Modelling non-point source pollution of rivers in the UK and Colombia

Martha Lucia Villamizar Velez

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University of York

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Abstract

Mathematical fate models have been developed and validated to simulate the transport of contaminants in temperate regions but little is known about their applicability in the tropics. Different models were applied to simulate brominated flame retardants in Colombia and the UK and to identify differences in model application and drivers of emissions in both regions.

Emissions of decabromodiphenyl ether (decaBDE) in Colombia and the UK were estimated and suggested large releases to wastewater textile back-coating and waste management stages. Emission data were used to study the partitioning of the flame retardant with a fugacity approach. Fugacity results from Colombia were in agreement with sediment concentrations from the literature for the outlet of the River Magdalena. GREAT-ER was also applied to simulate decaBDE emissions in the Calder catchment; the model showed good potential for the simulation of the flame retardant. Monitoring of polybrominated diphenyl ethers (PBDEs) in sediments in the Calder showed that decaBDE represented the vast majority of PBDEs analysed (>90%) with increasing concentrations moving downstream.

A modelling framework with field-scale models using MACRO was developed to simulate transport of six contrasting herbicides targeted by a management programme in the Wensum catchment in eastern England. The catchment-scale model SPIDER was also used for comparison. Preferential flow was the main driver of pesticide transport to water. A fairly good simulation of the flow was achieved (model efficiency, E = 0.6 for MACRO and 0.4 for SPIDER) but variability in pesticide simulations was observed due to uncertainties in input parameters. In-stream processes had little effect on pesticide simulations from either model. Modelling showed that most of the observed reductions in pesticide transport to the river (ca. 80% decrease between 2006 and 2011) can be explained by changes in weather and flow in the catchment during the study period, but an influence on management practices cannot be excluded.

AnnAGNPs was applied to simulate triazine loss to the River Cauca from sugarcane, maize and sorghum in the Cauca Valley of Colombia. Runoff was the main driver of pesticide emissions to water. Satisfactory simulation and validation of the hydrology was achieved after little calibration (E = 0.7). A fairly good simulation of pesticides was generally achieved, but some patterns in the measured data could not be simulated. Use of grab samples resulted in uncertainty in measured concentrations. Implementing best management practices was predicted to result in a 78% reduction in triazine losses, whilst replacing triazine herbicides resulted in an 87% reduction when expressed as a proportion of the total pesticide applied.

Uncertainty analyses of sensitive input parameters were carried out for the applied models. Their impact on simulations was chemical- and situation-specific. Recommendations for future research are provided to improve modelling of chemical fate in contrasting situations.

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Author’s declaration

I declare that the work contained in this thesis is my own and has not been submitted for any other degree or award.

1 Introduction to environmental contaminants and mathematical fate modelling

Human society has produced and released into the environment a wide variety of natural and synthetic chemicals for different purposes. When a chemical is introduced into the environment (mostly undesirable) or at concentrations above background levels, *contamination* may take place; however, the substance does not need to be harmful to be considered a contaminant. Some of those contaminants can cause environmental pollution by damaging human health and natural resources and disrupting important processes and cycles of ecosystems (Schwarzenbach et al., 2003). The introduction of undesirable elements into any of the natural resources and damage to ecosystems that arises as a consequence is called *pollution*. Therefore, a pollutant is any potential undesirable biological, physical or chemical substance that is likely to cause harm to the surrounding ecosystem. Waste management (e.g. dump sites, waste incineration, leaching of wastes from landfills, wastewater, direct discharge of industrial wastes to the soil), accidents (e.g. rupture of underground storage tanks, leaking from oil and fuel dumping), and leaching and runoff through soils into aquifers from the intensive use of pesticides are some of the most common sources of pollution (Schwarzenbach et al., 2003). The concern related to environmental pollution involves human health effects from direct contact with contaminants or following transport from their source to human settlements or to vulnerable ecosystems as well as disruption to natural cycles and other negative impacts on natural resources.

There are thousands of different types of chemical contaminants. Well known contaminants include heavy metals, synthetic organic substances, pesticides, persistent organic pollutants, petroleum hydrocarbons, solvents, components of detergents, dyes and varnishes, additives in plastics and textiles, chemicals used for construction, antifouling agents and radionuclides. Emerging contaminants such as veterinary and human antibiotics, pharmaceuticals, steroidal hormones, nanoparticles and brominated flame retardants (BFRs) are relatively new contaminants of concern, particularly because these chemicals are starting to be discovered in the environment where previously they had not been detected (US EPA, 2011).

Once contaminants are introduced into the environment, they are subject to complex physical, biological, and chemical processes that are highly variable in space and time, and which can transform and transport them within and between environmental compartments (soil, water, sediment, air and biota). The transport of contaminants in the environment is, in itself, very complex and is affected by many factors such as the weather, proximity to a water body, erosion, and presence of microorganisms. As a result, the fate of contaminants can only be elucidated and quantified after multiple and complicated measurements, followed by intensive experimentation, which is often complemented with the use of mathematical simulation models (Dosi and Fondazione, 2001). Mathematical fate modelling is the use of mathematical equations in order to describe the transport of contaminants in the environment. Models that are able to realistically represent the fate and behaviour of contaminants in the environment are useful tools for environmental studies (Brimicombe, 2010). Models can provide an understanding of the fundamental processes that control the fate and transport of contaminants in the environment. Physically-based models are the most comprehensive since they are more widely applicable to different environmental conditions; empirical or conceptual models can also be useful, but more attention should be taken in checking their applicability when being used in different regions.

1.1 Brominated flame retardants

Brominated flame retardants (BFRs) are organic chemicals containing bromine that are incorporated into polymeric materials such as plastics, textiles and furnishing foam in order to decrease their burning potential and achieve high levels of fire safety (Rahman et al., 2001; WHO, 1997). It is estimated that to date at least 75 different commercial BFRs have been produced (Covaci et al., 2011; Alaee et al., 2003). Health concerns for BFRs in humans include endocrine disruption, altered behaviour and learning, neurotoxicity and thyroid system perturbation (Viberg et al., 2006; US EPA, 2003b; Hallgren and Darnerud, 2002; Kester et al., 2002; Viberg et al., 2002; Eriksson et al., 2001; Hallgren et al., 2001). In addition, most of these chemicals are persistent, lipophilic and bio-accumulate in the environment (Covaci et al., 2011; Brooke et al., 2009; de Wit, 2002; Rahman et al., 2001).

Most of the studies on BFRs have focused on three groups: polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs) and tetrabromobisphenol-A (TBBPA). Polybrominated diphenyl ethers like pentabromodiphenyl ether and octabromodiphenyl ether formulations were banned in 2003 in the European Union (Directive EEC., 2003). Since 1 July 2008 decabromodiphenyl ether was also banned in electrical and electronic applications (European Court of Justice, 2008a). The components of the commercial formulations pentabromodiphenyl ether (tetra and pentabromodiphenyl ether) and octabromodiphenyl ether (hexa and heptabromodiphenyl ether) were added to the Persistent organic pollutants (POPs) list of the Stockholm Convention (Ashton et al., 2009). Even though the manufacturers Chemtura and Albermarle have announced that they will phase out production, import and sale of decabromodiphenyl ether for most uses in the USA by the end of 2013 (Albemarle, 2009; Chemtura., 2009; Hess, 2009), the chemical is still widely used for textile applications in Europe and particularly in the United Kingdom.

Most of the decabromodiphenyl ether currently commercialized in Europe is used in the UK (EU, 2002). Different studies carried out in rivers near to possible sources of release including the Rivers Skerne, Calder, Tees, Ribble, Humber and almost all the estuaries discharging into the North Sea, have shown detectable concentrations of decabromodiphenyl ether (decaBDE) (ECB, 2004). Studies in 1995 and 2001 indicated an increase in decaBDE concentration in sediment over the period by around 50 – 100% (ECB, 2004). However, no mathematical fate models have been applied to study either the dynamics of PBDEs in this country or estimation of decaBDE emissions to the environment. Palm et al. (2002) applied fugacity modelling as a first screening approach to estimate the partitioning of PBDE congeners using emission rates previously calculated for Denmark (Lassen et al., 1999) as an extrapolation of the behaviour in other European countries. Results showed that as the extent of bromination increased the intermediate transport from water to sediment becomes the dominant partitioning process and that the partitioning to air and water were insignificant regardless of the compartment of release. In addition, the former European Chemical Bureau (ECB, 2004, 2002) carried out risk assessments for decaBDE in Europe using emission information from the Bromine Science and Environmental Forum (BSEF, 2003b). The assessments demonstrated methodologies that can be useful to calculate decaBDE emission rates to the environment in other European countries.

1.2 Pesticides

The current world population is approximately 7.2 billion and this is expected to reach 9.6 billion by 2050 (United Nations, 2013). Global agricultural production relies on pest management for sustainable crop production to deal with the increasing food demand (Repetto and Baliga, 1996). Pesticides are nowadays the most viable option for crop protection despite the potential for negative impacts on the environment and particularly to water quality. Pesticides can contaminate water by point or non-point sources.

Point source pesticide pollution is characterized by very high peak concentrations at one point of the system, usually due to bad handling and management of pesticides. Examples of poor agricultural practices include spills from filling spraying equipment, cleaning equipment, using faulty spray equipment and the inadequate disposal of pesticide containers (Ongley, 1996). Studies in Europe have demonstrated that point source pollution is an important cause of pesticide loss in catchments in European countries (Navarro et al., 2010; Wittmer et al., 2010; Holvoet et al., 2007b; Yuce et al., 2006; Leu et al., 2004; Gerecke et al., 2002; Muller et al., 2002; Bach et al., 2001; Kreuger, 1998) including the UK (Mason, 2003; Rose et al., 2003; Hankinson and Welland, 2001). Point source pollution can be significantly reduced by providing adequate training and information to farmers (Prudent et al., 2007; Gerecke et al., 2002; Kreuger and Nilsson, 2001; Norvell and Hammig, 1999) as well as with the installation of biobeds in farm yards to collect and treat any spillage during handling and rinsing of pesticides (Fogg, 2001; Fogg and Carter, 1998).

Non-point source (or diffuse) pesticide pollution coming from farming operations is a critical and complex environmental issue which poses a major threat to surface and groundwater. Non-point sources respond to hydrological conditions and are not easily measured or controlled directly. Pesticides in the environment undergo different processes that influence their fate in the environment including volatilization, degradation, sorption-desorption, canopy interception, spray drift, surface runoff (in water or eroded soil) and leaching. These processes directly control the transport of pesticides after crop application and the eventual transfer from soil or plants to air and water (Arias-Estevez et al., 2008; Linn, 1993). Main diffuse pathways responsible for the largest pesticide losses are leaching, surface runoff (Zhang and Jorgensen, 2005; Ropke et al., 2004), interlayer flow and drain flow.

Leaching of pesticides into deep aquifers is an important contamination pathway to groundwater (Wehtje et al., 1983; Rothschild et al., 1982; Zaki et al., 1982; Peoples et al., 1980) and to a lesser degree to surface water by outflowing of contaminated groundwater from areas of recharge to discharge areas (Puckett et al., 2008; Puckett and Hughes, 2005; Gallagher et al., 1996; Broshears and Bradley, 1992). Factors contributing to pesticide leaching are well characterized (Rose and Carter, 2003; Zhang et al., 2000; Enfield et al., 1982; Selim et al., 1977; Wood and Davidson, 1975); pesticide solubility in water, soil sorption, degradation and pesticide formulation are among the most important. Mobile pesticides likely to contaminate groundwater are characterized by having small degradation rates and low soil sorption (Gardner, 2014). In addition, limited microbiological activity and pesticide degradation in deeper soil layers and the unsaturated zone is found due to low oxygen levels. Agronomic and environmental factors include weather, soil properties, land cover, irrigation and cropping practices. Soil characteristics that favour pesticide leaching include low organic matter which reduces potential for adsorption and highly permeable soils such as coarse-textured soils with high sand content that allow the rapid movement of water; in contrast clay-textured soils with small pore sizes slow the downward movement of pesticides (Gardner, 2014; Arias-Estevez et al., 2008; Carter, 2000). Loosely packed soils or the presence of fissures or cracks, earthworm and plant root holes may allow the rapid movement of water and solutes through the soil profile via preferential flow. In addition, the presence of microorganisms increases pesticide degradation, reducing the leaching potential (Carter, 2000).

Surface runoff (or overland flow) occurs when the rainfall rate exceeds the infiltration capacity of the soil or when saturated soil prevents the entry of all the rainfall received at the soil surface (Carter, 2000). The antecedent soil moisture content, weather and other site specific factors determine the amount of pesticide loss through runoff. For example, steep slopes, clay soils, sparse vegetation cover or the application of pesticide to a saturated soil followed by a rainfall event or heavy rain occurring soon after pesticide application can enhance pesticide runoff. During a runoff event pesticide can be transported either in solution or sorbed to soil particles. Physicochemical properties of pesticide also control the susceptibly to pesticide runoff (CIPM, 2006). Highly soluble pesticides are likely to be washed off by overland flow but may leach out of upper soil layers if there is a lag between application and surface runoff. In contrast, pesticides with high sorption to soil are prone to transport sorbed to soil particles during a runoff event. After water infiltrates, interlayer flow (or subsurface runoff) can also take place, which refers to the lateral movement of water through the soil and subsequently flow out of the soil profile to nearby surface water.

Drainage systems such as tile drainage (Figure 1-1) are a common practice in agricultural soils with low infiltration capacity; drainage consists of burying perforated drainage pipes (or tiles) into the soil to lower the water table and rapidly remove excess water in order to facilitate field operations and crop growth by enhancing soil oxygenation (Figure 1-1 a); the excess water is then transferred to a surface drainage ditch or directly to the stream network (Sheaffer and Moncada, 2009) (Figure 1-1 b). This drainage system benefits farming greatly and also helps to reduce surface runoff of pesticide and nutrients; however, pesticide leaching through drains via preferential flow is an important route for pesticide loss to surface water (Kladivko et al., 2001; Zehe and Fluhler, 2001; Flury, 1996; Brown et al., 1995a; Brown et al., 1995b; Kladivko et al., 1991) which can cause high pesticide concentrations in agricultural ditches and stream networks (Brown et al., 2004; Leu et al., 2004; Williams et al., 1996).

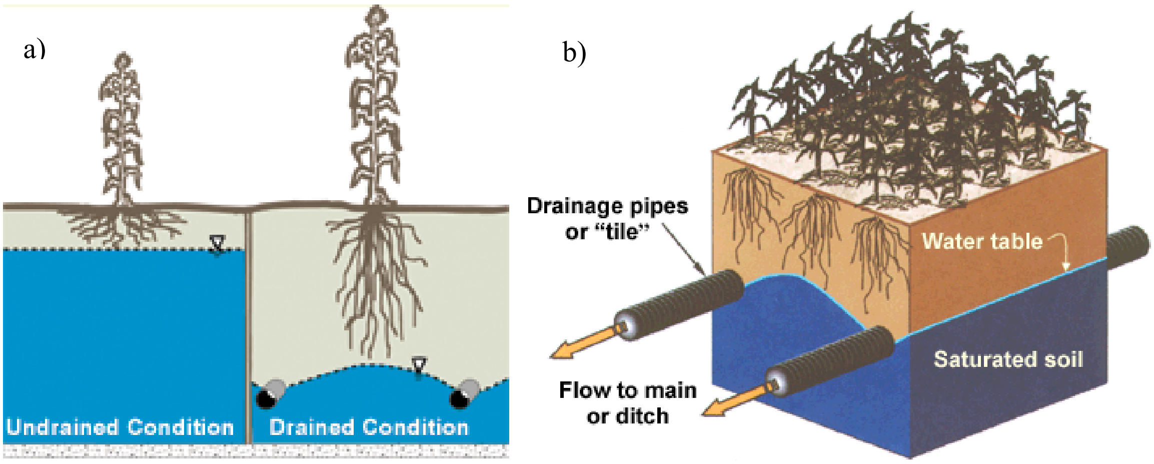


Figure 1-1 Effect of tile drainage system on a) crop growth and b) water table (Busman and Sands, 2012).

Efforts to reduce water contamination by pesticides in Europe are currently in place. In particular, the Water Framework Directive 2000/60/EC (WFD) came into force on December 22nd 2000 and requires Member States to comply with water quality objectives to secure water protection. Under WFD Article 7, Member States are required to characterise water quality and carry out risk assessments for Drinking Water Protected Areas (DrWPAs). DrWPAs are surface and groundwater bodies being or intended to be abstracted for human consumption at more than 10 m^3 per day. The assessment should also determine whether the protected areas objectives will be met by 2015. The EU Drinking Water Directive 98/83/EC states that no individual pesticide should reach tap water at concentrations above 0.1 μg/l and the total concentration must not exceed 0.5 μg/l (EC, 1998). However, in 2012 the Environment Agency has reported that 15% of the 647 surface water DrWPAs in England and Wales are at risk of failing to achieve WFD Article 7 because of contamination by pesticides (Pesticide Forum, 2012). In order to reduce water pollution from agricultural land, the Environment Agency initiated the Catchment Sensitive Farming programme (CSF) in December 2005. The programme provides advice to farmers on measures they can take to minimise risk and also provides them with finance to invest in infrastructure for this purpose. Several reports into the progress of the CSF have shown an apparent reduction in pesticide concentrations in rivers (CSF, 2012, 2011); however, no mathematical modelling has yet been applied to understand the dynamics of pesticides at the catchment level which would enable a better assessment of the impact of the programme.

1.3 Pesticide fate modelling

Pesticide fate models have been used for many years in a regulatory context as a cost-effective method to investigate pesticide management strategies for the reduction of pesticide emissions from non-point sources and to study the fate and behaviour of pesticides and their metabolites under different environmental conditions (FOCUS, 2000; Oreskes et al., 1994). The selection of the appropriate model will depend on several factors that include the identification of the most important processes that the chemical will undergo and which need to be considered in the model structure. For instance, a compound leaching in a strongly structured soil should be simulated using a model that accounts for preferential flow or the simulation of pesticides in an area with poor hydrological conditions or likely to exhibit overland flow should include a runoff description (FOCUS, 2000).

Mathematical modelling of pesticide fate in the environment has been applied at different scales, from edge-of-field to catchment-scale (Holvoet et al., 2007b). Renaud et al. (2008) presented a summary table with different types of pesticide fate models with potential use at the catchment-scale. Models included one-dimensional soil column leaching and surface runoff (e.g. MACRO and PRZM), field-scale (e.g. GLEAMS and RZWQM) and catchment-scale models (e.g. AnnAGNPS and SWAT). Generally, less complex models but with more detailed site-specific input data are required at smaller scales while at larger scales the use of average parameters can be applied but model complexity and amount of input data usually increases. In addition, spatially-variable landscape characteristics and temporally-variable meteorological input data are necessary for more accurate modelling results at the catchment level.

Model input and output parameters should be evaluated with as much rigor as possible in order to ensure reliable modelling results. When designed, pesticide transport models are usually first tested against laboratory data and then evaluated against field measurements which usually requires calibration and validation of the model. Calibration can be performed when applying the model to field data and consists in adjusting input parameters until an acceptable simulation is achieved. Then, the calibrated model is applied for a different simulation (usually for a different period of time or to similar environmental conditions) and if the results are also acceptable the model is considered to be validated for that situation (Loague and Green, 1991). If the model needs further adjustments then recalibrations can be considered. Model performance should be similar for calibration and validation. Different statistical and visual analyses against measured data can be applied to evaluate model performance. For example, analysis of residual errors is useful for characterising systematic under- and over-estimation of the simulation and the coefficient of determination can be used to evaluate the linear correlation between the observed and the simulated data. Visual analysis through the use of graphs and plots of the simulated and the observed data is used to identify types of errors and trends which cannot be easily detected with statistical tools (Loague and Green, 1991).

The incorporation of model evaluation against accurate monitoring data and uncertainty analysis is an essential procedure to provide realistic model outputs (Dubus et al., 2003b; Dubus and Brown, 2002; Sohrabi et al., 2002; Dubus et al., 2001). A poor sampling procedure can lead to the rejection of a good model or the acceptance of a poor one (Addiscott et al., 1995). Monitoring studies have shown that high temporal variation of pesticide concentrations in the river network can be expected (Seuntjens et al., 2008; Holvoet et al., 2007a). This finding demonstrates the practical constraints on the use of grab samples to assess water quality status or to evaluate modelling results; composite samples are more reliable and representative of the average concentration of sampling time interval but impose a financial limitation when monitoring programmes are required. The combination of sampling data and fate modelling is a more cost-effective approach for the optimisation of monitoring programmes (Vanrolleghem et al., 1999).

Mathematical models are simplified representations of the environment and by themselves must always be considered as uncertain. Some parameters cannot be measured directly or are difficult to obtain so the best option is to apply functions or models to the available data to obtain them (Addiscott et al., 1995). For instance, pedotransfer functions are useful to calculate non-available soil properties using the available data and series of regression analyses and data mining techniques (Bouma, 1989); such functions are frequently applied for estimation of water retention curves and hydraulic conductivity values.

Key input parameters in fate models usually vary spatially and/or temporally within a catchment. In assessing pesticide behaviour in soils, researchers have found high variability which results from the complex environmental factors involved. Various spatially variable soil characteristics that influence pesticide sorption in soils include organic carbon content, clay content, pH and Al/Fe oxides and hydroxides (Weber et al., 2004; Bailey and White, 1964). Similarly, pesticide degradation is influenced by soil organic content, pH, salinity, nutrients, soil temperature, oxygen content, soil moisture content, bioavailability, chemical structure and concentration (Alexander, 1999; Aislabie and Lloyd-Jones, 1995). This often leads to a highly heterogeneous spatial pattern of pesticide sorption and degradation within the same area. For example, field studies on the most commonly used herbicide in the USA, atrazine, have shown K_{oc} and half-lives ranging from 89 to 513 mL/g and from 6 to 108 days, respectively (AERU, 2007). Walker et al. (2001) found that within a single field the half-life of isoproturon and chlorotoluron varied from 6 to 30 days and from 34 to 203 days, respectively. In addition, climate data and particularly the precipitation falling over a location vary both spatially and temporally. The different influences on the variability of precipitation include the topography characteristics (mainly altitude, aspect and slope) and the presence of convective thunderstorms (Davie, 2008; Johnson and Hanson, 1995). The variability of input parameters should be considered if a realistic description of the dynamics of pesticides in the environment is to be obtained (Peck et al., 1977). The use of average input parameters instead of site-specific data is a common source of uncertainty when applying pesticide models. The uncertainty due to input parameters has produced large controversy concerning the use of models, so there is a clear need to assess the impact on model predictions (Haan et al., 1995a; Beven, 1993); understanding uncertainties and their causes is essential to interpret simulation results effectively (Sohrabi et al., 2002).

1.4 Pesticide fate and modelling under tropical conditions

Although there have been many advances in developing environmental models most of them have been designed and validated to be applicable to temperate regions. However, one-third of the earth's land corresponds to tropical regions (Racke et al., 1997). In addition, intensive use of pesticides under weak safety standards, poor pest management and limited monitoring programmes is a major issue for pesticide contamination in developing countries (Feola and Binder, 2010; Ramos et al., 2010; Hughes et al., 2006). FAO (2009) estimated that between 1999 and 2009 an average of 82,000 tonnes of pesticides were applied annually; most of this was herbicides (47%) followed by fungicides/bactericides (35%) and insecticides (17%). Main crops cultivated in tropical regions include sugarcane, corn, rice, cotton, coffee, cocoa beans, tobacco, rubber, spices, legumes, tropical and subtropical fruit and vegetables. The population of developing countries is at high risk of acute and chronic exposure to pesticides under both occupational and epidemiological conditions (el Sebae, 1993). There is also a global risk for pesticide dissipation and transportation across borders.

Tropical regions are situated near the equator, within the area bounded by latitudes 23.5° N (Tropic of Cancer) and 23.5° S (Tropic of Capricorn) (Cobley and Steele, 1976). Over 70 countries are located in this zone, most of them developing countries (Table 1-1) and most make significant use of pesticides (Racke et al., 1997).

Table 1-1 List of countries with land areas in the tropics (Racke et al., 1997).

America	Africa	Asia and Pacific
Bolivia	Angola	Australia (Northern)
Brazil	Cameroon	Bangladesh (Southern)
Colombia	Central African Republic	Cambodia
Costa Rica	Congo	China (Guangzhou)
Cuba	Ethiopia	India (Southern)
Dominican Republic	Ghana	Indonesia
Ecuador	Ivory Coast	Malaysia
Guatemala	Kenya	Myanmar
Honduras	Mali	Oman
Jamaica	Mozambique	Papua New Guinea
Mexico (Southern)	Nigeria	Philippines
Nicaragua	Somalia	Saudi Arabia
Panama	Sudan	Sri Lanka
Paraguay (Northern)	Tanzania	Taiwan (Southern)
Peru	Zaire	Thailand
Puerto Rico	Zambia	Vietnam
Venezuela	Zimbabwe	Yemen

The tropics are mainly characterized by the relative homogeneity of temperature throughout the year, length of daylight of approximately 12 hours which remains almost constant during the whole year and levels of solar radiation that are about twice those of temperate regions (Racke et al., 1997); some differences in the behaviour of precipitation are observed between tropical areas. Three areas are classified according to their moisture regime: (i) high and uniform precipitation (Udic), (ii) distinct wet and dry seasons (Ustic) and (iii) low or sporadic rainfall (Aridic), covering 25, 50 and 25% of the tropics, respectively (Cobley and Steele, 1976).

Studies have suggested that tropical and temperate soils do not differ significantly and that differences are mainly due to the variation of soil moisture and temperature over the year (Isbell, 1983; NAS, 1972). The formation of the soil is a complex process influenced by external factors and internal processes including climate, organisms, parent material, topography and the time over which these factors have acted on the parent material (Buol et al., 1973). Therefore, if soil forming factors are different in both regions then a different type of soil will develop. Table 1-2 shows the distribution of the major soil orders in the three tropical continents (Africa, America and Asia). All the eleven soil orders are present in the tropics; highly weathered and leached acid infertile soils (Oxisols and Ultisols) comprise about 43% of the tropics, soils with moderate to high fertility (Alfisols, Vertisols, Mollisols and Andisols) constitute 23% and dry sands (Entisols) and base-rich acidic soils (Aridisols) account for 18% of the tropical area (Nair, 1993).

Table 1-2 Distribution of soil orders in tropical countries, based on the dominant soil in FAO maps at a scale of 1:5 million. Areas are in million hectares (Szott et al., 1991).

Soils	**Tropical America**		**Tropical Africa**		**Tropical Asia and Pacific**		**Total**	
	Area	**%**	**Area**	**%**	**Area**	**%**	**Area**	**%**
Oxisols	502	33.6	316	27.6	15	1.4	833	22.7
Ultisols	320	21.4	135	11.8	294	28.4	749	20.4
Entisols	124	8.3	282	24.7	168	16.2	574	15.7
Inceptisols	204	13.7	156	13.7	172	16.6	532	14.2
Andisols	31	2.1	1	0.1	11	1.1	43	1.2
Alfisols	183	12.3	198	17.3	178	17.4	559	15.2
Vertisols	20	1.3	46	4.0	97	9.3	163	4.4
Aridisols	30	2.0	1	0.1	56	5.4	87	2.4
Mollisols	65	4.4	0	0	9	0.9	74	2.0
Histosols	4	0.2	5	0.4	27	2.6	36	1.0
Spodosols	10	0.7	3	0.3	7	0.7	20	0.5
Total	1493	100.0	1143	100.0	1034	100.0	3670	100.0

Oxisols and Ultisols in the tropics are also called low activity clay soils due to their high to medium acidity and low cation exchange capacity which in this region is due to the lack of nutrients since the soil itself is comprised of clay. Entisols are soils with little profile development (USDA, 1999) except an A horizon, commonly found in places of recent deposited material such as those that suffer from periodic flooding (e.g. alluvium), steep slopes or in parent materials resistant to tropical weathering (e.g. quartz sand). Thus, Entisols are characterized by a wide productivity potential, environmental surroundings and land use. Inceptisols have some profile development (more than Entisols) and the differences between horizons are just beginning to appear. Inceptisols are prominent in mountainous regions, fairly steep slopes, sites with high water table, young geomorphic surfaces, and on resistant parent material. The suborder Andepts within the Inceptisols has been used intensively in the tropics, particularly in volcanic areas. They are extensive in Central and South America along the Andes, isles of Oceania and in Africa (e.g. in the Republic of the Congo, Tanzania, Madagascar, Uganda, Kenya and Cameroon) (NAS, 1972). Volcanic ash produces allophane, an atypical kind of amorphous clay that in combination with organic matter provides the soil with high water-holding capacity and incomplete dispersibility that traps organic matter and protects it against rapid decomposition. Andepts have a low cation exchange capacity at low soil pH. However, these generalizations are only broad indications since a wide range of soils with different properties exist among soil orders.

The soils of the tropics are as diverse as those of temperate regions (Lal and Sanchez, 1992). A vast majority of tropical soils have a weak structure prone to crusting, compaction and slaking and are susceptible to erosion under heavy rain and sloping terrain (Nair, 1993). Acid soils will affect the sorption behaviour of pesticides with ionic equilibrium constant near the range of soil pH. For instance, triazines exhibit a sharp increase in the K_d in acidic soils, and carboxylic acids and sulfonylurea herbicides show increase mobility at higher soil pH (Wauchope et al., 2002).

Authors claim that pesticides exhibit high variability in physicochemical parameters such as pesticide degradation and sorption, and for this reason it is very difficult to establish whether differences in physicochemical properties from studies in temperate and tropical regions actually occur (Racke et al., 1997). Pesticide degradation is determined by different physical, chemical and biological mechanisms such as temperature, environmental pH, soil moisture content and the population of microorganisms (Wilson et al., 1997; Sandmann et al., 1988; Que Hee and Sutherland, 1981). Studies have shown increased degradation in tropical soils due to elevated temperatures (Daam and Van den Brink, 2010; Magallona, 1989; Zimdahl and Clark, 1982). Temperature has been considered as an important factor affecting pesticide hydrolysis, as described by the Arrhenius equation. Higher soil temperatures can increase pesticide hydrolysis (Getzin, 1981), so this process is expected to be more important in the tropics than in temperate regions. Korpraditskul et al. (1992) studied the hydrolytic degradation of atrazine in Thai soils at different temperatures and observed that after 90 days of incubation at 15, 25, 37 and 45°C the remaining percentage of atrazine for a Pak Chong and a Kamphaengsaen soil were 26, 8, 5 and 1% and 70, 58, 41 and 27%, respectively. Similarly aqueous photolysis of pesticides is enhanced in tropical regions since more solar radiation is obtained during the year (Racke et al., 1997; Magallona, 1989). In contrast, higher evapotranspiration rates due to high temperature and solar radiation can also reduce soil moisture and thus, pesticide degradation (Getzin, 1981). Perez et al. (2013) demonstrated the importance of soil moisture for the faster degradation of pesticides under tropical conditions. The authors found that the optimal conditions for the degradation of chlorpyrifos and diazinon in a tropical region in Colombia are 80 – 100% of humidity in relation to field capacity and a soil temperature of 10°C.

Nowadays there are some efforts to assess pesticides in tropical regions but little has been done to develop applicable models, to identify the difference between the fate and behaviour of contaminants under temperate and tropical conditions and to understand whether results from models applied in temperate zones can be extrapolated to the tropics. The IUPAC commission on agrochemicals and the environment recommends carrying out more studies in tropical environments including the application of contaminant fate modelling (Racke et al., 1997).

Perez and Paez (2010) studied the runoff potential of chlorpyrifos at the field-scale using simulated rainfall in potato crops under tropical humid conditions in Colombia. Soil moisture contents were measured and supplied to the runoff model GLEAMS (Leonard et al., 1987). Uncalibrated results showed good model efficiency (0.7) for pesticide runoff in soil but a poor simulation was obtained for concentrations in the water phase (model efficiency = 0.2). Good simulations were observed by Alavi et al. (2007) when applying two leaching models, S1D DUAL (Ray et al., 2004; Vogel et al., 2000) and MACRO 4.3

(Jarvis et al., 1991) to tropical soils. The study also showed that preferential transport was not significant due to reduced soil moisture; instead high saturated conductivity of micropores enhanced the water flow by this route. Good model performances obtained under tropical regions suggest that models designed in temperate regions can be applicable but more work is required on evaluation and validation of models.

The application of fate models in tropical regions will enable more definitive knowledge that accompanies the use of pesticides in these areas (e.g. sufficient pest efficiency, potential for pesticide loss, persistence, residual pesticide in soil and potential for damage to following crops, surface runoff and risk to water bodies) (Racke et al., 1997). However, the availability and easy access to regional pesticide usage, land cover, climate and soil information will be crucial for model application. The paucity of data available to evaluate and validate models in the tropical regions is mainly due to the high cost of producing data. Therefore, the use of models is helpful to assess the minimum data required and the most cost-effective alternatives to maximise the use of available data.

1.5 Aims and objectives

The aim of the present research is to apply and develop different modelling methodologies in order to describe the fate and behaviour of contrasting environmental contaminants; in particular, the research aims to extrapolate European models and practice to Colombian conditions. The specific objectives are to:

1. Evaluate models of the fate of brominated flame retardants to estimate emissions in the UK and Colombia and then apply results to investigate their presence in both regions.
2. Study the dynamics of pesticides in UK and Colombian catchments by using pesticide fate modelling.
3. Analyse the different sources of uncertainty arising from applying mathematical modelling to describe the complexity of environmental fate.
4. Identify major differences in contaminant behaviour in Colombia and the UK to determine the drivers for those differences and to understand the implications for model structure appropriate to the two countries.

1.6 Thesis structure

In the present study, several modelling tools have been applied to different environmental issues in the UK and Colombia.

In Chapter 2, studies into the emissions and fate of PBDEs, particularly decabromodiphenyl ether in the Calder catchment in the UK and at the mouth of the Magdalena River in Colombia are carried out using two models: 1) the Equilibrium Criterion model (EQC) which is a Mackay fugacity type model; and 2) the Geography-referenced Regional Exposure Assessment Tool for European Rivers model (GREAT-ER), a model that combines a geographical information system (GIS) with a steady-state fate model. A monitoring study was also carried out to study the dynamics of PBDEs in a highly industrialised area in the UK and to evaluate model results from GREAT-ER. The main aim is to investigate differences in environmental pollution and modelling approaches to study the fate of relatively new contaminants such as BFRs from both regions.

Chapter 3 presents a modelling framework to simulate pesticides in the Wensum catchment. The modelling methodology includes the use of the preferential flow model MACRO to simulate pesticide loss via tile drainage and leaching. In addition, a groundwater mixing model is developed to account for the groundwater and pesticide residence time before being transported to the river network. Overland flow from developed areas (hard surfaces) is also included into the simulation of the hydrology. RZWQM2 and PRZM are tested by including them into the model framework in order to determine which model better describe surface runoff and associated pesticide losses in the catchment. Simulation results are evaluated against existing monitoring data from 2006 – 2011. Modelling evaluation of pesticide simulations is used to decide to what extent the model can be used to fill gaps between monitoring dates.

Chapter 4 evaluates the modelling performance of the catchment-scale model SPIDER in modelling pesticide loss at the Wensum catchment and compares the results to the modelling framework developed in Chapter 3 using MACRO. Results are then used evaluate whether the Catchment Sensitive Farming (CSF) programme is reaching the goal of reducing pesticide emissions. Finally, an uncertainty analysis is carried out to identify and evaluate the different sources of uncertainty arising from the different assumptions and simplifications within the modelling methodology as well as to identify errors associated with the use of mean input parameters in the model.

Chapter 5 aims to assess the model applicability and predictive capacity of the catchment-scale model AnnAGNPS to predict pesticide loss in a nested catchment with intensive use of pesticides in the River Cauca in Colombia. The modelling methodology also includes different approaches to deal with the limited amount of regional input data as well as to simulate a sub-catchment which does not include the river source. Results are evaluated against available monitoring data from 2010 and 2011 and model validation is also applied for a different period of time (2008 – 2009). An uncertainty analysis of the most uncertain input parameters is also included. Finally, the simulation attempts to identify major differences in pesticide usage and practice between Colombia and the UK that can then help to understand their implications for the application of mathematical modelling in the two countries.

Chapter 6 discusses the main findings of the preceding chapters in a wider context and addresses the main thesis objectives particularly number four. Recommendations for future research about BFRs, pesticide management and fate modelling applications in the UK and Colombia at the catchment-scale are also presented along with final concluding remarks.

2 Brominated flame retardants in the UK and Colombia

2.1 Introduction

Flame retardants are chemical substances that are applied to polymers to reduce their ignition potential. Nowadays, there are more than 175 chemicals classified as flame retardants and among them 75 are brominated organic compounds (IPC, 1997). The annual production of brominated flame retardants was 150,000 tonnes in 2001 where about one-third of this figure corresponded to polybrominated diphenyl ethers (PBDEs). PBDEs have been used in a large variety of consumer products such as upholstery textiles, plastics, television sets, computers, vehicles, aircrafts and construction materials (e.g. wires, cables, pipes and carpets) (BSEF, 2013a). BFRs can be used as additives or reactive substances; PBDEs are additive flame retardants that are mixed into the products without any chemical bond which makes them more likely to leach out of products (Sjodin et al., 2003). Environmental pollution by PBDEs has become a well-known issue. PBDEs have passed from being emerging contaminants to widespread ubiquitous pollutants found in environmental media (Arellano et al., 2011; Hale et al., 2006), biota (Alaee, 2006; de Wit et al., 2006; de Wit, 2002) and humans (Wang et al., 2007; Hites, 2004).

Studies into PBDEs have proven their toxicity, persistence, bioaccumulation and long-range atmospheric transport potential which has led to the addition of the commercial products penta- and octabromodiphenyl ether to the list of persistent organic pollutants (POPs) of the Stockholm Convention (2008). Nowadays, the only commercially available PBDE is decabromodiphenyl ether (decaBDE). A recent inventory study estimated that from 1970 to 2010 between 185,000 and 250,000 tonnes of decaBDE were consumed in Europe (Earnshaw et al., 2014). PBDE producers claim decaBDE is neither mobile nor bioavailable (BSEF, 2013b), but studies have found them in a large variety of abiotic media (Baron et al., 2013; Darnerud et al., 2001), biota (Kuo et al., 2010) and human samples including breast milk samples (Lunder and Sharp, 2003; Schecter et al., 2003; She et al., 2002). Increasing concentrations in the Artic atmosphere have also demonstrated the long-range transport of decaBDE (Vorkamp and Riget, 2014; Moller et al., 2011; de Wit et al., 2010) and it has also been shown to be a potential endocrine disruptor (Patisaul et al., 2013; Sosa-Ferrera et al., 2013; Johnson and Jurgens, 2003). There is growing evidence that decaBDE can degrade in the environment into lower and more toxic congeners which themselves are

POPs listed in the Stockholm Convention (POP-PBDEs) (ECHA, 2012b; Environment Canada, 2010).

In 2008, the EU banned decaBDE from its use in electrical and electronic equipment (EEE) (European Court of Justice, 2008b) and in 2009 chemical companies in the US agreed to phase out and eliminate its production, import and sale by 2013 as part of the “decaBDE Phase-Out Initiative” (Wager et al., 2012; US EPA, 2010) (Wager et al., 2012). More recently, a proposal was submitted by Norway to list commercial decaBDE as a Persistent Organic Pollutant (POP) in the Stockholm Convention (UNEP, 2013). Based on the existing information, decaBDE meets the POP criteria of the Stockholm Convention under Annex D due to persistence, bioaccumulation, long-range transport and adverse effects. Despite these actions, no further restrictions have been applied to other uses of decaBDE in Europe such as on textile applications and even more worrying, no regulations have been applied in other countries particularly in developing countries.

A European risk assessment has identified that the country with the highest consumption of decaBDE in textile application is the UK (ECB, 2004, 2002). Monitoring data in this country have shown high levels of decaBDE near sewage treatment plants and processing sites that use this flame retardant (Allchin et al., 1999; Law et al., 1996). DecaBDE can be released into the environment from production sites, from finished articles during their lifetime and at disposal (Earnshaw et al., 2013; Shaw et al., 2010; Imm et al., 2009; Wong et al., 2007; ECB, 2004, 2002). Despite the extensive usage and the high concentrations in the environment, no further assessments in the emissions of decaBDE or mathematical fate modelling have been carried out in the UK. Estimating the main emission pathways in the environment is valuable for identifying the most important sources of release. In addition, these estimates can also be used to assess the environmental partitioning of the flame retardant in the UK, using fugacity level III modelling. Studies into the partitioning of decaBDE using fugacity modelling and risk assessments by the European Union have shown the high emission potential that decaBDE pose to air, surface water and the aquatic environment (ECB, 2004, 2002). However, transport modelling of decaBDE in the environment has mainly focused on the simulation of long-range atmospheric transport (Bogdal et al., 2010; Schenker et al., 2008; Breivik et al., 2006; Wania and Dugani, 2003). Catchment-scale modelling can provide an understanding of the dynamics of decaBDE in the aquatic environment, particularly in high industrialised areas with a significant usage of this flame retardant.

Since most of the monitoring studies and assessments of BFRs have been focused on industrialised countries, there is little knowledge on PBDE usage and levels in developing countries. Furthermore, restrictions about their use are limited and there is an increasing generation of e-waste and PBDEs containing products without adequate waste management or recycling plants (Weber et al., 2011). A recent monitoring study of PBDEs in the mouth of the River Magdalena in Colombia has shown the presence of different congeners in sediment and biota samples with decaBDE being the most detected congener and with the highest levels (Baron et al., 2013). No regulations about the usage of PBDEs are currently in place in this country and there is little information about the usage and consumption figures of this flame retardant. The Stockholm Convention has published guidelines that can help countries to undertake inventories of the POP-PBDEs which is a first step to acquiring an understanding of the situation at a national level (Stockholm Convention, 2012). This inventory methodology can also be applied to estimate levels of decaBDE which can then be used to estimate its emissions and partitioning in the environment.

2.1.1 Aims and objectives

The aim of the work reported in this chapter is to study the dynamics of decabromodiphenyl ether in a temperate and in a tropical region by application of fugacity and catchment-scale models. The specific objectives to meet this aim are to:

1. Estimate emissions of decabromodiphenyl ether to different environmental compartments in the UK and Colombia.
2. Use estimated emissions to determine the general environmental partitioning of decabromodiphenyl ether in both countries using fugacity modelling.
3. Evaluate fugacity model results against reported concentrations in the environment for both countries.
4. Investigate the presence and levels of decabromodiphenyl ether in the Calder catchment in the UK.
5. Study the fate of decabromodiphenyl ether in the Calder catchment using the catchment model GREAT-ER.
6. Evaluate the predictive capacity of GREAT-ER to simulate spatially distributed concentrations of decabromodiphenyl ether in the Calder against measured data.

2.2 Background information

2.2.1 Brominated flame retardants

Brominated flame retardants (BFRs) are industrial chemicals containing bromine atoms in their structure which are incorporated in different products to reduce the risk from fires. There are different kinds of BFRs but most environmental concerns have focused on polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA) (Figure 2-1) as they have been shown to bioaccumulate in fatty tissues and to be persistent in the environment (Covaci et al., 2011; Alaee et al., 2003; de Boer et al., 2001; Allchin et al., 1999; Law et al., 1996). Flame retardants can be classified as additives or reactives depending on the process of incorporation into the polymers. Reactive flame retardants are covalently bonded to the polymer, e.g. TBBPA, whilst the additives such as PBDEs and HBCD are added to the polymeric material which make them more likely to leach out of the products and more readily enter the environment (Alaee et al., 2003; Rahman et al., 2001).

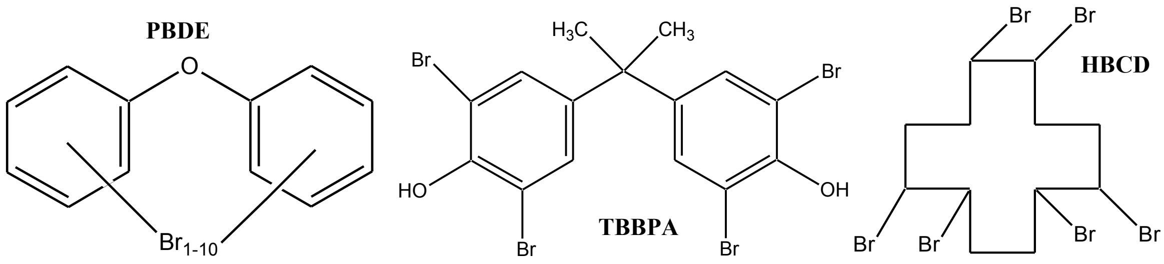


Figure 2-1 Structural formulas of polybrominated diphenyl ethers (PBDE), tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCDD).

The structure and properties of the polybrominated diphenyl ethers are similar to polychlorinated biphenyls (PCBs) and polybrominated biphenyls (PBBs), specifically in their high level of persistence and bioaccumulation in the environment. PBDEs are diphenyl ether molecules where hydrogen atoms can be substituted with bromine, resulting in 209 different compounds or congeners that differ in the number and position of the bromine atoms on the two phenyl rings (WHO, 1994). Not all the possible PBDE congeners are commercially available and also they do not come as a single congener. PBDE formulations are a mixture of congeners with one of them as the major component, which gives the commercial name to the product (WHO, 1994). Commercially available PBDEs included congeners with different degrees of bromination; pentaBDE, octaBDE and decaBDE (Prevedouros et al., 2004; Alaee et al., 2003) i.e., five, eight and the fully brominated molecule, respectively. The Stockholm convention has included the penta- and octa-formulations in the list of persistent organic pollutants (POPs) (Stockholm Convention, 2008). The decaBDE formulation has not yet been included but debromination due to degradation can generate some of the listed POP congeners (UNEP, 2010b, a).

2.2.2 Environmental fate of polybrominated diphenyl ethers

Table 2-1 lists several physicochemical properties for the most common PBDE congeners that have been commercially available. PBDEs have low water solubility (≤ 0.1 mg/l) and high log octanol water partition coefficients (> 5.0) which enables high sorption to soils and sediments and a tendency to bioaccumulate. The Henry's law constant (H) and the vapour pressure (Vp) values show that PBDEs have low tendency to volatilize (H $<10^{-5}$ and Vp $<10^{-4}$ Pa) and volatilisation decreases with increasing molecular weight and degree of bromination (US EPA, 2010).

Table 2-1 Physicochemical properties of most common commercially available polybrominated flame retardants.

Compound	Molecular mass (amu)	Vapour pressure (Pa)[h]	Log K_{ow}	Solubility (mg/l) 25 °C	Henry's law constant (10^{-5})[a]
tetraBDE	485.8	(2.6 – 3.3) x 10^{-4}, 25°C	6.81[b] 5.9 – 6.2[h]	0.011[g]	
pentaBDE	564.8	(2.9 – 7.3) x 10^{-5}, 25°C	6.64 – 6.97[a] 6.57[d] 6.5 – 7.0[h]	0.013[d]	0.35 – 1.2
hexaBDE	643.6	(4.2 – 9.4) x 10^{-6}, 25°C	6.9 – 7.9[h]	0.9[b]	
octaBDE	801.5	(1.2 – 2.2) x 10^{-7}, 25°C	6.29[a,f] 8.4 – 8.9[h]	0.002[a] 0.0005[f]	0.0075 – 0.026
decaBDE	959.2	< 10^{-4}, 20°C < 100, 250°C 270, 278°C 670, 300°C	6.27[a,f] 10[i]	< 0.001[e]	0.0012 – 0.0395[c]

[a]ATSDR (2002); [b]ATSDR (2004); [c]Cetin and Odabasi (2005); [d]ECB (2001); [e]ECB (2002); [f]ECB (2003); [g]Stenzel and Markley (1997); [h]Watanabe and Tatsukawa (1989); [i]WHO (1994)

The aquatic toxicity and bioaccumulation potential of PBDEs decreases with increasing degree of bromination (Brooke et al., 2009). However, fish can debrominate higher brominated PBDEs to lower and more toxic congeners (UNEP, 2013). Invertebrates are expected to have lower debromination potential due to the low solubility of higher PBDEs. The EU Water Frame Directive (2013) stipulated Environmental Quality Standards (EQS) to protect the aquatic environment of 0.14 µg/l and 0.0085 µg/kg for the sum of PBDEs in inland surface waters and biota, respectively.

2.2.3 Decabromodiphenyl ether

Decabromodiphenyl ether (decaBDE) is the fully brominated PBDE. It is widely used in virtually any type of polymer including rubber, polyvinyl chloride, polyamides, polyoleofins, polycarbonates, polyester resins, ABS (acrylonitrile, butadiene and styrene), polyamindes, polyvinyl chloride, and rubber. Table 2-2 presents the typical composition for the commercial decaBDE formulation. The commercial formulation is a technical mixture of decabromodiphenyl ether and other congeners in a small amount, the major congener after decaBDE is nonaBDE (2.5%) and past formulations used to have the octa- congener (ECB, 2002).

Table 2-2 Typical composition of commercial decaBDE formulation (ECB, 2002).

Type of Congener	Congener identity	DecaBDE Commercial formulation (mass % composition)
TriBDE	Total TriBDE	0.00001
TetraBDE	BDE 47	0.00003
PentaBDE	BDE 99	0.002
HexaBDE	BDE 153	0.001
HeptaBDE	Total HeptaBDE	0.003
	BDE 206	2.2
NonaBDE	BDE 207	0.24
	BDE 208	0.06
	Total NonaBDE	2.5
DecaBDE	BDE 209	97.5

In recent years, there have been increasing concerns about the degradation of decaBDE to its lower and more toxic congeners such as tetraBDE, pentaBDE and octaBDE. However, this mechanism is still not completely understood. A few studies have shown that higher PBDE congeners can be fragmented by photodegradation into lower congeners under a variety of conditions (Darnerud et al., 2001) but the reaction is slower in water than in organic solvents (Mas et al., 2008). Table 2-3 shows some of the reported degradation half-lives for different media and degradation conditions. DecaBDE is a persistent contaminant with half-lives in soil and sediment greater than six months.

Table 2-3 Degradation half-lives for decaBDE (ECHA, 2012a).

Media	**DT_{50} (days)**
Soil - High	365
Soil - Low	180
Air - High	153.6
Air - Low	15.4
Surface water - High	365
Surface water - Low	180
Ground water - High	730
Ground water - Low	360
Sediment	365

2.2.4 Polybrominated diphenyl ethers in the UK

The only PBDE currently in use in the European Union is decaBDE. It is mostly used as an additive flame retardant in the plastic and textile industries (ECB, 2002). This flame retardant is no longer produced in the UK but imported. The European Chemicals Bureau (ECB) (2002) reported that there was one producer of decaBDE in the UK that operated intermittently and not in large quantities. This site ceased its operations in 1999. DecaBDE was imported without restrictions to be applied to polymers and textile applications until the Directive 2002/95/EC (2003), banned its use in EEE and required the new products placed on the market to not contain polybrominated diphenyl ethers from 1st July 2006. A remaining amount of decaBDE is present in existing EEE until disposal and the compound is still used without restrictions in other polymeric and textile applications (European Commission, 2003).

Decabromodiphenyl ether was applied in a large number of polymeric items with EEE such as computers, wire and cables, electrical boxes etc. and the major application was in high impact polystyrene (HIPS) which is used in the television industry for cabinet backs. The quantity used depended on the type of finished product, usually ranging between 10 and 15% by weight of the polymer application and it was always applied in combination with antimony trioxide (ECB, 2002).

The current use of decaBDE in textiles relates to upholstery fabric and polypropylene drapery applications; it is not used for clothing (ECB, 2002). The United Kingdom Furniture and Furnishing (Fire) (Safety) Regulations (1993, 1989; 1988) regulate furniture, covers and upholstery materials to comply with specified ignition requirements. The UK and Eire are the only countries in the EU with this kind of regulation; therefore, the UK is the country with the largest consumption of decaBDE and upholstered fabrics containing flame retardants in the European Union (ECB, 2004).

According to the ECB (2002), there are thought to be three or four major manufacturers and formulators and three or four smaller ones in the UK. In addition, finishers are considered to account for four large contract coaters and around six smaller ones and also two in-house weaver/coaters. The process of adding the flame retardant to the textiles consists in back coating the flame retardant in a latex binder or in the case of synthetic carpets, it is encapsulated within the polymer fibres (ECB, 2002).

2.2.4.1 Consumption figures

The world demand for decabromodiphenyl ether was 56,100 tonnes in 2001 (BSEF, 2003a). In the 1990s, the total consumption of decaBDE in Europe was estimated to be 9,600 tonnes/year, with 2,500 tonnes/year being used for textiles, 5,800 tonnes/year used in plastics (mostly from EEE) and 1,300 tonnes/year imported as finished articles (ECB, 2002). The industry producing flame retardants estimated that this figure has fallen in the 2000s to between 6,900 and 8,600 tonnes/year (BSEF, 2010; VECAP, 2010). As decaBDE is currently banned for EEE, these figures may have decreased subsequently; however, it may also still be used in some polymer items not associated with EEE like foams and hotmelt adhesives, although the amounts are likely to be small (Brooke et al., 2009; ECB, 2002). It is also indicated that the amount of decaBDE used in textiles in the EU may remain reasonably stable (ECB, 2004). The UK consumption figure for decaBDE used for textile applications is reported to be 1,250 tonnes per year (ECB, 2004); which corresponds to half the consumption figure in the EU. This figure suggests that emissions from textile consumption in the UK might be much higher than in other EU countries.

2.2.4.2 Monitoring in the UK

There have been several monitoring studies on PBDE concentrations in water and sediments in different UK rivers and estuaries, particularly near to possible sources of release.

However, understanding and comparing PBDE monitoring data is complicated because some studies provide concentrations without specifying whether the concentration relates to an individual congener or to the commercial formulation which is a mixture of two or more congeners. Current commercial decabromodiphenyl ether formulation mainly consists of decaBDE (>97%), but older commercial products had much higher levels of other PBDE congeners particularly octaBDE (ECB, 2002). Some of the detectable concentrations are presented below. Monitoring studies demonstrate that decaBDE is a common contaminant in environmental samples and is present in some samples up to levels of milligram per kilogram.

Levels of decabromodiphenyl ether in water

DecaBDE is either non-detectable or present at very small concentrations in surface water in line with its low solubility and high K_{ow} value. Table 2-4 shows levels of decaBDE in water samples reported by the UK Environment Agency (2002). The samples were collected from the Aycliffe sewage treatment plant influent and effluent that receives water from a supplier of PBDEs as well as upstream and downstream of the sewage treatment plant (ECB, 2002). In most of the samples decaBDE was either not detected or detected at concentrations between 0.005 and 0.015 µg/l of dissolved decaBDE and one estimated concentration of 1.2 µg/l in suspended solids.

Table 2-4 Levels of decaBDE in water samples in the UK (ECB, 2002).

Location		Concentration (µg/l)
Aycliffe sewage treatment plant influent		Dissolved – ND Suspended solids – 1.2 (estimated concentration)
Sewage treatment plant effluent		Dissolved – 0.005 Suspended solids – ND
River Skerne	Upstream Aycliffe SWTP)	Dissolved – 0.005 Suspended solids – ND
Demons Beck	Upstream Aycliffe SWTP	Dissolved – 0.015 Suspended solids – ND
Howden Beck	Upstream Aycliffe SWTP	Dissolved – ND Suspended solids – ND
River Skerne	Two locations downstream Aycliffe SWTP	Dissolved – ND Suspended solids – ND
River Tees	Downstream Aycliffe SWTP	Dissolved – ND Suspended solids – ND

ND: Not detected. LOD: 0.005 µg/l.

Levels of decabromodiphenyl ether in sediments

Monitoring data for sediments have been generated in rivers and estuaries near to possible sources of release in the UK. Detectable concentrations are presented in Table 2-5. As expected from its physicochemical properties, decaBDE is more likely to be detected in sediments than in water samples. Detectable concentrations ranged between 5 and 3,190 µg/kg (ECB, 2002). The locations exhibiting the highest concentration were both on the River Calder at Cock Bridge and downstream of a sewage treatment works (STW). The results suggested that the sources of contamination might be via the STW and also from an industrial site upstream (Allchin et al., 1999). The rivers Skerne and Tees also showed high concentrations of decaBDE in the sediments near to decaBDE suppliers and industrial sites in the lower Tees estuary. Allchin et al. (1999) suggested that the major source might be the suppliers of decaBDE at Newton Aycliffe, more than 40 km upstream from the mouth of the Tees.

The ECB (2002) has estimated that the Tees estuary may contain about 0.1 tonnes of decaBDE and that the overall input of this contaminant from the estuary into the North Sea would be a mean of 0.15 tonnes per year (interval limits 0.06 - 0.45 tonnes/year). It is also calculated that the input to the North Sea is 0.2 – 0.8 tonnes/year. In addition, de Boer et al. (2001) carried out a trend study in sediments located in different European rivers where van Zeijl’s (1997) performed an earlier study. The results showed that between 1995 and 2001 almost all the decaBDE concentrations increased by around 50 – 100% (ECB, 2002).

Table 2-5 Detectable concentrations of decabromodiphenyl ether in sediment samples in the UK.

Location		**Concentration** (µg/kg dry wt.)
Avonmouth, furthest upstream[a]		7
River Skerne at Croft-on-Tees[a]	Near to a decaBDE supplier	7
River Skerne at Newton Aycliffe[a]	Near to a decaBDE supplier	64
Howden Beck[a]	Near to a decaBDE supplier	23
Howden Beck[a]	Near to a decaBDE supplier	60
River Skerne, upstream of Howden Beck[a]	Near to a decaBDE supplier	294
River Skerne, downstream of Howden Beck[a]	Near to a decaBDE supplier	95
River Calder at Cock Bridge[a]	Near to a foam manufacturing site	399
River Calder, downstream of STW[a]	Near to a foam manufacturing site	3,190
River Tees at Stockton[b]	Near to a decaBDE supplier	209
Tees estuary, Portrack STW[a]	Industrial area	5
Tees stuary, No. 23 buoy[a]	Industrial area	9
Tees estuary, Philips approach buoy[a]	Industrial area	8
River Ribble, Freckleton saltings[a]	Near to a foam manufacturing site	111
River Humber, Paull[a]		17
Demons Beck[b]	Upstream of a decaBDE supplier	5.8

[a] Allchin et al. (1999) and Law et al. (1996) [b] ECB (2002). LOD: 0.6 µg/kg dry wt.

2.2.5 Polybrominated diphenyl ethers in Colombia

There has not been any known production decaBDE in the Colombia (Ministerio de ambiente y desarrollo sostenible, 2012); however, similarly to other countries, decaBDE has been used as an additive flame retardant in plastics including acrylonitrile butadiene styrene (ABS), high impact polystyrene (HIPS) and polycarbonate (PC) and in the back-coating of textiles (Blaser, 2009). There are no local figures of the amount of decaBDE usage, exports or imports. Inventory studies for the global market in 1999 and 2001 show that the American continent (including North, Central and South America) along with Asia are the main consumers of decaBDE (Table 2-6), about 44% of the global market demand in 2001.

Table 2-6 Global market demand for decaBDE in 1999 and 2001 (tonnes).

	Americas	**Asia**	**Europe**	**Rest of the world**	**Total**	**Reference**
1999	24,300	23,000	7,500	-	54,800	de Boer (2000)
2001	24,500	23,000	7,600	1050	56,100	BSEF (2003a)

In contrast to the high use of decaBDE in textiles in the UK, in Colombia a major source of pollution is thought to come from the inadequate disposal of EEE (Blaser, 2009; Ott, 2008). Each year, large amounts of obsolete electronic products are discarded and accumulate in landfills and illegal dump sites. Given the continuous and rapid development of this industry, most of EEE become obsolete in just two years (Blaser, 2009). One of the biggest concerns about e-waste is the environmental impact when chemicals are released to contaminate soils and then can infiltrate into groundwater or runoff to surface waters. In many developing countries, the extent of the problem associated with e-waste has not yet been determined.

2.2.5.1 Monitoring in Colombia

Information about levels of flame retardants in Colombia is scarce. The only known study was carried out by Baron et al. (2013) in the outlet of the river Magdalena to the Caribbean Sea near the city of Barranquilla, the major port of the country and a highly industrialized and urbanized area. The river Magdalena is one of the most important rivers of the country flowing for approximately 1,500 km with more than 32.5 million people living throughout the basin and covering 24% of the national territory (269,129 km^2) (IDEAM, 2012b). Sediment samples were taken in 2010 and 2011 for 13 sampling stations along the river mouth, the coast and the estuarine area (Baron et al., 2013). The samples were analysed for brominated flame retardants (BFRs) including 38 PBDEs congeners. Large variation of the concentrations was observed between sampling locations and campaigns. In 2010, BFRs were detected in five out of 13 samples with the highest concentration found for decaBDE; detected decaBDE concentrations ranged between 0.59 to 143 µg/kg dwt. In 2011, decaBDE was found in most of the collected samples (8 out of 9 samples) but in smaller concentrations than in 2010, between 0.18 and 1.98 µg/kg dwt (Paez, 2012).

2.2.6 Modelling decabromodiphenyl ether in the environment

Since decaBDE is a widely used flame retardant that has been found in high concentrations in sediments in the UK and Colombia, the present work is focused on this PBDE congener. The modelling tools used in this chapter include 1) fugacity modelling (Mackay, 1979), to assess the potential distribution of decaBDE in environmental compartments in the UK and Colombia; and 2) the GREAT-ER model (CEFIC, 1999), a catchment model coupling a GIS module and a fate model. GREAT-ER is used to simulate the fate of decaBDE in the Calder catchment in the UK.

2.2.6.1 Fugacity modelling

The calculation of the environmental distribution of a substance is a useful tool in assessing the potential environmental impact which provides an understanding of the environmental compartments that can be affected and the expected levels of contamination. Fugacity models also called Mackay-type models are based on the principle of environmental partitioning. This principle states that all substances move between environmental compartments (air, soil, water, sediment and biota) and are subject to environmental partitioning (Mackay, 1979). A chemical substance will move from the compartment of its entry point towards the ones to which it has a higher affinity. From there, the substance can be transferred back to other compartments until reaching equilibrium. A substance can also undergo chemical transformations in each environmental compartment.

The affinity of a substance to a particular compartment depends on its chemical properties. A substance whose solubility (S) in water is high will tend to stay in this compartment. On the other hand, if a substance with high soil adsorption coefficient (K_{oc}) is discharged into the surface water, it will be rapidly adsorbed to the sediment. Volatile substances will have high Henry's constant (H) and can move with air currents reaching areas far from their place of origin, a process called long-range atmospheric transportation. Substances with high n-octanol-water coefficient (K_{ow}) will have high affinity with living organisms and can accumulate in plants and animals, either directly or through food chains.

Fugacity (f) is a physicochemical concept, which has been defined as the tendency of a chemical to escape from one phase to another (Mackay, 1979). This property is measured in pressure units (Pa). Fugacity modelling is applied to an evaluation model of 1 km^2, called "world unit", which is divided into the different environmental compartments. This model introduces the concept of environmental capacity, Z, for each compartment which is related to the chemical concentration at small values (Mackay and Paterson, 1982). Fugacity modelling is divided into levels of increasing complexity. A system in equilibrium is simulated in Level I, where 100,000 kg of the chemical is released to each compartment (Mackay and Paterson, 1991; Mackay et al., 1985a; Mackay et al., 1985b). For this stage, chemical transformation is not taken into account. The results from this level are useful to identify the main compartments where the chemical is most likely to be found. In Level II, degradation and advection losses are included. For this level, a fixed emission amount of 1,000 kg/h is used and the system is also in equilibrium. Results for Level II provide an idea of the overall residence time of the chemical or its persistence and it also identifies the dominant loss processes.

Fugacity Level III calculates the partitioning of a pollutant amongst environmental compartments using more complex and realistic assumptions than the two lower fugacity levels (Mackay and Paterson, 1991; Mackay et al., 1985a; Mackay et al., 1985b). Level III is a non-equilibrium model where the chemical is continuously discharged at a constant rate. The loss processes are advection, degradation reactions and inter-media transport processes.

The fugacity Equilibrium Criterion model (EQC) includes fugacity level III calculations (CEMC, 2003, 2002; Mackay et al., 1996). The user must define emission amounts for each compartment; therefore the distribution and residence times now depend on the model of entry. This simulation is regarded as the most realistic. It provides information on the likely relative importance of inter-compartmental transport rates and a more realistic description of the fate and the expected concentrations in the environment. Input data include the pollutant physicochemical properties. There are options for three types of chemicals: Type 1 is for chemicals that partition into all media; Type 2 non-volatile chemicals; and Type 3 chemicals with zero, or near-zero, water solubility. Other data required are half-life estimates for different environmental compartments (air, water, sediment, aerosols, suspended sediment and aquatic biota), and emission data for each compartment, i.e. how and how much of the chemical enters into the environment. The simulation outputs are the partition coefficients, capacity constant (Z) values and compartmental rate constants and fluxes, known as D-values.

Palm et al. (2002) used a level III simulation to evaluate the partitioning of different PBDEs in environmental compartments. Two simulations were carried out, the first using emission for each individual compartment and then emissions for all of them simultaneously. The typical emission rate of 1000 kg/h was used assuming each chemical to be emitted to the air, water, and soil. Individual emissions in the compartments predicted that nonaBDE tends to remain in the medium to which is discharged. However, for most of the other chemicals when emitted to air, they are predicted to be transported to soil and sediment. When emitted to water the contaminants are transported to sediments with increasing proportion as bromination increases; this is expected since their water solubility decreases as bromination increases. If emitted to soil, brominated compounds tend to stay there due to their high adsorption coefficient. Finally, as bromination extent increases, the contaminants’ affinity for organic carbon and lipid media increases.

2.2.6.2 GREAT-ER model

The GREAT-ER model (Geography-referenced Regional Exposure Assessment Tool for European Rivers) (CEFIC, 1999) combines GIS with a steady-state fate model to predict 'down-the-drain' chemical concentrations in European surface waters along a river or a catchment area. The model is most suited for modelling contaminants that are emitted down the drain from wide dispersive consumer use, or from defined point sources such as SWTP. It can be used for environmental risk assessment and management of chemical in river basins. GREAT-ER permits the evaluation of specific zones, to visualize PECs in specific points and identify hot spots as well as regional averages with a small amount of input data compared to other more complex dynamic river models. This allows the model to achieve “a high degree of accuracy in chemical exposure assessments” for river basins (Schowanek, 2012). This model also uses European regulations and methodology to calculate predicted environmental concentration (PEC) values. The sediment module for GREAT-ER is able to predict concentrations of contaminants in both water and sediments phases along the river network. Input data include basic chemical properties, degradation data for different environmental compartments, river and WWTP removal data, and the emission data per capita (Koormann et al., 2006).

Monitoring programmes to evaluate GREAT-ER have been carried out in European catchments including studies in Yorkshire (UK), Lambro (Italy), Itter (Germany) and Rupel (Belgium). The studies have shown very good agreements between modelling results and monitoring data (CEFIC, 1999). The model has been used successfully to assess the exposure of personal care products, detergents and pharmaceuticals (Pistocchi et al., 2012; Cunningham et al., 2009). More than 175 publications using GREAT-ER have been published to date for different environmental issues. However, there are no reported studies using GREAT-ER for brominated flame retardants. In the present project GREAT-ER will be used to assess the chemical concentrations of BFRs in the Calder catchment in the UK and the results will be evaluated against sediment data generated in this study.

2.2.7 Calder catchment

The Calder catchment is located in West Yorkshire, Northern England. The catchment comprises 957 km^2 and its main river, the Calder, flows for approximately 72 km from its source at Heald Moor near Todmorden to its confluence with the River Aire near Castleford. The main river tributaries include the River Hebble and Colne. Nearly 770,000 people live within the catchment area (UK Environment Agency, 2010). Major urbanised areas in the catchment are located in Huddersfield, Dewsbury, Halifax, Todmorden and these heavily pollute the river. Organizations such as Calder Future, local industries and Yorkshire Water have worked together to improve the water quality of the river (Calder Future, 2014). Despite these efforts the catchment continues to be a heavily industrialized area including textile and polymeric sites with a potential environmental input of flame retardants.

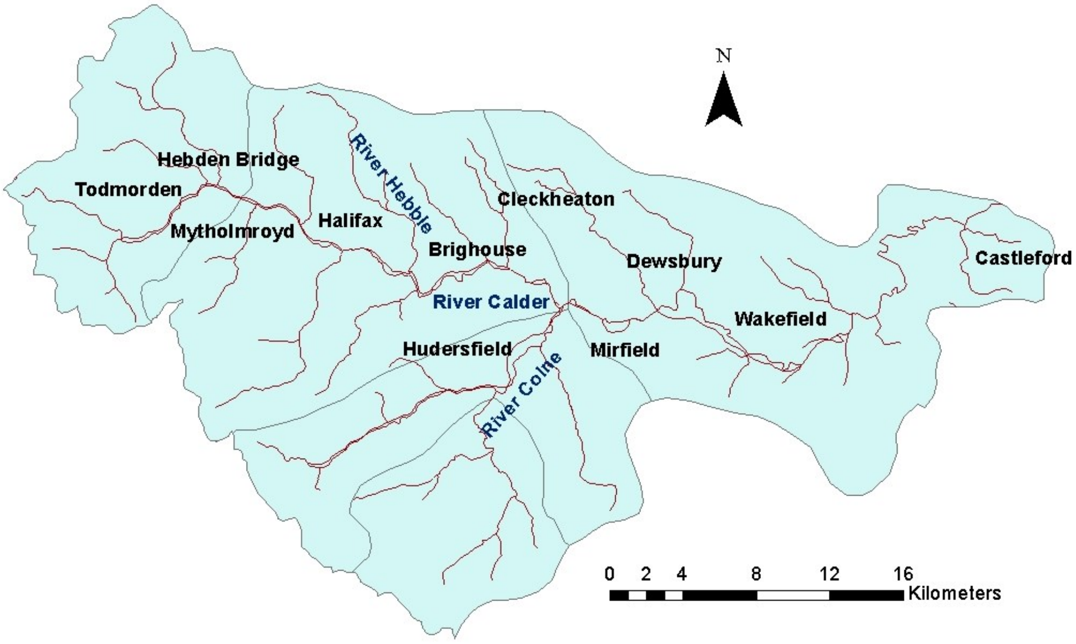


Figure 2-2 Location of the Calder catchment and its subareas.

2.3 Methodology

2.3.1 Decabromodiphenyl ether in the UK

2.3.1.1 Emission calculations

Consumption estimates are derived from the latest reported global European figures which range between 6,900 and 8,600 tonnes/year (BSEF, 2010; VECAP, 2010). The smallest value of the range was used in the calculations since a reduced consumption is expected nowadays due to increasing restrictions and improvements in the recycling and disposal of WEEE. Since decaBDE consumption in textile is expect to remain constant (ECB, 2002), polymeric consumption could have fallen to 4,200 tonnes/year of which 20% were estimated to be imported as finished articles, following relative estimates from the ECB (2002).

European methodologies to calculate emissions of decaBDE (ECB, 2004, 2002) including global and per capita consumption figures for Europe and the UK are used to estimate emissions of decaBDE in the UK. European emission values of decaBDE were calculated by the European Chemicals Bureau (ECB) (2004) using results from different studies including one carried out by the industry producing flame retardants, the Bromine Environmental Science Forum (BSEF), which investigated emissions to air and water from six plastic and three textile sites using decaBDE in the EU.

In the present study, individual emissions for each processing stage of polymers and textiles in the UK are calculated and then added together to estimate global emission values of decaBDE for each environmental compartment. Emissions from production are not calculated since there is no current production of decaBDE in the UK.

Polymeric applications

Emissions from polymeric applications are expected to be considerably reduced since decaBDE was banned for electric and electronic applications; however, this flame retardant is used in other polymer items like foams and hotmelt adhesives (Brooke et al., 2009; ECB, 2002). Emissions from polymeric applications are expected to come from the processing sites, their service life and recycling (Figure 2-3) (ECB, 2002). Since no consumption figures of decaBDE are available for polymeric applications in the UK, this figure is calculated considering the estimated EU consumption figure of decaBDE for plastic and polymer applications of 4,200 tonnes per year. In 2010, the EU27 population was about 501 million and in the UK 62 million (United Nations, 2010). Based on the consumption per capita in Europe, the UK consumption of decaBDE is estimated to be 520 tonnes/year of which 104 tonnes/year would enter the country as finished articles.

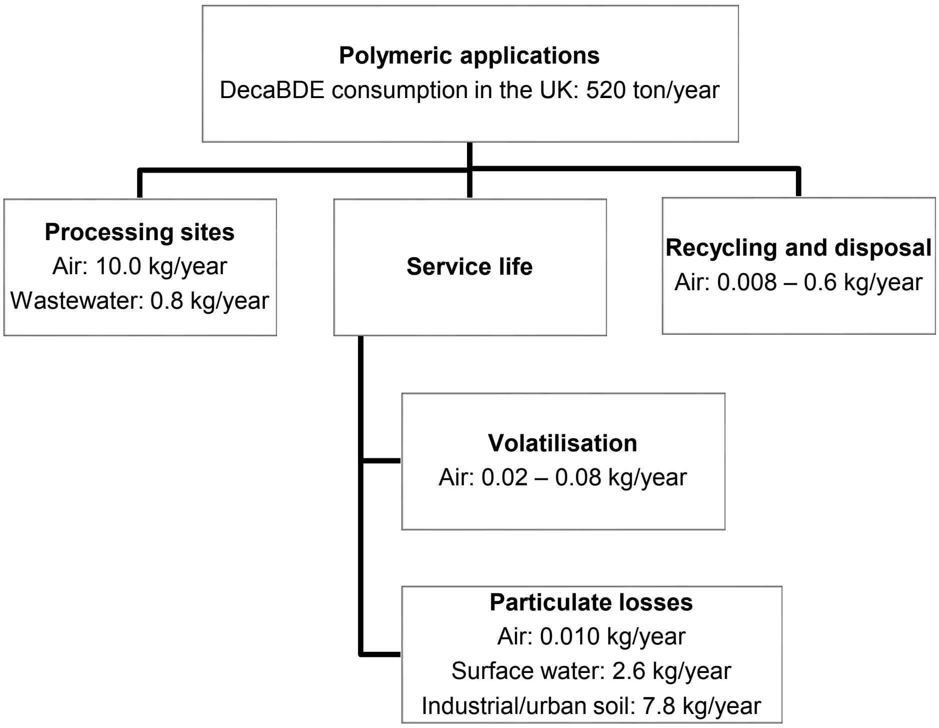


Figure 2-3 Consumption figure and losses of decaBDE from different stages in polymeric applications.

Emissions of decaBDE coming from polymer processing sites are reported to be due to losses of powders when handling raw material and also from the compounding stage. Both processes are susceptible to dust generation. Losses will be as dust to solid waste (which could be recycled or disposed), wastewater and small amounts to wastewater streams (when washing or cleaning down floors and equipment). In addition, there will also be an emission from the volatilisation of the flame retardant at high processing temperatures (ECB, 2002).

The ECB (2004) reported calculated emissions of decaBDE from processing sites to air and water in the continent to be 81.0 and 6.6 kg per year, respectively. Assuming that the UK has 12.4% of the total European consumption, the emission in this country to air and water would be 10.0 and 0.8 kg/year, respectively.

Emissions of decaBDE from polymers during service come from volatilisation and particulate losses from products in use and particulate losses during recycling and disposal (ECB, 2004). The ECB (2004) calculated emissions from volatilisation from polymeric products using the results from research carried out by Kemmlein et al. (2003), which determined the volatile emissions of PBDEs from a variety of products including insulation materials, assembly foam, upholstery/mattresses and electronic equipment. Emission factors of between 0.29 and 1.05 kg/year were calculated for Europe from plastic articles for 7,100 tonnes/year (i.e. the consumption figure and the imported product). Therefore, the volatilisation emission of decaBDE for the UK, which has a consumption plus import figure of 520 tonnes of polymers with decaBDE per year, would be 0.02 – 0.08 kg/year.

The particle losses from products in use are primarily released to industrial/urban soil, air and surface water. This type of waste is generated when using outdoor products and during polymer disposal. Particulate losses of 0.14 kg/year to air, 35.3 kg/year to surface water and 106.5 kg/year to industrial/urban soil were calculated for Europe (ECB, 2004). Therefore, the expected particulate losses from products in use in the UK would be 0.010, 2.6 and 7.8 kg/year to air, surface water and industrial/urban soil, respectively. Finally, the estimated emission to air from the recycling of polymers in Europe is reported to be 0.11 – 8.8 kg/year (ECB, 2004). Therefore, this emission for the UK would be 0.008 – 0.6 kg/year.

Textile applications

Emissions from textile applications are expected to come from the processes of formulation and back-coating at processing sites, their service life and recycling (Figure 2-4) (ECB, 2002). The sources of release during formulation and application of decaBDE to textiles are the dust generated when adding the flame retardant powder into the pre-mixer and also release to wastewater during the back-coating process and when washing out equipment (ECB, 2002). The ECB (2004) reported emissions of decaBDE from textile sites to air and water in Europe to be 3.7 and 166 kg per year, respectively. It is considered that the consumption figure of decaBDE for textile applications is 2,500 tonnes per year in Europe, where 1,250 tonnes per year correspond to the UK. Therefore, the emission in the UK to air and water would be 1.8 kg/year and 83 kg/year, respectively.

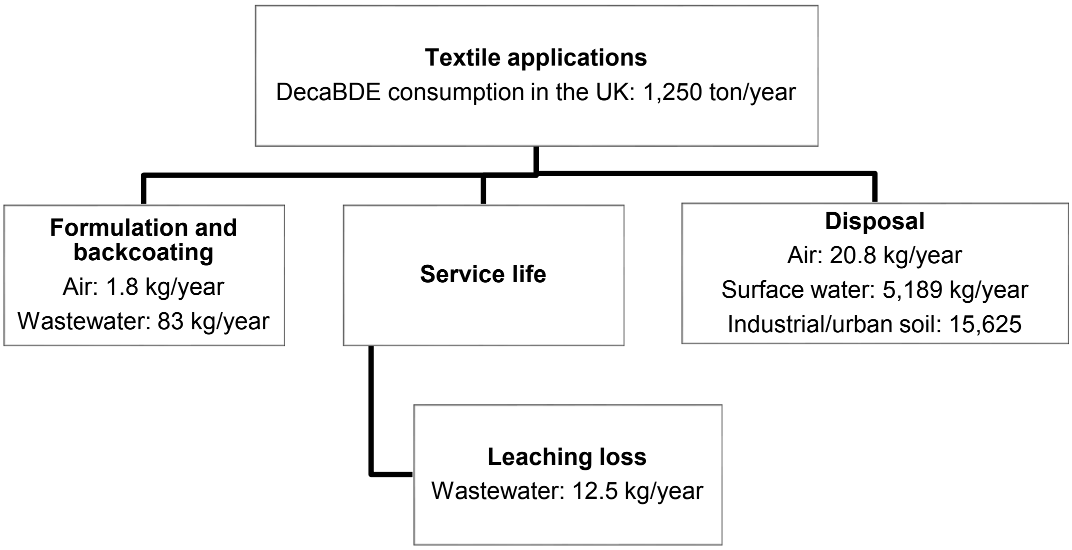


Figure 2-4 Consumption figure and losses of decaBDE from different stages in textile applications.

The ECB (2004) considered that 2% of the textiles with decaBDE are subject to washing and that the leaching loss of decaBDE over a textile lifetime is 0.05%. Considering these figures, the emission of total decaBDE can be estimated to be 12.5 kg/year to wastewater in the UK. Finally, the ECB (2002) suggested a particulate loss of decaBDE in textiles from disposal of 2%, and the releases are thought to end up to industrial/urban soil (75%), surface water (24.9%) and air (0.1%). Using these assumptions to calculate for the UK, the calculated emissions are 20.8 kg/year to air as dust, 5,189 kg/year to surface water and 15,625 kg/year to industrial/urban soil.

2.3.1.2 Fugacity modelling

The fugacity Equilibrium Criterion model (EQC) version 2.02 was used to estimate the environmental partitioning of decaBDE in different environmental compartments in the UK. Levels I, II and III were applied using reported physicochemical parameters for decaBDE (Table 2-1 and Table 2-3). The predicted concentrations and release amounts for level III should be interpreted as an average for an area of 10,000 km^2. The input emission data used for level III are the ones calculated from the methodology in Section 2.3.1.1. Wastewater and surface water emissions were added to the water compartment in the model.

2.3.1.3 Simulation of decaBDE in the Calder catchment using GREAT-ER

The GREAT-ER model was used to study the fate and behaviour of decabromodiphenyl ether in the Calder catchment in the UK. Before running the model it was necessary to collect information about: 1) the geographical location of the population settled in the catchment and 2) geographical location of the possible sources of decaBDE release such as flame retardant suppliers, foam manufacturing, textiles and other industrial sites. This information was brought together from an online survey map of the study area from the UK Environment Agency (2011). The map includes annual information about the location of industrial sites including a description of their processing activities, type of industry and concentrations released to the environment for authorised substances.

Potential release sites were identified according to the type of industries (Table 2-7). Emissions figures were calculated using the emission data from processing sites from the EU risk assessment (0.5 kg of decaBDE per year to wastewater for a polymer site and 7 kg of decaBDE per year to wastewater for a textile site) (ECB, 2004; BSEF, 2003b). Emission of decaBDE to surface and wastewater per capita for the UK were also calculated using the results from the calculated emissions (Section 2.3.1.1) and added as input data in GREAT-ER. The total decaBDE released to water sources (surface water and wastewater) for the UK is 5,288 kg/year. Therefore, the emission of decaBDE surface and wastewater per capita for the UK is 8.53×10^{-5} kg/(year.cap).

Table 2-7 Potential sites for decaBDE releases in the Calder catchment.

Location	**Sites**	**Estimated releases to wastewater (kg/year)**
Sowerby Bridge	A polymer site (polyurethane foam)	0.5
Halifax	A polymer industry	0.5
Ripponden	A chemical site with textiles (carpets)	7
Huddersfield	A textile site	7
Dewsbury (Batley)	A textile site carpet, compounds and foam	7
Dewsbury (Batley)	A plastic, polymer and coating industry	0.5
Dewsbury	Two textile site carpet industry	14
Dewsbury (Heckmondwike)	A textile site – carpets and rugs manufacturer	7
Cleckheaton	A plastic, adhesives and coating industry polymer	0.5

Additional input parameters included information about the removal of decaBDE from treating wastewater which was gathered from a mass balance of decaBDE carried out in a WWTP in Stockholm which calculated removal values from the different treatment stages in the plant (Ricklund et al., 2009) (Table 2-8). The removal for sewer was estimate from the difference between these values and the total estimated removal during wastewater treatment reported by Kolic et al. (2005) of 93%. Following this methodology, GREAT-ER was used to generate a concentration map with decaBDE concentrations for the Calder catchment.

Table 2-8 Removal input values included in GREAT-ER for the simulation of decaBDE in the Calder (Ricklund et al., 2009).

Removal stage	Removal (%)
Sewer*	25
WWTP primary settler	57
Activated sludge plant	8
Trickling filter plant	3

*Estimated

2.3.1.4 *Sediment monitoring in the Calder Catchment*

Seven sediment samples were collected on May 11th 2014 from different locations in the Calder catchment to study the occurrence of PBDEs in sediments and to generate data for model evaluation. The sampling locations (Figure 2-5) were selected according to model results covering different concentration ranges; locations are shown. A Van Veen grab of 0.5 liter was used to collect surface sediment samples from the top of bridges. Pre-treatment of the samples involved air-drying and passing through a 2 mm-mesh sieve. Sample sizes varied along the river due to issues with the high river depth, flow, presence of rubbish and stony bottom when moving downstream in the catchment. Sample sizes sent for analysis were 100.0 g from locations between Luddenden and Mirfield, 22.2 g from Bride Road, 9.69 g from Wakefield and 12.7 g from Stanley. However, due to the high sensitivity of the analytical method and expected large concentrations, samples sizes were not an issue for the analysis. Samples were sent for analysis of decaBDE and other congeners at the Food and Environmental Research Agency (FERA) in York.

The target PBDE analytes included tri- (BDE-17 and BDE-28/33), tetra- (BDE-47, BDE-49, BDE-66, BDE-71 and BDE-77), penta- (BDE-85, BDE-99, BDE-100, BDE-119 and BDE-126), hexa- (BDE-138, BDE-153 and BDE-154), hepta- (BDE-183), and deca- (BDE-209) bromodiphenyl ether congeners. These PBDE congeners were selected on the basis of their relatively high content in the commercial products (SFT, 2009; Schlummer et al., 2007; La Guardia et al., 2006; Hites et al., 2004) and others which can only occur from debromination since they were not reported in formulations. This would help to identify profile patterns and signs of debromination. They are also the most frequently detected congeners in the environment.

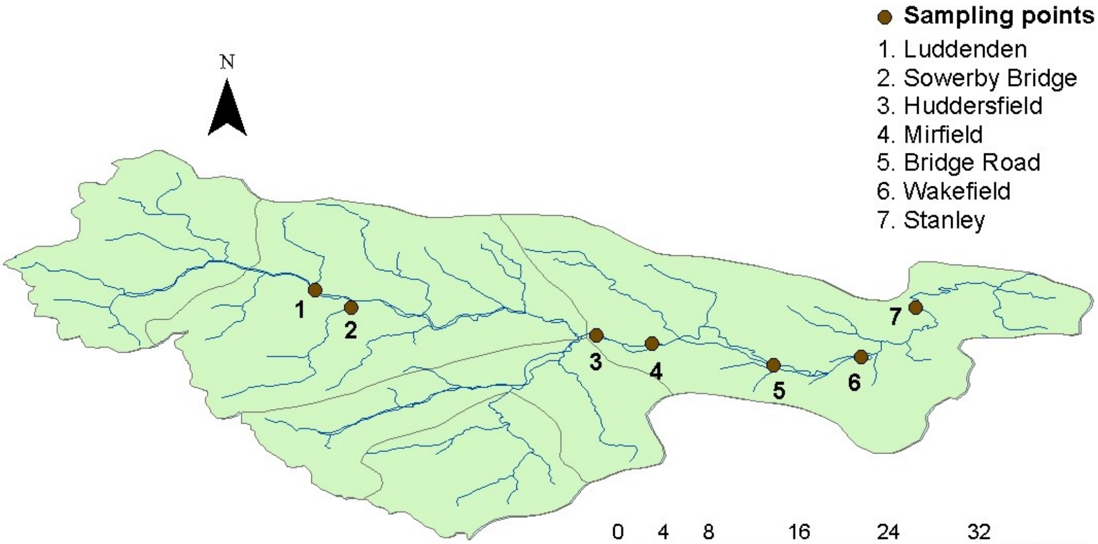


Figure 2-5 Map with the location of the sediment samples collected in the Calder catchment.

2.3.2 Decabromodiphenyl ether in Colombia

2.3.2.1 Inventory of decaBDE in Colombia

An inventory on decaBDE is the first step to acquire an understanding of the national situation concerning this chemical. The Stockholm convention has provided technical guidance for inventory of POP-PBDEs (UNEP, 2012). The inventory aims to gather information related to the past and current production and uses, present products containing the chemical in finished articles on the market, recycling and disposal. In the present study an initial assessment and preliminary inventory of decaBDE in Colombia were carried out (Tier I and II, respectively) for polymer and textile applications; the inventory was focused on the use of decaBDE in EEE and carpets, respectively.

Inventory of decaBDE in EEE/WEEE

The inventory commenced by gathering existing information about usage of decaBDE in Colombia and inventory data on articles contain decaBDE mainly EEE, waste EEE (WEEE) and textiles. The main EEE/WEEE devices that contain decaBDE in Colombia belong to categories 1 (large household appliances), 3 (IT and telecommunications equipment) and 4 (consumer equipment) covered by the EU WEEE Directive (European Commission, 2003). In Colombia, Blaser (2009) has undertaken an inventory of EEE/WEEE for the first (refrigerators and washing machines) and the fourth (televisions), video (VHS, Betamax and DVD) and audio (radios, stereos, Hi-Fi, DVD discs and cassettes, speakers and amplifiers) categories and Ott (2008) for the third (computers and mobile phones) category. The total amount of decaBDE in EEE was calculated using Equation 2-1:

Equation 2-1 $M_{\mathrm{decaBDE}} = M_{\mathrm{EEE}(j)} \times f_{\mathrm{Polymer(k)}} \times C_{\mathrm{decaBDE}(i);\mathrm{Polymer(k)}}$

where M_{decBDE} is the amount of decaBDE in kg (in the polymer (*k*) of EEE (*j*)), $M_{\mathrm{EEE}(j)}$ is the amount of EEE (*j*) in tonnes (either imported, stockpiled or disposed), f_{Polymer} is the total polymer fraction in the EEE, and $C_{\mathrm{decaBDE}(i);\mathrm{Polymer(k)}}$ is the content of decaBDE (*i*) in the total polymer fraction in kg/tonne (UNEP, 2012). Therefore, the information needed includes the amount of EEE/WEEE in Colombia (Table A2– 1) and their weight (Table A2– 2), information about the amount of polymers in the different EEE/WEEE (Table A2– 3) and the content of decaBDE in those polymers (Table A2– 4). DecaBDE contents in finished products usually ranges between 10 and 15% by weight of the polymer application (ECB, 2002).

Inventory of decaBDE in textiles

Reported information about the production, imports and exports figures of carpets in Colombia from 1999 to 2009 was the base of the inventory (Table A2– 5). The apparent consumption of carpets in 2010 was 101,936 tonnes. DecaBDE is reported to be applied to textiles by back-coating in the range of 7.5 and 20% (ECHA, 2012a, b). Reported amounts of decaBDE used for back-coating textiles range were used in the inventory since there is no regulation of the maximum amount of decaBDE used in Colombia.

2.3.2.2 Emission calculations

Polymer applications in EEE/WEE

Emissions of decaBDE were calculated following the methodology described by the ECB (2002, 2004) since there is no available information about emissions of this compound in Colombia. The estimated amount of decaBDE used for EEE production in 2010 was 3.8 tonnes based on production figures and using Equation 2-1. Emissions from use in polymer applications can occur during handling of the chemical, compounding and conversion, volatilisation and waste remaining in the environment from the use of products containing the flame retardant and from disposal (Figure 2-6).

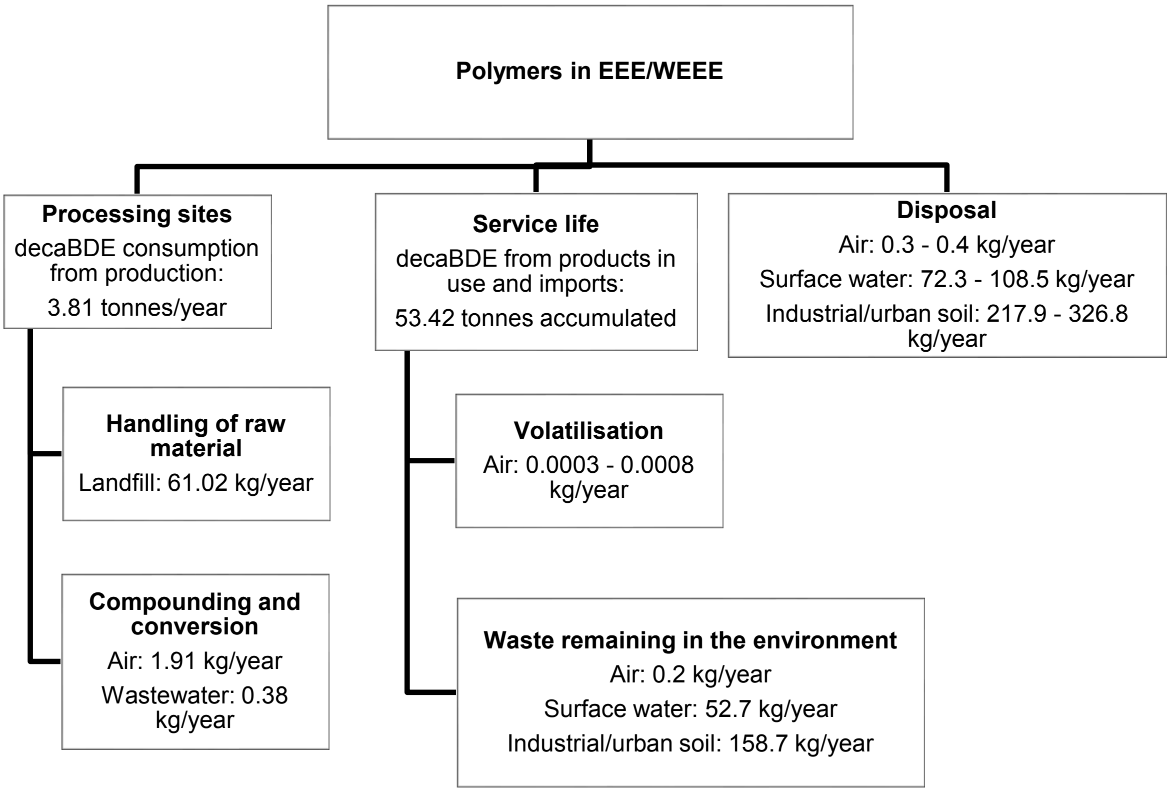


Figure 2-6 Consumption figure and losses of decaBDE from different stages of polymers in EEE/WEEE applications in Colombia.

Losses of powders during the handling of raw flame retardant can account for up to 1.6% of the handled material; this is expected to be disposed to landfill but it is possible that a small amount could reach wastewater. Compounding is thought to contribute to dust generation but in lower amounts than in the handling stage which in a worst case scenario can be around 0.06% (UCD, 1994) (0.05% to wastewater and 0.01% to air).

Kemmlein et al. (2003) studied the volatilisation behaviour of PBDEs including decaBDE. This study found an emission rate of decaBDE of 0.28 ng/m^2/hour for a TV casing which was used by ECB (2002) to calculate emission to air from this route in Europe. This emission rate was also used to calculate the emission rate in kg per year due to volatilisation of decaBDE from EEE in Colombia using a similar methodology to that in Europe (ECB, 2004, 2002): i) the total amount of polymer in EEE equipment from articles imported and in use in 2010 was estimated to be 534 tonnes (from the inventory data); ii) the amount of decaBDE in those plastics was estimated to range between 53.4 and 80.1 tonnes (the typical concentration of decaBDE in plastics is between 10 and 15%); iii) assuming a density of 800 kg/m^3 and that the plastic used in finished EEE articles has a typical thickness of 2 to 5 mm, the total surface area of plastic containing decaBDE can be estimated to be between 1.34 x 10^5 and 3.34 x 10^5 m^2 in 2010. Therefore, using the reported emission factor of 0.28 ng/m^2/hour, the total emission of decaBDE due to volatilisation in Colombia would be between 3.28 x 10^{-4} and 8.19 x 10^{-4} kg/year.

The waste remaining in the environment refers to any particulate loss of decaBDE from the normal use of products containing the flame retardant. These particles are thought to end up mainly in industrial/urban soil but some could also be released to surface water and air. A similar approach to the one taken in a risk assessment for di-(2-ethylhexyl) phthalate (RAR, 2000) was used to estimate decaBDE losses in Europe (ECB, 2002) was used here. The approach involves several assumptions, some of them include: i) the amount of decaBDE in articles disposed each year is the same as for new articles; this would be true for the case of Colombia until the phase out of EEE products containing decaBDE in 2013; ii) only outdoor applications are considered to contribute significantly to the emissions; emission products for outdoor use are 10%; iii) the total release of decaBDE from articles over their service life is 2%; iv) emissions can also occur at disposal; v) the partitioning of emissions to soil, surface water and air is 75, 24.9 and 0.1%. Therefore, the calculation steps and the estimated waste remaining in the environment from EEE in Colombia are shown in Table 2-9.

Table 2-9 Calculation steps of waste remaining in the environment over the lifetime of products containing decaBDE in Colombia.

Calculation step	Amount (kg)
Remaining decaBDE after volatilisation	53,427
Total amount in plastics for outdoor applications (10%)	5,343
Amount loss of 2% over lifetime	106.9
Total amount remaining in plastics at disposal	5,236
Emissions at disposal of 2%	104.7
Amount in EEE for disposal	5,131
Estimated amount of waste remaining in the environment	211.6
75% to industrial/urban soil	158.7
24.9 to surface water	52.7
0.1% to air	0.2

The ECB (2004) calculated emissions of decaBDE from plastic articles using data from a recycling facility of WEEE in Japan. However, in Colombia the WEEE is normally sent to landfill since recycling of these articles continues to be minimal. A similar approach to the one used previously about emissions from waste remaining in the environment was used to calculate the emissions from WEEE at disposal (Table 2-10). In this case, the calculated decaBDE in WEEE in 2010 at the inventory stage was used. Then, the amount loss during the service life of outdoor applications was removed to avoid double counting. A 2% emission at disposal was also applied to estimate the total decaBDE loss at this stage which was then partitioned using the pattern, 75% to industrial/urban soil, 24.9% to surface water and 0.1% to air.

Table 2-10 Calculation steps of waste remaining in the environment at disposal of products containing decaBDE in Colombia.

Calculation step	Amount in (kg)
Amount of decaBDE in WEEE in 2010	14,555 – 21,832
Amount from previous outdoor applications (10%)	1,455 – 2,183
Amount loss of 2% over lifetime	29.1 – 43.7
Amount loss from outdoor applications	14,526 – 21,788
Emissions at disposal of 2%	290.5 – 435.8
75% to industrial/urban soil	217.9 – 326.8
24.9% to surface water	72.3 – 108.5
0.1% to air	0.3 – 0.4

Textile applications in carpets

The estimated amount of decaBDE used in textiles in 2010 in Colombia would be around 7,645 to 20,387 tonnes (Section 2.4.2.1). Emissions of decaBDE from formulation and back-coating of carpets in Colombia are thought to have a similar behaviour to the UK since this process is not expected to differ significantly between countries (Figure 2-7). Therefore, for a decaBDE usage between 7,645 and 20,387 tonnes in 2010 for back-coating of carpets the estimated emissions to air and water would be 11 – 29 kg/year and 508 – 1,355 kg/year, respectively.

Leaching loss from products in use was estimated assuming that textiles subject to washing account for 2% of the total decaBDE usage and the total decaBDE loss from washing is 0.05% over the life time of the product. Therefore, a total leaching loss of 76 – 203 kg/year could be released to wastewater.

Particulate losses at disposal can be estimated following the procedure used for polymers. A 2% loss was assumed to occur from products containing decaBDE, and their releases were thought to end up in industrial/urban soil (75%), surface water (24.9%) and air (0.1%). The estimated decaBDE released to those media are 115 – 306, 38 – 102 and 0.1 – 0.3 kg/year, respectively.

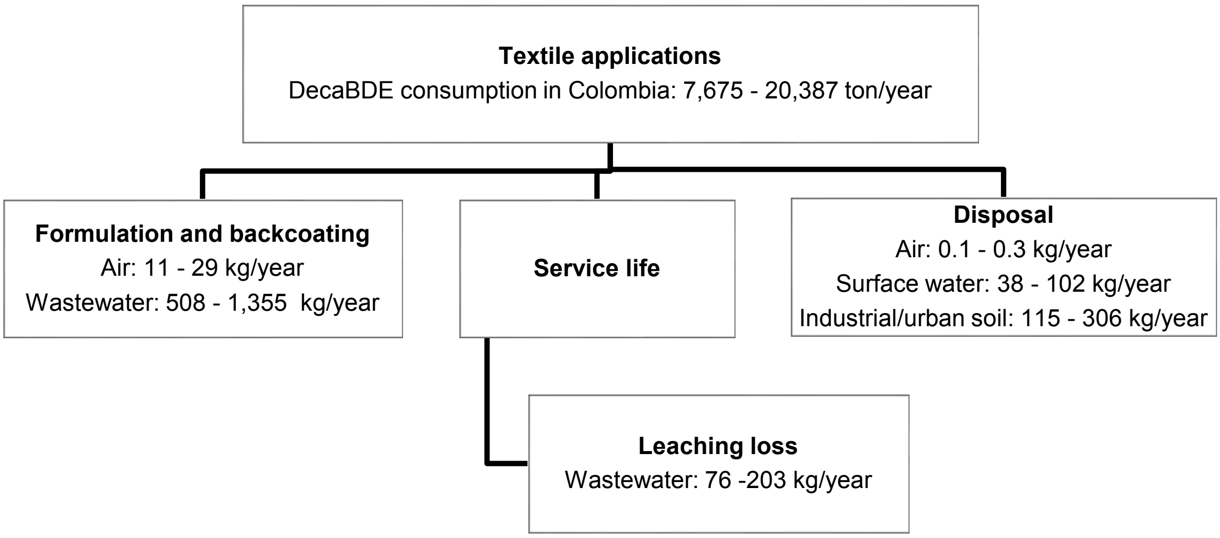


Figure 2-7 Consumption figure and losses of decaBDE from different stages in textile applications in 2010 in Colombia.

2.3.2.3 Fugacity model

Similarly to the UK modelling, fugacity level III was applied to estimate the environmental partitioning of decaBDE in different environmental compartments from emissions due to EEE/WEEE and carpets in Colombia using the emission estimated in Section 2.3.2.2. Modelling results were evaluated against reported monitoring data in the outlet of the River Magdalena (Section 2.2.5.1).

2.4 Results

2.4.1 Decabromodiphenyl ether in the UK

2.4.1.1 Estimated emissions

The estimated emissions of decaBDE for the UK are summarised in Table 2-11. Emission results showed that decaBDE can be released into the environment during its incorporation process into products, products use and after disposal. The most important source of release is the particulate loss during textile disposal (99.4% of the global emissions). Considering expected behaviour of the contaminant from its physicochemical properties, the decaBDE in soil is expected to be strongly absorbed to the soil particles and therefore will remain unmovable. Thus, the main concern to the environment is when decaBDE is released to surface water and wastewater.

Table 2-11 Calculated emissions of decabromodiphenyl ether in the UK.

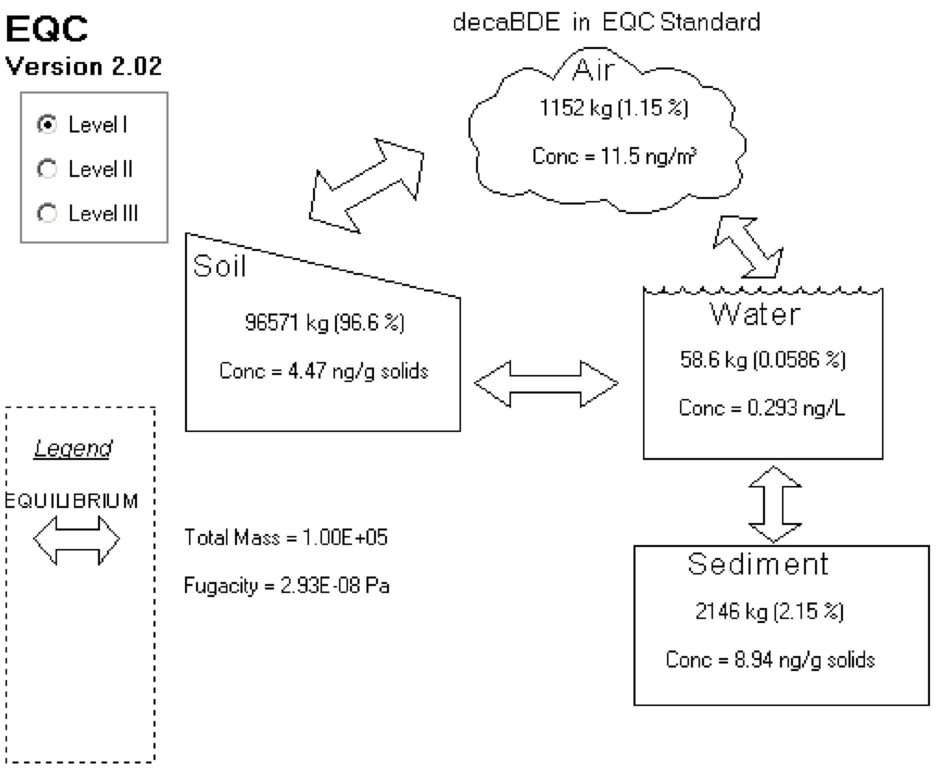
	Scenario	**Releases in the UK (kg/year)**	
Polymers	Processing sites	10.0	to air
		0.8	to wastewater
	Volatilisation	0.02 – 0.08	to air
	Particulate loss	0.01	to air
		2.6	to surface water
		7.8	to industrial/urban soil
	Recycling	0.008 – 0.6	to air
Textiles	Formulation and back-coating	1.8	to air
		83	to waste water
	Leaching loss	12.5	to wastewater
	Particulate loss during disposal	20.8	to air
		5,189	to surface water
		15,625	to industrial/urban soil
	Maximum global emission figures for the UK	33	to air
		5,211	to surface water
		77	to WWTP
		15,633	to industrial/urban soil

2.4.1.2 Fugacity Model

The fugacity distribution diagram for level I when the system is in equilibrium (Figure 2-8) showed that the vast majority of the decaBDE is predicted to be partitioned into soil (96.6%) and sediment (2.15%). A noticeable amount of 1.15% is partitioned to air. Partitioning to water was small 0.06%.

The introduction of degradation and advective outflows in the compartments (Level II) (Figure 2-9) showed the same partitioning as at level I. The dominant loss process was degradation in soil. The high advective value to air demonstrates the long-range atmospheric transport potential of decaBDE which agrees with studies that have reported the contaminant to be present in the Polar regions (Desonie, 2008; Gouin and Harner, 2003).

The fugacity distribution diagram for level III when using the calculated emissions to different compartments in the UK (Figure 2-10) showed that most of the decaBDE was partitioned to soil (86.2%) and sediment (12.9%). Partitioning to water and air were small (0.74 and 0.066%, respectively). The most important inter-media exchange was from water to sediment (0.367 kg/h) and from water to air (0.128 kg/h). The estimated decaBDE concentration in sediment was 10.5 µg/kg which is within the range of detectable concentrations in sediment in the UK (5 – 3,191 µg/kg).

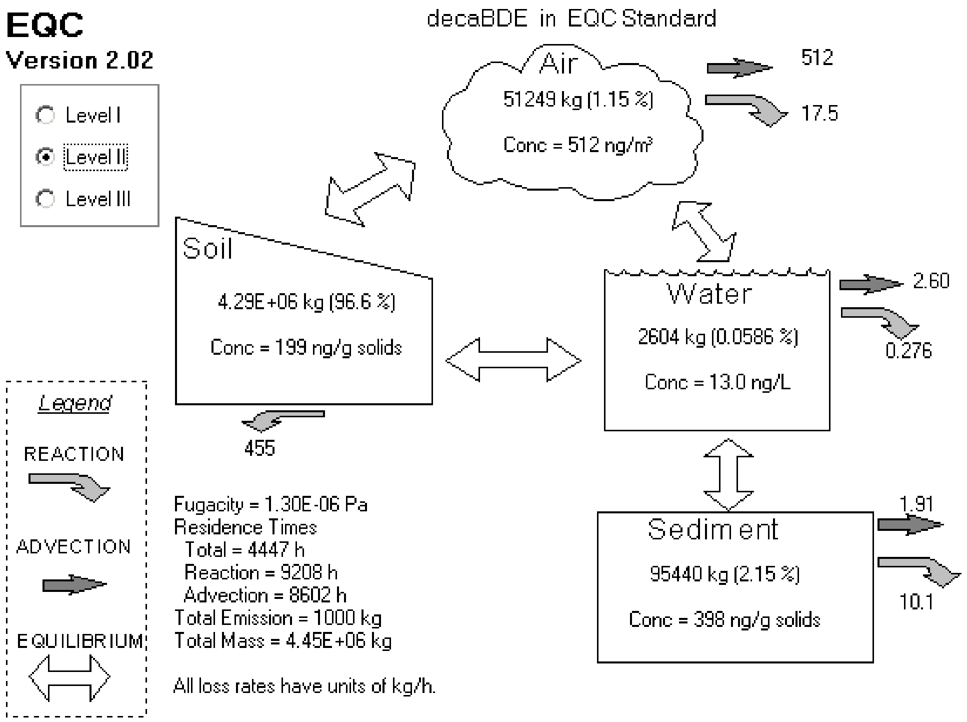


● Level I
○ Level II
○ Level III

Total Mass = 1.00E+05

Fugacity = 2.93E-08 Pa

Figure 2-8 Fugacity distribution diagram for level I.

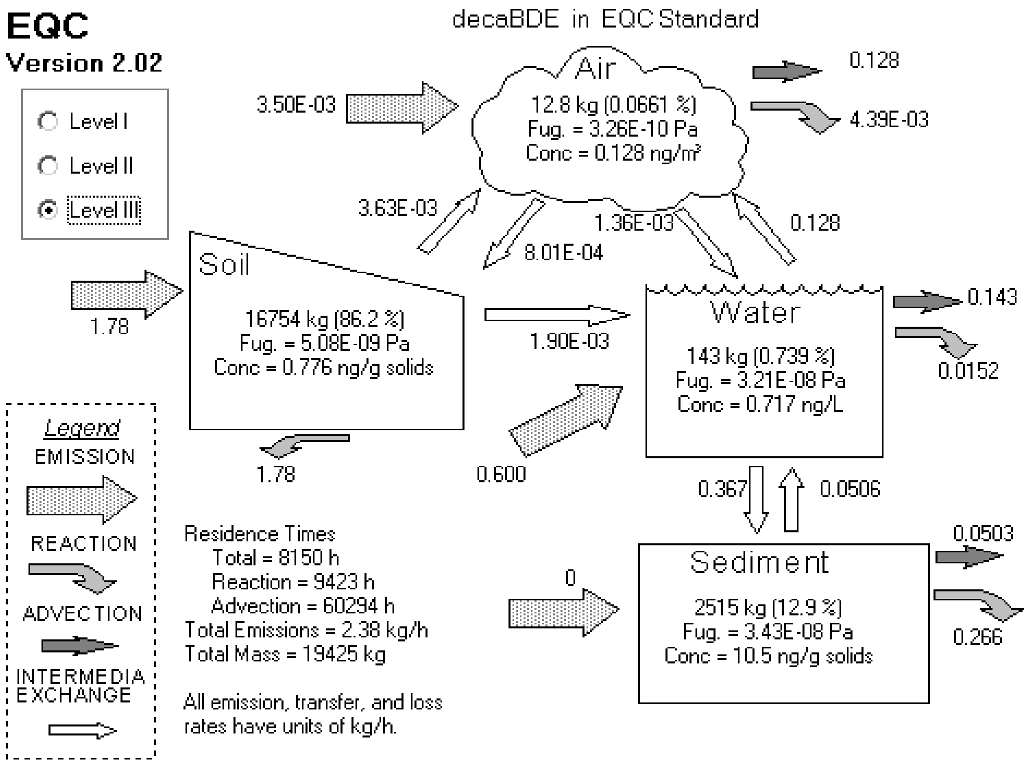


○ Level I
● Level II
○ Level III

Fugacity = 1.30E-06 Pa
Residence Times
Total = 4447 h
Reaction = 9208 h
Advection = 8602 h
Total Emission = 1000 kg
Total Mass = 4.45E+06 kg

All loss rates have units of kg/h.

Figure 2-9 Fugacity distribution diagram for level II.



○ Level I
○ Level II
● Level III

Residence Times
Total = 8150 h
Reaction = 9423 h
Advection = 60294 h
Total Emissions = 2.38 kg/h
Total Mass = 19425 kg

All emission, transfer, and loss rates have units of kg/h.

Figure 2-10 Fugacity distribution diagram for level III in the UK.

2.4.1.3 Monitoring decaBDE in sediments in the Calder catchment

Monitoring concentrations from sediment samples along the Calder catchment are shown in Table 2-12. Unfortunately, some of the concentrations were under-estimated in the analysis due to saturation of the detector so they are presented as indicative concentrations. Diluted extracts are also indicative as at these concentrations, the measurement of the internal standard was affected and the value would be beyond the measured linearity range. This was the case for decaBDE in most of the samples and for BDE-47 and BDE-99 at Stanley. Indicative concentrations have different levels of under-estimation (small, medium or large marked as *, ** and *** in Table 2-12), based on the relative response of the analytes. The worst under-estimation is likely to be for BDE-209 measurement for the sediment sample at Stanley; the reported value of 2,622 µg/kg could actually be between 25,000 and 100,000 µg/kg. In addition, some of the concentrations were under-estimated because of the contribution to the measurement of the internal standard (^{13}C) from the native (^{12}C) since the concentration of the natives was very large for some of the samples (i.e. the calculated recovery of BDE-209 appeared to be much higher than it should be) so in the worst case the native concentration could be under-estimated by a factor of up to 50 times.

Table 2-12 Concentration of PBDEs in sediment samples (in µg/kg dwt) from the Calder catchment.

PBDE	Luddenden	Sowerby Bridge	Huddersfield	Mirfield	Bridge Road	Wakefield	Stanley	Percentage in samples (% of the total)
				(µg/kg dwt)				
17	<0.002	0.002	0.040	0.045	0.045	0.109	2.10	0.05
28/33	0.005	0.007	0.065	0.078	0.073	0.241	4.84	0.11
47	0.168	0.149	1.14	1.47	1.52	7.65	85.2**	2.05
49	0.011	0.015	0.143	0.188	0.177	0.615	13.9	0.32
66	0.010	0.012	0.068	0.094	0.090	0.342	6.01	0.14
71	<0.002	0.002	0.020	0.040	0.022	0.091	1.81	0.04
77	<0.002	<0.002	0.002	0.004	0.004	0.015	0.201	<0.00
85	0.007	0.007	0.068	0.074	0.069	0.447	10.6	0.24
99	0.152	0.164	1.81	2.04	1.821	11.6	150**	3.54
100	0.028	0.030	0.325	0.370	0.308	2.11	64.1	1.42
119	<0.002	0.003	0.005	0.009	0.006	0.028	0.471	0.01
126	<0.002	<0.002	<0.002	<0.003	<0.002	<0.002	<0.007	0.0
153	0.014	0.024	0.184	0.259	0.156	1.23	31.6	0.71
138	<0.003	<0.005	0.032	0.047	0.021	0.152	3.11	0.07
154	0.010	0.016	0.111	0.162	0.106	0.871	28.36	0.63
183	0.014	0.023	0.028	0.078	0.034	0.228	2.15	0.05
209	10.9	49.7*	41.3 *	468***	164*	935***	2620***	90.6

* Indicative results - they are likely to be underestimates due to contribution to the measurement of the internal standard (^{13}C) from the native (^{12}C). ** Indicative results - these are underestimated because the detector was saturated. *** Indicative results - these are highly underestimated due to saturation of the detector and also from the contribution to the measurement of the internal standard (^{13}C) from the native (^{12}C)

The concentration of some of the PBDEs in the samples was higher than expected; particularly at the downstream points (Mirfield, Wakefield and Stanley). Samples were treated using an internal standard method which is commonly used for analysing samples using chromatography separation. This method aims to compensate for potential sources of error during the analysis by adding a known amount of a surrogate compound (similar to the chemical of interest) to samples and analytical standards, prior to any sample preparation and/or analysis. Then, the internal standard would experience the same changes as the target analytes and when developing a calibration curve based on the relative response of the analytes to the amount of the internal standard, most of the errors can be removed. In this case, a ^{13}C labelled internal standard was used in the analysis.

The amount of internal standard that should be added to samples would be the one that produces a concentration close to that expected for the target analytes or at least within one order of magnitude (Harris, 2010). Calibration curves are generally prepared over a linear range of analytical response vs. concentration but when the concentration in the samples exceeds the linear range, the accuracy of the results is affected. The laboratory where samples were sent for analysis usually carries out routine analysis of food samples with very low concentrations using very sensitive methods. Unfortunately, the analyst in the laboratory was not prepared or not advised that the sediment samples should have been treated differently due to higher concentrations of PBDEs. Therefore, the analysis of lower brominated congeners with small concentrations was more accurate than for congeners with the highest concentrations. Multiple internal standards that covered the range of concentrations for all PBDEs congeners should have been applied in this case where the potential concentration between lower and higher brominated congeners spans several orders of magnitude. An initial screening analysis could have also been carried out to determine the right amount of internal standard and to avoid the saturation of the detector.

Increasing PBDE concentrations were found from the top to the bottom of the catchment. The largest PBDE concentration was found for decaBDE (BDE-209) in all the sampling locations, representing more than 90% of the total PBDEs in each point. A fluctuation of the concentration of decaBDE was observed in Mirfield and Bridge Road. High concentrations of other lower congeners were observed particularly for BDE-99, BDE-47, BDE-100, BDE-153 and BDE-154 at Wakefield and Stanley.

Most of the lower brominated congeners found in the sediment samples are reported to be part of the banned commercial formulations of pentaBDE and octaBDE (SFT, 2009; Schlummer et al., 2007; La Guardia et al., 2006; Hites et al., 2004). PentaBDE formulation mostly contained BDE-99 (~58%) and BDE-47 (~33%), in minor amounts BDE-100/85 and BDE-153 (~8%), and traces of BDE-17, BDE-28, BDE-15 and BDE-183. Marker congeners for pentaBDE formulations when analysing PBDE patterns are actually BDE-47, BDE-99, BDE-100, BDE-153, and BDE-154. The octaBDE formulation had major concentrations of BDE-183 (~43%), BDE-197 (~35%), with minor concentrations of nonaBDE (~10%) and other octaBDE congeners, BDE-153 (11%) and traces of BDE-154, BDE-180 and BDE-209. BDE-183 is considered a marker congener for commercial formulations of octaBDE since it is the major component in this formulation and is not found in penta- or decaBDE formulations (Zegers et al., 2003).

The relatively large percentage of BDE-99, BDE-47 and BDE-100 would be likely to come from historical releases of pentaBDE formulation rather that from debromination of other more brominated congeners. Similarly, the high percentage of BDE-153, and the presence of BDE-183 were likely to come from historical emissions of octaBDE formulation from previous uses in the catchment. Some congeners found in appreciable concentrations such as BDE-17 and BDE-28/33 which only appeared as tracers in pentaBDE and octaBDE formulations could have also come from degradation of more highly brominated PBDEs. The rest of the congeners which were not reported to be part of the any PBDE formulation are most likely to be originated from debromination of higher PBDEs; this includes three tetra- (BDE-49/66/77), one penta- (BDE-119) and one hexa- (BDE-138) congeners.

2.4.1.4 Simulation of decaBDE in the Calder catchment using GREAT-ER

Simulated concentrations of decaBDE in sediment and water in the Calder catchment using GREAT-ER are shown in the map in Figure 2-11. As expected from the physicochemical properties of decaBDE, the simulated concentrations in sediment (280 – 3,800 µg/kg) were significantly higher than the simulated values in water (0.007 – 0.082 µg/l). Simulated concentrations generally increased in the main river from the top to the bottom of the catchment with some fluctuations near discharge sites. The tributaries showed a different behaviour concentrations generally decreased from the top to the confluence with the Calder due to the presence of populated and discharge areas nearby. A profile of the sediment concentrations across the main river from Luddenden to the river outlet (Figure 2-12) shows that the concentrations between discharge values tended to remain constant until the discharge sites when abrupt changes to higher concentrations were observed. A slight decrease in concentrations was observed immediately before reaching the discharge sites maybe due to removal processes in STW at those points. Increases in concentrations at discharge sites were predicted to be up to a factor of two.

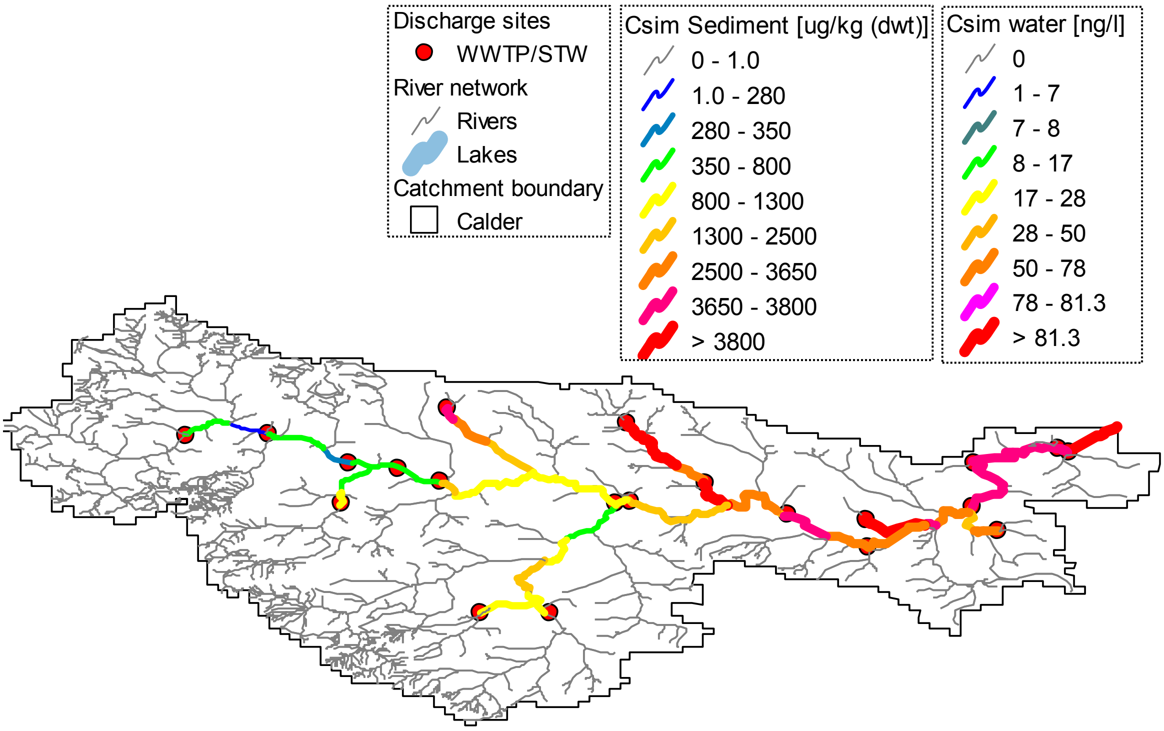


Figure 2-11 Map of predicted concentrations of decaBDE in sediment (Csim sediment) and water (Csim water) in the Calder catchment using GREAT-ER model.

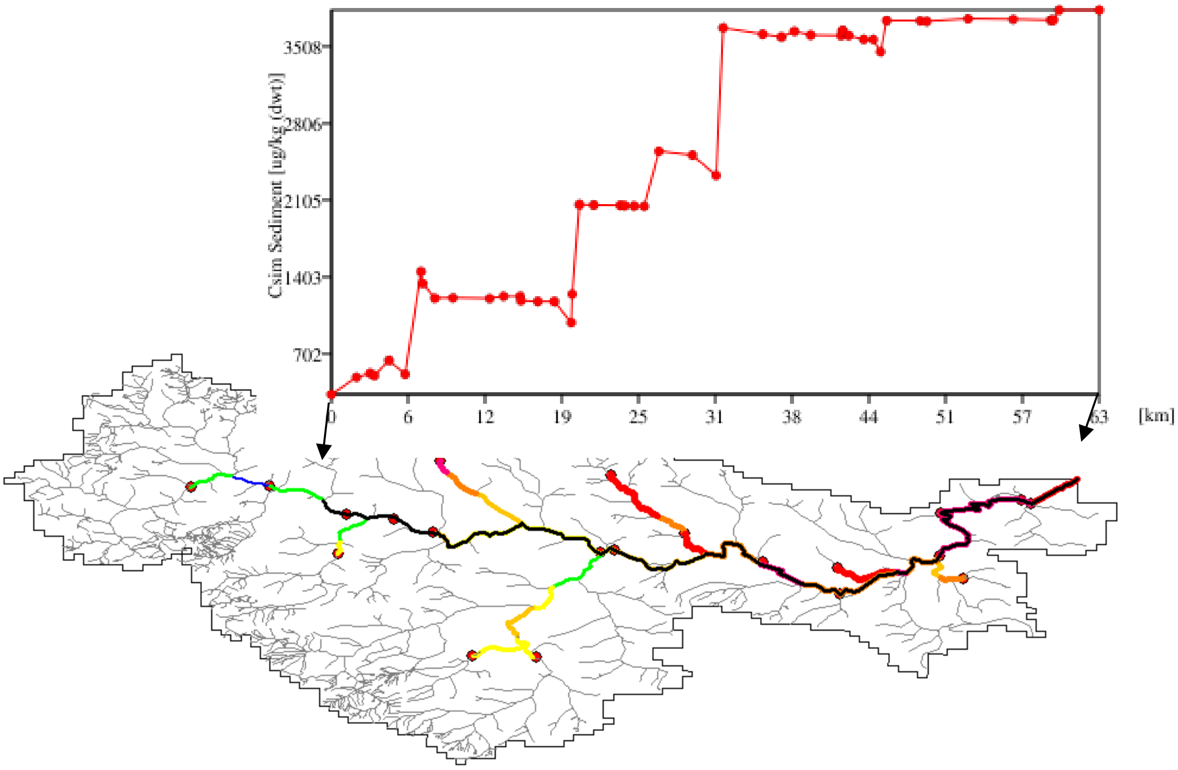


Figure 2-12 Profile of sediment concentrations (Csim Sediment) along the River Calder starting in Luddenden. The black line indicates the river section represented on the graph.

Simulated sediment concentrations of decaBDE using GREAT-ER appeared to be larger than the observed data for most of the locations; however, most of the reported measurements were considered by the analyst under-estimate the true concentrations so there is uncertainty about the level of agreement between the model and measured values (Table 2-13). The concentration for Stanley is likely to have been under-estimated by the model since great under-estimation was expected for the measured concentration in this location (the observed concentration is expected to range between 25,000 and 100,000 μg/kg dwt). The only non-indicative concentration was for Luddenden which was over-estimated by more than one order of magnitude. The model generally simulated well the pattern of increasing concentrations along the river; the exception was for Bridge Road where the model could not capture the observed decrease in the concentration.

Table 2-13 Observed and simulated decaBDE concentration in sediments in the Calder using GREAT-ER.

Location	**Simulated**	**Observed**
	(μg/kg dwt)	
Luddenden	325	11
Sowerby Bridge	405	50*
Huddersfield	1,225	41*
Mirfield	2,022	468***
Bridge Road	3,572	164*
Wakefield	3,610	935***
Stanley	3,737	2,621***

* Indicative results - they are likely to be underestimates due to contribution to the measurement of the internal standard (^{13}C) from the native (12C)

** Indicative results - these are highly underestimated due to saturation of the detector and also from the contribution to the measurement of the internal standard (^{13}C) from the native (^{12}C)

*** Indicative results - these are underestimated because the detector was saturated

2.4.2 Decabromodiphenyl ether in Colombia

2.4.2.1 Inventory

A preliminary inventory of decaBDE in EEE and WEEE was carried out using estimated consumption figures for these articles in 2010, their plastic content and the typical content of the flame retardant in plastics (Table 2-14). Refrigerators, cathode ray tube (CRT) TVs and washing machines are the articles containing most of the decaBDE, about 48, 20 and 16% of the total decaBDE in EEE/WEEE articles, respectively. Despite the extensive use of mobile phones in the country (about one mobile per habitant in 2010), this article gave the smallest contribution of decaBDE consumption.

Table 2-14 Estimated amount of decaBDE in EEE and WEEE in Colombia in 2010.

Articles	Apparent consumption of EEE	EEE in use/stock	WEEE	decaBDE
		kg/year		%
Refrigerators	2,181 – 3,271	25,933 – 38,900	5,473 – 8,209	48.2
Washing machine	1,154 – 1,732	8,032 – 12,049	1,715 – 2,572	15.6
Desktop computer	374 - 561	1,247 – 1,871	3,528 – 5,292	7.4
Laptop computer	37 - 55	37 - 55		0.1
Mobile phone	3 - 5	55 - 82	143 - 214	0.3
CRT TVs	165 - 247	11,880 – 17,820	1,800 – 2,700	19.9
LCD TVs	1,086 – 1,629			1.6
DVD/TCR	126 - 189	619 - 929	216 - 324	1.4
Audio equipment	375 - 562	1,830 – 2,745	1,680 – 2,520	5.6
Total	5,501 – 8,252	49,634 – 74,451	14,555 – 21,833	

The amount of decaBDE in carpets was estimated between 1999 and 2010 from the apparent consumption of this article in Colombia and the reported range of decaBDE content in textiles. The increasing demand for carpets in Colombia has also increased the amount of decaBDE used in the country from 1999 to 2010 (Table 2-15); decaBDE consumption has more than doubled during this period (225% increase). Greater consumption figures of decaBDE were observed in carpets than in EEE equipment in 2010.

Table 2-15 Amount of decaBDE used for the apparent consumption of carpets in Colombia.

Year	**decaBDE used** (tonnes/year)
1999	3,390 - 9,040
2000	3,576 - 9,535
2001	4,027 - 10,737
2002	4,600 - 12,267
2003	4,718 - 12,582
2004	4,605 - 12,281
2005	5,661 - 15,096
2006	5,918 - 15,781
2007	5,815 - 15,508
2008	6,691 - 17,842
2009	8,106 - 21,616
2010	7,645 - 20,387

2.4.2.2 Estimated emissions

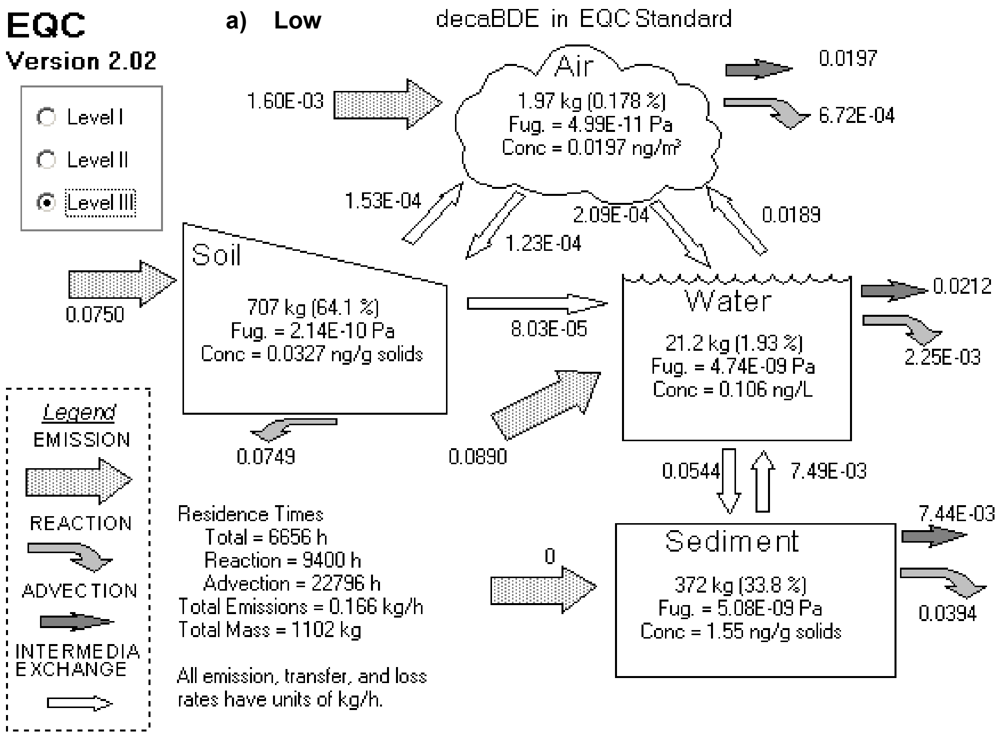
Emissions of decaBDE were estimated for different environmental compartments from polymer and textile applications in EEE and carpets, respectively (Table 2-16); global and individual emissions for each scenario are shown. The most important source of release was to wastewater during formulation and back-coating of carpets. Results also show that decaBDE was mainly released to wastewater, industrial/urban soil and surface water with emission ranges of 46 – 58%, 29 – 36% and 10 – 12% of the total decaBDE emitted, respectively. Emissions to air are very small at between 1.0 and 1.2%. These results show that the main compartment of concern due to decaBDE emissions is surface water where wastewater is expected to be discharged.

Table 2-16 Calculated emissions of decaBDE in Colombia.

	Scenario	**Releases in the Colombia (kg/year)**	
Polymers	Handling of raw material	61.02	to landfill
	Compounding and conversion	1.9	to air
		0.4	to wastewater
	Volatilisation	0.0003 – 0.0008	to air
	Particulate loss, waste remaining in the environment	0.2	to air
		52.7	to surface water
		158.7	to industrial/urban soil
	Particulate loss during disposal	0.3 – 0.4	to air
		72.3 – 108.5	to surface water
		217.9 – 326.8	to industrial/urban soil
Textiles	Formulation and back-coating	11 - 29	to air
		508 – 1,355	to waste water
	Leaching loss	76 – 203	to wastewater
	Particulate loss during disposal	0.1 – 0.3	to air
		38 – 102	to surface water
		115 – 306	to industrial/urban soil
Global estimated emissions of decaBDE to each environmental media		13 – 32	to air
		163 – 263	to surface water
		622 – 1,558	to WWTP
		492 – 791	to industrial/urban soil
		61	to landfill

2.4.2.3 Fugacity model

The fugacity distribution diagram for level III when using the estimated emission to different compartments in Colombia (Figure 2-13) showed that most of the decaBDE partitioned to soil (49.8 – 64.1%) and sediment (33.8 – 47.2%). Partitioning to air (0.18 – 0.25%) was smaller than to water (1.9 – 2.7%) due to the small estimated emission to the air compartment. The most important inter-media exchange was from water to sediment (0.054 – 0.13 kg/h) and from water to air (0.019 – 0.042 kg/h). The estimated concentration in sediment ranges between 1.55 and 3.62 µg/kg for low and high emission scenarios, respectively.



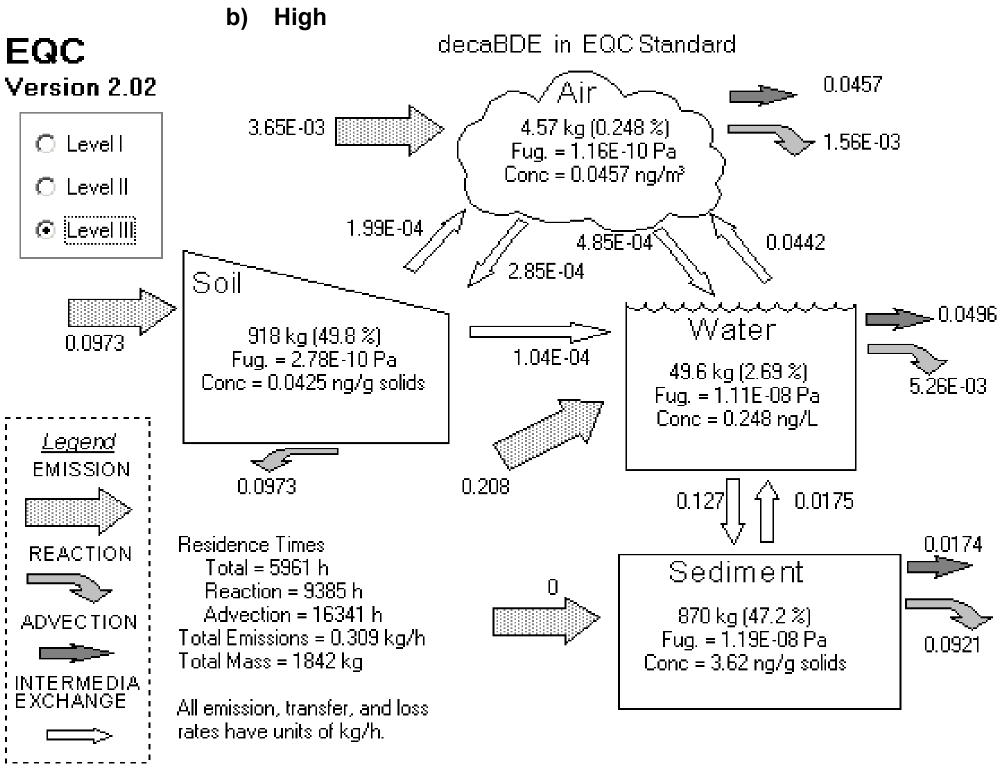


Figure 2-13 Fugacity distribution diagram for level III in Colombia for a) low and b) high emissions.

Simulated concentrations in sediment (1.55 – 3.62 μg/kg) were under-estimated by up to two orders of magnitude compared to maximum reported concentrations of decaBDE found at the outlet of the River Magdalena and the coastal line nearby in 2010 (143.0 and 55.8

µg/kg, respectively). However, the concentrations matched well the maximum observed data for the monitoring campaign carried out in 2011 in the same area; observed detected concentrations of decaBDE at that time varied between 0.2 and 2.0 µg/kg (Paez, 2012). The reasons for the variability in monitoring results are discussed in Section 2.5.2.3.

2.5 Discussion

2.5.1 Decabromodiphenyl ether in the UK

2.5.1.1 Emissions

Consumption figures for decaBDE used in this assessment were estimated from the global reported EU consumption in the 2000s by the flame retardant's industry (BSEF, 2003b) and the relative consumption distribution in polymers, textiles and imported finished articles reported in (ECB, 2004) since no updated figures are available either for the EU or the UK. The latest official assessments in the UK and in the EU have also highlighted this lack of information (ECHA, 2013; Brooke et al., 2009). Recently, Earnshaw et al. (2013) carried out estimations about the consumption and emissions of decaBDE in Europe between 1970 and 2020 using historical consumption data from different sources and a dynamic substance flow analysis. Earnshaw et al. (2013) estimated consumption at between 4,800 and 8,500 tonnes in 2010 which spans the value assumed in the present study (6,900 tonnes/year).

The flow analysis for decaBDE by Earnshaw et al. (2013) identified 26 emission pathways of decaBDE where 12 assumed that contaminant would be released to air, seven to water and seven to soil. In contrast, this study which followed the methodology of the ECB (2004) only identified a total of 15 emission pathways; seven to air, six to water and two to soil. Differences in the number of pathways were due to a more complex breakdown of the production, use and disposal of products containing decaBDE as well as different assumptions about the media of release. For instance, Earnshaw et al. (2014) considered that emission to air either as gas or particulate-bound material would be more important despite the low vapour pressure of decaBDE. In addition, the waste management stage was described in more detail; their analysis considered emissions from incineration, sewerage and landfill, export and recycling of products and material containing the flame retardant was also considered in the analysis (Earnshaw et al., 2013). Landfill has decreased in most European countries with an increase in incineration and recycling, but waste management differs between European countries. For example, Sweden has almost eliminated landfill operations from household waste (<1% in 2011) (Sverige Avfall, 2012). In the UK, the recycling and incineration rates reached 43.2 and 13% of the total household waste in 2012/13, respectively with variation across local authorities (DEFRA, 2013).

Estimated emissions for the UK were higher than the estimated regional values in the EU risk assessment (ECB, 2004) by a factor of 1.7 due to high usage of decaBDE in textiles. Waste management was the dominant source of release of decaBDE, particularly from particulate loss during textile disposal (99.4% of the total estimated loss) but mainly to soil and only to a lesser extent to surface water and air. Other studies for the EU also identified the disposal stage as the most critical in term of decaBDE emissions (Earnshaw et al., 2013; ECHA, 2013; ECB, 2004).

Figure 2-14 compares the estimated decaBDE emissions in the UK with results from other studies. Emission data from the original studies were modified to a per capita basis for comparison. The distribution of the estimated emissions for the different environmental media in the UK was similar to that obtained by the ECB (2004) since the methodology of this EU risk assessment was followed for the UK calculations. Estimated emissions to water and soil in the UK were higher than for other European studies by up to one and two orders of magnitude, respectively. Calculated emissions from the EU (Earnshaw et al., 2013; ECB, 2004) scaled down to a per capita basis would represent the behaviour of an average European country. However, the UK is expected to have a different behaviour and higher emissions due to differences in usage pattern from the high use of decaBDE in textiles (ECB, 2004; UK Legislation, 1993). The calculated emission for Denmark (Palm et al., 2002) and the recent estimations for the EU (Earnshaw et al., 2013)found emission to air as the most important route of release which is due to similar assumptions used in both flow analyses.

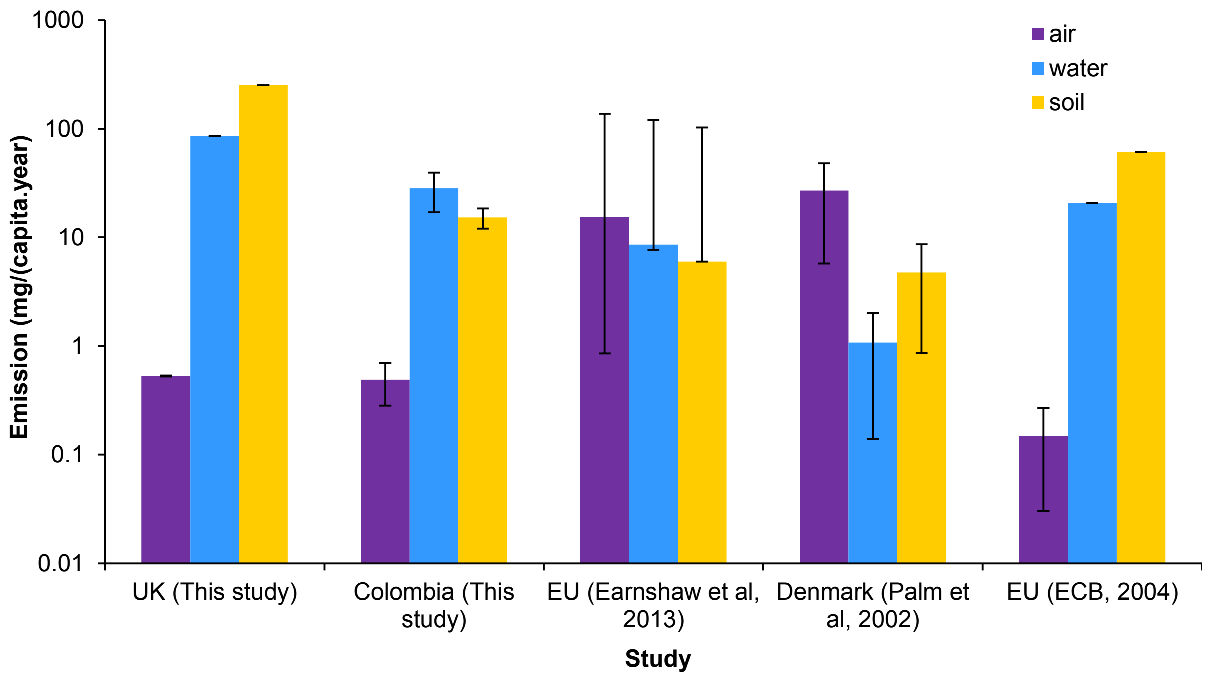


Figure 2-14 Comparison of estimated per capita decaBDE emissions to air, soil and water for the UK and Colombia to other studies. Data are presented in a logarithmic scale.

The lack of data for the UK is a source of uncertainty in the emission analysis. Estimated emissions could have been under-estimated particularly from the waste management stage since emissions from incineration and recycling stages were not included in the analysis. In addition, the static approach undertaken for decaBDE releases from products instead of accounting for changes over their lifetime can also under-estimate emissions since the stability of decaBDE attached to a product could be affected with product aging resulting in greater flame retardant release (Earnshaw et al., 2013). This study highlights the importance of generating consumption and emission data at the country scale, particularly for the UK which is likely to differ from an average European country.

2.5.1.2 *Fugacity modelling*

The partitioning of decaBDE was studied using fugacity modelling by supplying recently-generated physicochemical information for decaBDE. Palm et al. (2002) provided a general picture of the likely fate of PBDEs in the environment. However, when this study was conducted there was little information about the chemical properties of PBDEs and some of these properties were estimated using the with the EPIWIN method (US EPA, 2000). Fugacity level I showed similar distribution of contaminants in environmental media; most of the flame retardant was predicted to partition to soil (> 96%).

Results from level II evidenced the high potential for debromination and long-range atmospheric transport since the most important processes predicted in this level were degradation in soil and advection to air. Debromination of decaBDE into lower congeners has been demonstrated in different monitoring studies (UNEP, 2010a) and is the main reason for the proposal submitted by Norway to include this congener in the Stockholm Convention list of POPs (UNEP, 2013). However, debromination has only occurred in small amounts in different studies (Song et al., 2004; Voorspoels et al., 2003; Zegers et al., 2003) including this one; monitoring data from sediments collected at different locations of the Calder catchment showed that the vast majority of the congeners was decaBDE (>90%), followed by congeners found in commercial mixtures used in the past (penta and octaBDE formulations) (~7%) while congeners from debromination represented less than 3% of the PBDEs found in the samples. In addition, the long-range transport potential found from the fugacity model agrees with studies that have found decaBDE in the Polar regions (Desonie, 2008; Gouin and Harner, 2003).

The partitioning of decaBDE in the UK was studied using fugacity level III by supplying to the model estimated emissions to environmental media for this country. Fugacity results showed an increase in partition to sediment (13%) and a decrease in partitioning to air (0.07%) compared to the lower fugacity levels due to the high estimated emissions to water. Estimated concentrations from this level were compared to monitoring data reported for the UK (Table 2–17). Simulated concentrations for water and sediment were within the lower end of the range of observed data. Monitoring data for water and sediment have been normally collected near possible sources of release where concentrations are expected to be high. These concentrations are thus not representative of an average regional scenario. For air, the model predicted concentrations of the same order of magnitude as the maximum observed data from a semi-rural area in north-west England (Wilford et al., 2008) with only a slightly over-estimation by a factor of 1.3. The simulated concentration in soil could not be evaluated since no monitoring data were available. These results suggest that the calculated emissions were adequate to estimate environmental partitioning in the UK.

Table 2-17 Comparison between predicted and observed environmental concentrations for the UK.

	Air (pg/m^3)	**Water (µg/l)**	**Sediment (µg/kg dwt)**
Simulated	128	0.007	10.5
Observed	<0.49 – 100[a]	<0.005 – 0.015[b]	5 – 3,191[c] 11 – <2,621*

[a] Wilford et al. (2008); [b]ECB (2002); [c](ECB, 2002; Allchin et al., 1999; Law et al., 1996); *Measured in the present study for the River Calder

2.5.1.3 Monitoring decaBDE in sediments

Concentrations for decaBDE from monitoring of the River Calder (11 – 2,621 µg/kg) were within the range reported for sediments in the UK (5 – 3,191 µg/kg) (ECB, 2002; Allchin et al., 1999; Law et al., 1996). However, there is some uncertainty over some of measured decaBDE concentrations in the present study due to issues with the analysis; larger than expected concentrations in the samples mean that the maximum concentration in the range could be under-estimated. Maximum concentration of BDE-47 in sediments in the UK taken near potential PBDE sources were within the same order of magnitude (368 µg/kg dwt by Allchin et al. (1999)) than in the present study (85.18 µg/kg); however, this concentration was also under-estimated but to a lesser level than decaBDE concentrations.

A large variety of PBDEs were found in sediments of the Calder catchment with different levels of bromination. DecaBDE represented the vast majority of the PBDEs found in the catchment (< 90%), followed by BDE-99 (3.54%) and BDE-44 (2.07%) (Table 2-12). Other studies have also found these three congeners to be the most abundant in sediments (e.g. (Zegers et al., 2003) for Western Europe and in the Belgium North Sea and (Song et al., 2004) for the Great Lakes). Song et al. (2004) found that decaBDE represented between 83 and 94% of the 10 congeners analysed in sediment samples (congeners including BDE-28, BDE-47, BDE-66, BDE-85, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209). The second most important congeners were BDE-47 and BDE-99; however, the first was more abundant. Congeners BDE-100, BDE-153, BDE-154 and BDE-183 were also found in all the samples (Song et al., 2004). The presence of congeners that were normally found in penta- and octaBDE formulations suggests that they are due to historical releases of these formulations in the Calder. Other congeners that were not used in any PBDE formulation were also detected in smaller amounts (<3%) which are an indication of debromination of highly brominated congeners. However, the vast majority of PBDEs found in the samples corresponded to decaBDE which demonstrates that this flame retardant is intensively used in the catchment and emissions are very likely to come mainly from industry in the area rather than from residential usage.

2.5.1.4 Simulation of decaBDE in the Calder catchment using GREAT-ER

Results from estimated emissions to surface water and waste water as well as the extensive partitioning to sediment demonstrate the high emission potential of decaBDE from this route. However, most of the modelling studies into PBDEs have focused on the simulation of air emissions; to the best of our knowledge no fate modelling has been applied to study the dynamics of decaBDE at the catchment level. For this reason, fate modelling and monitoring of sediments were carried out in an industrialised area where levels of PBDEs were expected to be high. GREAT-ER results (280 – 3,800 μg/kg) agreed with previously reported monitoring data (5 – 3,190 μg/kg) for sediments from different rivers in the UK (ECB, 2002; Allchin et al., 1999; Law et al., 1996).

Monitoring studies in the UK have reported only a small number of detectable concentrations of decaBDE in water (detection limit: 0.0005 μg/l) as expected from its physicochemical properties (solubility in water < 0.001 g/m^3; Cetin and Odabasi (2005)); detectable concentrations in water as dissolved ranged between 0.005 and 0.015 μg/l and for suspended solids one sample reported a concentration of 1.2 μg/kg. However, the model predicts larger concentrations than the detection limit in these earlier studies (0.007 – 0.082 μg/l). The present results show the importance of generating monitoring data for this catchment to support model evaluation.

Sediment concentration data from the Calder were used in model evaluation. Unfortunately, monitoring concentrations had some uncertainty due to suspected under-estimation of the concentrations in samples where decaBDE concentrations were very large. This issue did not allow the proper evaluation of modelling results; however, indicative concentrations suggested a fairly good modelling performance. The model showed a good agreement in the pattern of the concentrations down the catchment. However, upstream concentrations were over-estimated by more than one order of magnitude. This suggests that: i) the emissions per capita to water could have been over-estimated, ii) the sewer system is actually removing more decaBDE than the removal value used in the model, iii) emissions from industry could have been less than the average values reported by the BSEF (2003b) or iv) degradation rates were under-estimated. Concentrations downstream appeared to be under-estimated since indicative measured concentrations are expected to be higher particularly at Stanley were they are expected to range between 25,000 to 100,000 μg/kg dwt. Under-estimation of concentrations downstream could be due to higher emission of decaBDE from industries using the flame retardant than expected or due to the presence of additional industries that were not taken into account in the model. Annual emissions of decaBDE to wastewater from two textile processing sites in the UK between 2002 and 2007 were reported to range between 86 and 2,440 kg/year according to ECB (2007); however, this report mentions that it was not clear if these figures represent the total mass of bromine or the mass of decaBDE itself; since decaBDE has a bromine content of around 83% emissions could be larger (Brooke et al., 2009).

2.5.2 Decabromodiphenyl ether in Colombia

2.5.2.1 Inventory

A preliminary inventory about decaBDE in EEE/WEEE and carpets was carried out using available historical consumption data of individual articles. Carpets were the only textiles considered in the inventory due to the lack of information for other products. The consumption of decaBDE in carpets is an important contributor to estimated decaBDE in Colombia with comparable figures to the ones obtained for EEE. Estimated consumption in carpets was based on the reported range of application for back-coating in textiles (7.5 – 20%) (ECHA, 2012a, b). This range is very wide and the real value will depend on the type of textile and national legislation. There is no national legislation that regulates the amount of decaBDE in products in Colombia, so the actual amount of decaBDE applied in the country is very uncertain. However, fire safety regulations in Colombia do not require high levels of flame retardants and the applied dose is also not specified. Therefore, it is expected that the application would be less than the maximum of the range (<20%), but finished articles that are exported to other countries would have to comply with regulations of the destination country.

Inventory for EEE/WEEE is expected to be less uncertain than for textiles since a wide range of products were covered with a decent amount of information about consumption in Colombia. Articles from EEE category 1 such as refrigerators, CRT TVs and washing machines had most of the total decaBDE in EEE/WEEE. Other studies have found that CRT TVs are an important source of decaBDE and POP-PBDEs (Sindiku et al., 2014; UNEP, 2012, 2010a). An inventory of PBDEs in Nigeria estimated 1,880 tonnes (about 10.8 g per capita) of decaBDE in the current stock of CRT casings. This figure is far higher than the estimate for Colombia (about 0.38 g per capita). In Colombia, sales of LCD TVs have seen a large increase since 2005; they accounted for 30% of the TV market in 2008 (DIAN, 2009) and nowadays, CRT TVs have almost disappeared from the market (Bustamante, 2012).

Most of the decaBDE in the inventory was estimated to be in EEE in use or stock (~71%) which would be disposed after their service life. DecaBDE in WEEE has also significant quantities (~21%). The adequate disposal of e-waste is a major problem in developing countries and is a major source of pollution (Sindiku et al., 2014; Blaser, 2009). Emissions from these countries are expected to be higher than in industrialised countries since appropriate management of WEEE containing BFRs is lacking and there are not enough facilities for treating current and future amounts of e-waste (Babayemi et al., 2014; Sindiku et al., 2014; Weber et al., 2013). In Colombia, there are some initial efforts to improve e-waste management; the governmental environment department has set guidelines for the appropriate disposal and recycling of WEEE (MAVDT, 2010) but more effort should be made to ensure national implementation in the short term. Studies in developing countries (Sindiku et al., 2014; Baron et al., 2013; Blaser, 2009; Ott, 2008), including this one, have highlighted the urgent need to develop adequate WEEE management for the expected large amount of material containing flame retardants that is expected to flow in the waste system at the end of service life of products (approximately during the next 20 years).

2.5.2.2 Emissions

Emissions of decaBDE from two relevant products containing decaBDE were estimated (EEE/WEEE and carpets); however, there is a wide range of other products containing this flame retardant that were not included in the analysis. Estimated emissions only represent a fraction of the total decaBDE emissions in Colombia. For example, in the USA the total decaBDE consumption was estimated to be divided by weight into 26% for textiles, 26% for automotive or transportation, 26% for construction material, 13% for EEE and 9% for other uses (Levchik, 2010). Considering individual product types for the calculation of emissions requires considerable amounts of data for a wide variety of products. Studies of emissions from other countries normally used the total sale of flame retardants as the starting point to avoid uncertainty of using individual product types (Earnshaw et al., 2013), but this information was not available for Colombia. However, emission figures from these two important products would be a starting point to understand the fate of decaBDE in the country.

Figure 2-14 compares decaBDE emission results estimated for Colombia with per capita results from other countries. Emissions to air were comparable to results for the UK and emission to water and soil showed similar figures as those for average European countries (Earnshaw et al., 2013; ECB, 2004); however, values for Colombia are likely to be under-estimated.

2.5.2.3 Fugacity model

Fugacity results greatly agreed with monitoring data of sediments in 2011, at the outlet of the main River Magdalena (the main of the country). However, under-estimation was observed for results from the previous year of between one and two orders of magnitude. The high temporal variability in measured concentrations between years could be an indication of degradation, sediment transport, dilution or spatial variability. High dispersion of BFRs concentrations was observed particularly in 2010 which can be explained by strong currents generated by trade winds (Baron et al., 2013).

Simulated concentrations in sediment for Colombia were smaller than fugacity estimations for the UK by one order of magnitude due to smaller releases to water estimated for Colombia. Segui et al. (2013) compared concentrations from two Ebro tributaries in Spain to concentrations found in coastal areas in Chile and Colombia; this study also found that sediment concentrations in the Spain were larger than in Latin America.

2.6 Conclusions

Data availability is a crucial factor in model applications. Brominated flame retardants are relatively new contaminants and their fate in their environment is still uncertain. This study highlights the need for updated consumption and emission data at the country level as well as for more consistent methods for producing emission calculations. This is particularly the case for decaBDE since it is very likely to be included soon in the POPs list of the Stockholm convention (UNEP, 2013). Per capita basis calculations from EU data can under-or over-estimate activity and emissions depending on the country, particular because waste management systems in the EU are very different between member states especially for landfill. DecaBDE emissions estimated in the UK from available information and assumptions predicted high emissions to water from STP's and industries; this was confirmed with a monitoring study and fate modelling for the Calder catchment. Sediment concentrations along the river Calder were higher than reported values for different locations near possible sources of release in the UK. The pattern of monitoring results for lower brominated congeners showed evidence of historical usage of penta- and octaBDE formulations in the Calder catchment as well as debromination of higher brominated PBDEs.

DecaBDE is strongly sorbed to sediments which reduces its mobility and bioavailability. Understanding of the dynamics of this flame retardant in the river system is particularly important to assess its behaviour in the environment and the implications for aquatic exposure. Fate modelling to study the dynamics of decaBDE in river systems at the catchment-scale was applied for the first time using GREAT-ER. Modelling results generally showed a good agreement in the simulation with GREAT-ER; however, uncertainty in the measured data did not allow proper model evaluation. GREAT-ER showed good potential to simulate emissions of BFRs from STP's and other point-sources such as industries, though this could be improved with more accurate emission data.

Information about the consumption of BFRs in Colombia is not available. An inventory based on individual products was needed to estimate emissions in this country. However, under-estimation of the emissions is expected since there is a wide range of products containing decaBDE that could not be included in the inventory due to the lack of consumption information. Total consumption data for decaBDE would be more useful in the calculation of emissions. Emissions estimated for Colombia showed large contribution from textiles which is expected to be comparable or higher than from EEE. More information about the amount of decaBDE applied to different textile applications is also necessary to reduce uncertainty in emission calculations. Fugacity results were in good agreement with observed concentrations reported for sediments in the outlet of the River Magdalena in 2011; however, high spatial and temporal variability on PBDE concentrations has been reported in this area from studies in 2010 and 2011.

3 Modelling pesticides in the Wensum catchment using field-scale models

3.1 Introduction

Surface and groundwater contamination due to farming operations in the UK is a source of concern for compliance with the European standards of water quality. Under the European Water Framework Directive (WFD) 2000/60/EC (2000), extra treatment of drinking water at treatment plants should be avoided and more attention should be taken to reduce pollution from the source by managing catchments sustainably. The Directive aims to protect and improve the quality of water bodies. The WFD came into force on December 22nd 2000 and then transposed to the English legislation, which applies in England and Wales, in December 2003 (DEFRA, 2003). In 2012, the Environment Agency in the UK reported that about 15% of the Drinking Water Protected Areas (DrWPAs) in England and Wales designated for abstraction of water for human consumption under Article 7 of the WFD were at risk of not compliance with European standards (Pesticide Forum, 2012), particularly in eastern and southern England. Pesticides currently in use that are most frequently detected at high concentrations in surface water include metaldehyde, MCPA, chlorotoluron, mecoprop, carbetamide, 2,4-D, asulam, propyzamide and clopyralid (DEFRA, 2012; Pesticide Forum, 2012) and in groundwater bentazone and mecoprop (DEFRA, 2012). These pesticides have been found in catchments in England and Wales at concentrations exceeding the 0.1 μg/l maximum acceptable concentration in drinking water set by the European Commission (1998) (EU Drinking Water Directive: 98/83/EC).

Priority catchments in England and Wales have been targeted under the Catchment Sensitive Farming programme (CSF), to reduce diffuse water pollution from farming activities. As part of this programme, pesticide monitoring has been conducted on a regular basis since 2006 in six catchments in England, comprising the Wensum, Yare, Waveney, Teme, Lugg and Ouse, to evaluate the effectiveness of the management actions. Monitoring frequency varies within the year; in some periods samples are taken every two or three days and in others every week (CSF, 2012). Despite the high sampling frequency, it is likely that some important pesticide peaks are missed when occurring on days when no samples are taken. One way to address this issue is to carry out pesticide fate modelling to understand the dynamics of pesticides in the catchments as well as to evaluate their trends between years during the programme.

Modelling studies into non-point source pollution of pesticides have been focused mainly on the edge-of-field rather than the catchment-scale. Modelling the fate of pesticides at the catchment-scale is an important tool for pesticide management in order to have a holistic picture of what occurs with pesticides at this scale and so it can be used to evaluate pesticide usage and management practices. Monitoring studies of diffuse water pollution by pesticides at different hydrological scales have shown that pesticide emissions normally occur as pulses of fluctuating concentrations with similarities in their pattern (Brock et al., 2010). For example, a comparison of isoproturon peak concentrations measured at edge-of-field and in small streams showed similarities in the timing and duration of peaks (Ashauer and Brown, 2007). These patterns are largely dependent on rainfall behaviour and the effect of the river network is suspected to not have a significant impact on pesticide patterns in surface waters.

Catchment-scale models such us SWAT (Arnold et al., 1998) and AnnAGNPS (USDA ARS, 2006) have shown good results in modelling pesticide runoff at the catchment-scale but the description of tile drainage is oversimplified. A few studies have applied field-scale models in catchment modelling by considering that the fate of pesticides in the catchment would be the result of the sum of multiple field-scale processes that pesticides undergo, in addition to the dynamics due to water balances, rainfall and the river network (Tediosi et al., 2013; Tediosi et al., 2012; Lindahl et al., 2005; Loague, 1992; Loague et al., 1989a; Loague et al., 1989b). Several field-scale models are available which differ in the physical approach used to describe hydrological processes. The selection of a modelling tool to simulate emissions from non-point source pollution requires an understanding of the major routes of pesticide loss in the study area. Many factors may influence pesticide loss which would mainly depend on topography, weather and practice conditions in the area.

Pesticide loss through subsurface drainage (when tile drains are present) and surface runoff constitute the most important routes for pesticide emission in the UK (DEFRA, 2012; Pesticide Forum, 2012; Ashauer and Brown, 2007; Evans et al., 1999; Harris and Catt, 1999; Johnson et al., 1996). Most heavy clay soils with artificially drained arable lands frequently experience pesticide transport via preferential flow causing surface water contamination (Kohne et al., 2009; Jarvis, 2007; Gardenas et al., 2006; Larsbo and Jarvis, 2005; Harris and Catt, 1999; Larsson and Jarvis, 1999; Johnson et al., 1996; Brown et al., 1995b; Haria et al., 1994). Simunek et al. (2003) reviewed different approaches for modelling preferential flow which included single- and dual-porosity models (with single- or dual-permeability). Both methods use Richards' equation but differ in their level of complexity and amount input data required of. Single-porosity models are the simpler of the two approaches where the entire flow domain conducts water according to Richards' equation and transports the solute according to the advection–dispersion equation. Dual-porosity models divide the soil into micropores and macropores with first-order advection and diffusion between the two domains. Single-permeability refers to when the mobile water is carried in the macropores while the micropores only exchange and retain water. In a dual-permeability model both micropores and macropores conduct water. Models using dual-porosity/dual permeability approaches have been shown to better describe subsurface water and solute drainage (Gerke et al., 2009; Haws et al., 2005). MACRO (Jarvis et al., 1991) is the most well-known and widely used dual-porosity/dual-permeability model in Europe.

In the simulation of runoff, models using the Green-Ampt equation (Green and Ampt, 1911) or the Soil Conservative Service (SCS) runoff curve numbers are the most commonly implemented (NRCS, 2008; Soil Conservation Service, 1972). The Green-Ampt method is a mechanistic model based on infiltration principles which requires more input data than the curve number approach. The equation calculates the infiltration rate based on the ponding time as a function of rainfall, the pressure-head, soil-water content and the saturated hydraulic conductivity. The RZWQM model (Ma et al., 2004) is an example of a mechanistic model which describes soil infiltration using the Green-Ampt method.

In contrast, the curve number method is an empirical runoff estimator developed in the USA in the 1950s. Several models use the SCS curve number approach such as CREAMS (Knisel, 1980), PRZM (Carsel et al., 1985) and SWAT (Tuppad et al., 2011). This method has been widely applied because of its simplicity and the requirement of a relatively small amount of data; in some cases the approach has shown better results than more complex mechanistic models such as the Green-Ampt method (Wilcox et al., 1990). Runoff volume is calculated based on the amount of rainfall, soil type, land cover and antecedent soil moisture condition prior to a rainfall event (Ponce and Hawkins, 1996). Models based on the curve number method are generally applied for fields with scarce data or for larger catchments (Van den Putte et al., 2013). Physically-based models, such as those using the Green-Ampt method, are preferred for detailed studies accounting for rainfall variation at a sub-hourly time scale which is particularly useful for the simulation of runoff generated during short rainfall events of high-intensity (Van den Putte et al., 2013).

The fate of pesticides is a complex system which is still not completely understood. When a pesticide is applied to soil, it undergoes various complex and interacting physical, chemical and biological processes that are difficult to predict. For instance, most of the models usually assume constant degradation and sorption values across large areas since the causes of spatial variability of these parameters in soil still cannot be either mathematically or empirically described at the field or catchment scale. Several available models can describe pesticide loss from tile drains or surface runoff but none is able to satisfactorily simulate water flow rates and their associated pesticide losses by both routes. Setting a model framework (i.e. coupling models) is an important alternative to overcome model limitations. The FOCUS (2000) framework selected four models for EU review of active substances including MACRO (Jarvis et al., 1991) and PRZM (Carsel et al., 1985). These models have been widely tested and evaluated in the past with good results in the simulation of the hydrology and pesticide losses at different hydrological scales (Beulke et al., 2004; Beulke et al., 2002a; Dubus and Brown, 2002; Beulke et al., 2001a; Beulke et al., 2001b; Jarvis et al., 2000; Vanclooster et al., 2000; Besien et al., 1997; Brown et al., 1996; Jarvis et al., 1994; Mueller, 1994; Nicholls, 1994; Parrish et al., 1992; Jarvis et al., 1991; Carsel et al., 1986; Carsel et al., 1985). However, at the moment there is no established or evaluated model framework, combining these models to simulate different sources of pesticide loss at the catchment level. The establishment of accurate modelling strategies would provide valuable tools for catchment management programmes currently being undertaken in the EU as part of the WFD (Holvoet et al., 2007b).

3.1.1 Aim and objectives

The aim of this chapter is to investigate the driving processes of pesticide transport to surface water from agricultural fields in the Wensum catchment by application of field-scale fate models. The specific objectives to meet this aim are to:

1. Develop a modelling framework based on detailed field-scale modelling to study the different routes of pesticide entry in the catchment

2. Evaluate the simulation capacity and applicability of the framework to simulate water flow and transport of pesticides against measured data
3. Use the framework to determine the drivers controlling catchment-scale losses of pesticide in the Wensum
4. Evaluate whether the modelling framework can be used to fill the gaps between measured monitoring data

3.2 Study area and background information

3.2.1 Study area

The Wensum catchment is located in the eastern region of the UK, to the north west of Norwich and covers an area of approximately 650 km^2 (Figure 3-1). The landscape is principally influenced by agriculture with intensive arable farming with 62% arable land on the plateau and valley sides, whilst the floodplain is largely managed grazing marsh, fen reedbed, scrub and scattered woodland (Sear et al., 2006; Coombes et al., 1999). The River Wensum flows approximately 78 km through the county of Norfolk at an average gradient of 0.00082 m/m, from its source on Colkirk Heath to its influence with the River Yare in Norwich. The principal tributaries are the River Tat, Langor Drain, Guist Drain, Wendling Beck (Whitewater/Blackwater), Penny Spot Beck, Blackwater, Swannington Beck and the River Tud. The catchment is underlain by a major Chalk aquifer. River flow results from the drain network, groundwater baseflow, direct recharge to the river and surface runoff (Sear et al., 2006). The entire hydrological response unit of the Wensum was simulated until the monitoring point located in Sweet Briar Road Bridge (TG 206 095).

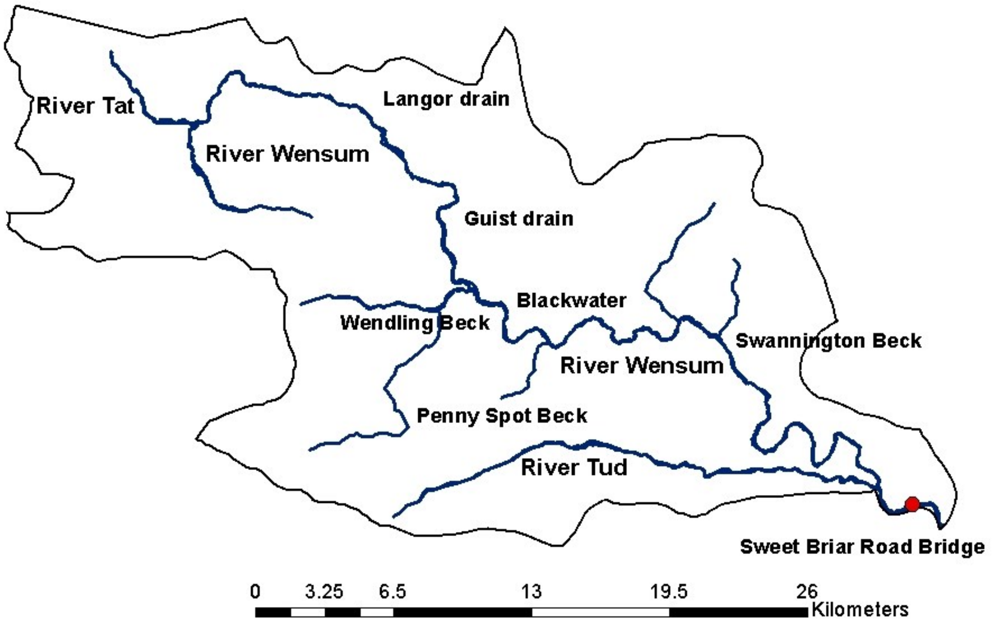


Figure 3-1 Rivers and streams in the Wensum catchment.

3.2.2 MACRO model

The flow pathways of water through soil profiles can be highly irregular under certain conditions. In macroporous soils, usually well structured, loamy to clayey soils, water percolation may rapidly move along regions of enhanced flux such as fissures, cracks, wormholes or root holes (Bouma, 1991; Beven and Germann, 1982). Such preferential movement of water and solutes is common in field soils and constitutes an important route of pesticide entry into surface water especially when field drains are present (Kladivko et al., 2001). There are several mechanistic models available that describe pesticide transport via preferential flow through drains such as DRAINAGE (Kumar and Kanwar, 1997), RZWQM (Ma et al., 2004), MACRO (Jarvis et al., 1991), HYDRUS-2D (Gardenas et al., 2006) and SPIDER (Renaud et al., 2008). The MACRO model is the most widely used and evaluated of these models under European conditions (Larsbo and Jarvis, 2005; Beulke et al., 2001a; Vanclooster et al., 2000; Villholth et al., 2000). This model has been recognized by the FOCUS working group on leaching (FOCUS, 2000) for pesticide registration to assess the potential to pollute both groundwater and surface water via drain flow. Version 5.2 of the model was used in the present study to simulate pesticide loss through drains.

The MACRO model is a one-dimensional physically based model of water flow and solute transport that divides the soil porosity into two flow domains, micropores and macropores.

A full description of the governing equations and the model parameters has been given elsewhere (Jarvis et al., 1997; Jarvis et al., 1991). The model undertakes a complete water balance including canopy interception, unsaturated and saturated water flow and root water uptake. Water and solute transport in the micropores are predicted by solving Richards' equation and the convection-dispersion equation, respectively, whilst for the macropores gravity flow of water is assumed using Darcy's law. The two flow domains operate separately with an interaction flow region calculated according to physically-based expressions characterised by soil water content, hydraulic conductivity and soil tension. As water saturation is approached, the hydraulic conductivity of the macropores rapidly increases. Pesticide sorption is described by a Freundlich isotherm and degradation is simulated assuming first-order kinetics. Surface runoff in the model only occurs when the surface layer is saturated, so MACRO cannot be used to simulate pesticide loss by this route. Pesticide volatilization is also not considered in the model.

3.2.3 RZWQM model

The RZWQM model is a one-dimensional (vertical) physically-based model that integrates physical, biological and chemical processes to simulate water flow and solute transport in macroporous soils (Ahuja et al., 2000). A detailed model description is given in the RZWQM documentation (Ma et al., 2004; Hanson et al., 1998; Ahuja et al., 1993). The model also allows simulation of a wide spectrum of management practices and scenarios. Water infiltration is described by the Green-Ampt equation until saturation; water excess in the soil matrix is routed into macropores if present. Poiseuille's law and the lateral Green-Ampt equation simulate the maximum macropore flow rate and the lateral movement, respectively (Ahuja et al., 1993). When rainfall or irrigation exceeds the infiltration rate, water excess surface runoff is generated. A numerical solution of the Richard's equation is used after infiltration for the redistribution of water within the soil profile. If evapotranspiration is not supplied, the model uses a modification of the double-layer Penman-Monteith model for its calculation. Pesticide sorption is not simulated in the macropores, only in the soil matrix, by either a linear or Freundlich isotherm (Malone et al., 2004). There is also the option of simulating pesticide sorption by a two-site partitioning, where a defined fraction of the sorption sites in instantaneous equilibrium is simulated using equilibrium-kinetic sorption and the other fraction is described by first-order reversible adsorption kinetics (Ma et al., 2004; Wauchope et al., 2002). Lumped first-order kinetics is used to simulate pesticide degradation which is adjusted for soil water content, temperature, and depth. Additional dissipation and degradation pathways such as volatilization, hydrolysis, photolysis, and oxidation, anaerobic and aerobic biodegradation can be modelled if input data are supplied.

Previous studies have shown fairly accurate predictions of pesticide loss by surface runoff when using site-specific input parameters (Chinkuyu et al., 2005) or after minimal calibration (Malone et al., 2004). RZWQM version 2.0 is used in this study in an attempt to simulate pesticide loss through surface runoff in the catchment.

3.2.4 PRZM model

The pesticide root zone model (PRZM), including PRZM-3 (the most recent version of the model) is a one-dimensional model to simulate chemical movement in soil by chromatographic leaching (Carsel et al., 1985). Preferential flow and pesticide loss through tile drainage are not considered by the model. Full descriptions of the model components are provided elsewhere (Suárez, 2006; Carsel et al., 1985) and only a summary is presented below. Soil hydrology is described by a “tipping-bucket” approach; water will only move to the next soil layer when field capacity is exceeded. Generalised soil parameters such as field capacity, wilting point and saturated water content are used to calculate water movement in the soil profile. Runoff and erosion are based on the Soil Conservation Service (1972) curve number technique and the universal soil loss equation, respectively. The curve number method is an empirical estimator of runoff that relates the amount of runoff to rainfall volume, the potential maximum soil moisture retention after runoff and the “initial abstraction” of rainfall by interception, infiltration and surface storage before runoff. Evapotranspiration is either estimated from pan evaporation data or from an empirical formula. Chemical transport is simulated using the convection-dispersion equation. Pesticide sorption is described by the Freundlich equation and first-order kinetics is implemented for degradation with option of bi-phasic degradation accounting for soil moisture and soil temperature. The model allows biodegradation in the root zone. Pesticide volatilization is considered by the model.

PRZM was developed and is currently used by the US Environment Protection Agency (EPA) for assessing pesticide transport to surface water from agricultural fields (US EPA, 2013; Carsel et al., 1985). Despite the simplicity of the curve number approach, studies have shown that runoff predictions can be equal to or better than those obtained by more complex mechanistic runoff models such as those based on Green-Ampt infiltration (Wilcox et al., 1990). In Europe, PRZM model was integrated into the group of FOCUS surface water models for pesticide registration (FOCUS, 2000). PRZM-3 version 3.12.2 was also tested in this study to simulate pesticide runoff in the catchment.

3.3 Methodology

3.3.1 Data acquisition

Information for use in deriving modelling parameters including meteorology, soils, crops and pesticides data for the Wensum catchment was compiled from different data sources.

- Meteorological data were obtained from the British Atmospheric Data Centre, BADC (UK Meteorological Office, 2012) and in communication with the UK Meteorological Office. Relevant data included global radiation, daily and hourly rainfall, daily maximum and minimum temperature, vapour pressure and wind speed.
- Soil information was taken from the Soil Survey of England and Wales Bulletin for Eastern England (Hodge et al., 1984) and from the SEISMIC information system (Hallett et al., 1995).
- Pesticide usage information including crop information and pesticide application data were gathered from the Food and Environment Research Agency (DEFRA, 2009). This information has been reported every two years for arable crops or every four years for grassland and fodder crops in the UK.
- Information about water flow and pesticide monitoring in the catchments was supplied by the Environment Agency (Environment Agency Evidence Directorate and Catchment Sensitive Farming, 2012).
- GIS vector data for the Wensum catchment were taken from the earlier analysis carried out by Farrow (2013).

3.3.2 Pesticide modelling in the Wensum catchment

The proposed modelling methodology comprised several steps. First, MACRO was used to simulated water flow and pesticide loss through deep percolation and tile drainage. A groundwater mixing model was developed to simulate the baseflow behaviour of the river and to allow deep aquifers, leaching water and pesticide to mix before being routed to the river. Runoff coming from urban areas was also estimated and added to the simulation. Then, RZWQM and PRZM were used to simulate surface run off from arable land and to evaluate which of the two models achieved better simulations. Since all models were set up to simulate 1 ha of land (field-scale), the modelling results were then scaled-up to the whole catchment. The conceptual model in Figure 3-2 summarises this strategy.

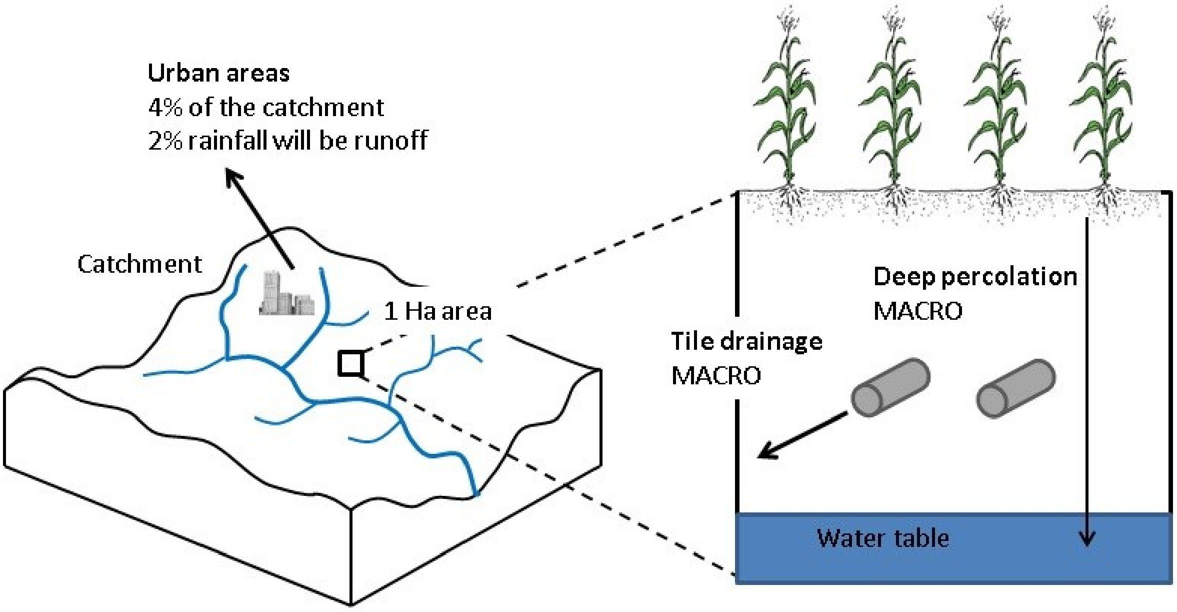


Figure 3-2 Conceptual model.

3.3.3 Groundwater mixing model

The groundwater mixing model is important to simulate water flow in the catchment especially for the simulation of periods dominated by baseflow (periods of low flow). The groundwater mixing model performs a mass balance of water flow and pesticide amounts. Figure 3-3 and Equation 3-1 show a diagram of the processes and the governing equations involved in the model, respectively. Input data are the inflow (*i*) of percolating volume of water ($V_{i,t}$) in m^3 day^{-1} and pesticide leaching that reaches the groundwater (and did not exit via tile drains, when tiles are present) ($m_{i,t}$) in mg day^{-1}, predicted by MACRO at a daily time-step ($t \geq 1\ day$). The aquifer is represented as a mixing tank (T) with the same base area as the catchment. The tank depth was nominally set at 3 m. The daily volume of water ($V_{T,t}$), pesticide mass ($m_{T,t}$) and concentration ($C_{T,t}$) in the aquifer are also calculated on a daily basis (in m^3 day^{-1}, mg day^{-1} and mg m^{-3}day^{-1}, respectively). The outputs (o) from the model are the volume of water ($V_{o,t}$), pesticide mass ($m_{o,t}$) and concentration ($C_{o,t}$) outflow (in m^3 day^{-1}, mg day^{-1} and mg m^{-3}day^{-1}, respectively) moving from the groundwater (or tank) to the river at the rate of the outflow factor, OF. This outflow factor and the initial tank volume ($V_{T,1}$) can be set by calibration to match measured flow during periods dominated by baseflow as well as the flow at the beginning of the simulation, respectively. In the model, pesticide degradation and sorption are assumed to be negligible in the saturated groundwater zone.

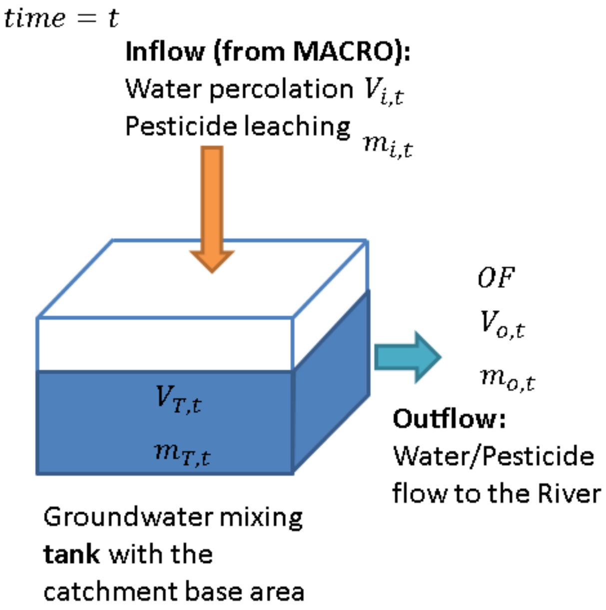


Figure 3-3 Groundwater mixing conceptual model.

Equation 3-1 $Inflow\ (i) \quad V_{i,t}\ ;\ m_{i,t}\ \ (from\ MACRO)$

$$Tank\ (T)\begin{cases} V_{T,t}\ (calib.);\ m_{T,t} = m_{i,t}; C_{T,t} = m_{T,t}/V_{T,t}\,, & if\ t = 1 \\ V_{T,t} = V_{T,t-1} - V_{o,t-1} + V_{i,t}\ ;\ m_{T,t} = m_{T,t-1} - m_{o,t-1} + m_{i,t}\ ; C_{T,t} = m_{T,t}/V_{T,t}, & if\ t > 1 \end{cases}$$

$$Outflow\ (o) \quad V_{o,t} = \left(V_{T,t} + V_{i,t}\right) \times OF;\ m_{o,t} = C_{T,t} \times V_{o,t}$$

3.3.4 Soil associations

A soil association is comprised of multiple soil series which are typical found occurring together in the landscape which generally take place in areas with similar environmental conditions (Clayden and Hollis, 1984; Avery, 1980, 1973). Information about the soil associations in the catchment was required to run the models. A spatial analysis using ArcGIS version 10.0 was carried out to identify and classify the soils in the catchment. For this purpose, information about soils in the Wensum (Hodge et al., 1984) along with spatial data including catchment boundaries and soil maps for the UK (Hallett et al., 1995) was used. The soil associations and their areas are shown in Table 3-1 and their distribution along the catchment in Figure 3-4. Low permeable soils with tile drainage systems located on the river valley constitute the main soils in the catchment (Beccles and Burlingham). In the source, the soils are a combination of well drained mainly loamy soils (Barrow) with patches of sandy soils (Newport). The opposite occurs at the base of the catchment where the Newport association predominates. The floodplains are dominated by peaty soils (Adventurers) and loamy and sandy soils with naturally high groundwater and peaty surface (Isleham). In order to simplify the simulation, the soils that only account for a small area of the catchment were combined into other soil associations with similar drainage properties; Adventures and Gresham were combined into Isleham simulation, and Wick soils into Newport. Therefore five soils were included in the simulation: Isleham, Newport, Barrow, Beccles and Burlingham.

Table 3-1 Soil association areas at the Wensum catchment.

Soil association	**Area (km^2)**	**Area (%)**
Gresham	0.9	0.1
Adventurers	8.5	1.3
Wick	12.3	1.9
Isleham	56.7	8.8
Newport	95.7	14.9
Barrow	100.9	15.7
Beccles	137.4	21.4
Burlingham	230.0	35.8
Total	642.5	100.0

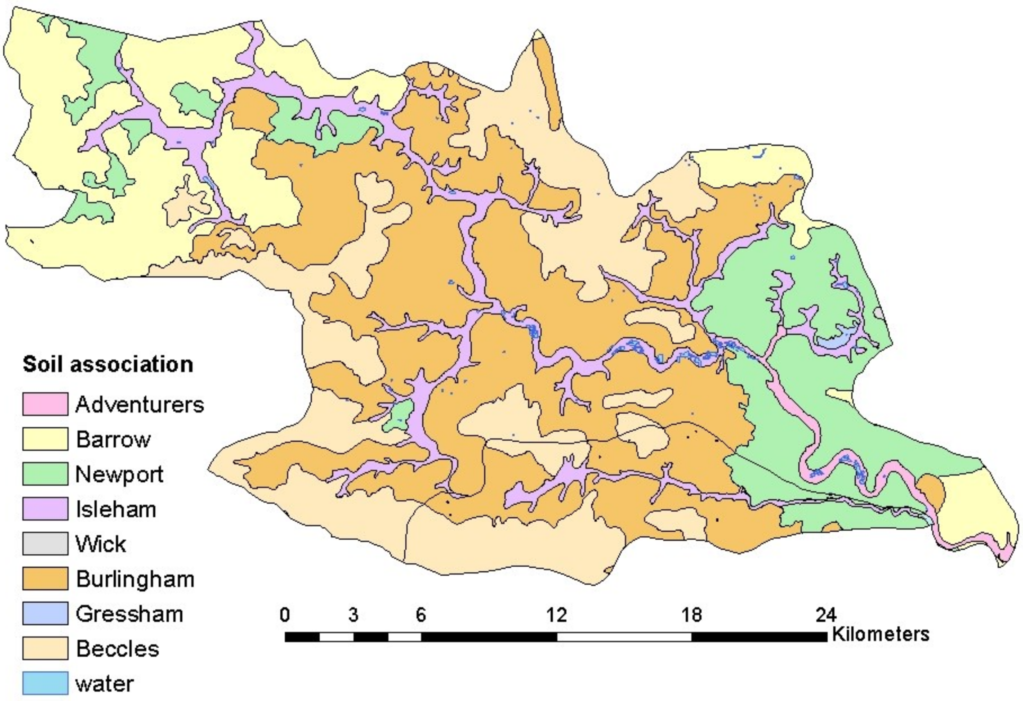


Figure 3-4 Spatial distribution of soil associations in the Wensum catchment.

3.3.5 Meteorological data

Combined daily and hourly meteorological data including rainfall, wind speed, vapour pressure, maximum and minimum temperature and solar radiation from 2006 to 2011 were used in the simulation. As there is no single meteorological station near the catchment recording all the required parameters, it was necessary to use information from more than one station from the Eastern region of the UK. The selected stations were the ones closest to the catchment with hourly or daily information available (see Table 3-2 and Figure 3-5).

Additional data processing included: (i) linear interpolation for the days without recorded information by using the data from the previous and the following day; (ii) mean calculation for days with more than one measurement recorded; (iii) sum or average calculation for available hourly data in order to calculate corresponding daily value; (iv) there were missing hourly rainfall data for 2006 and 2007 for Norwich Airport station so monthly and yearly rainfall values for this station along with Mannington Hall daily rainfall information were used to estimate daily rainfall for these years; then a rate of 2 mm per hour from midday was applied to generate hourly rainfall.

Table 3-2 Meteorological stations and parameters used in the model.

Meteorological station	Frequency recorded	Parameter
Norwich Airport	Hourly	Rainfall (2008 – 2011)
Mannington Hall	Daily	Rainfall*
Wattisham	Hourly	Solar radiation
	Hourly	Rainfall
	Daily	Maximum and minimum temperature
Marham	Hourly	Wind speed
	Hourly	Vapour pressure

*Used to calculate missing data from Norwich airport

Figure 3-5 Location of meteorological stations.

3.3.6 Modelling pesticide loss via tile drains and percolation using MACRO

The MACRO model was used to estimate pesticide concentrations at the field-scale in the Wensum catchment between 2006 and 2011. The fate of six pesticides including chlorotoluron, carbetamide, clopyralid, MCPA, mecoprop and propyzamide was simulated for the catchment. These pesticides were chosen because they are all included within the compounds causing 15% of Surface water Drinking Water Protected Areas (DrWPAs) to be at risk of non-compliance with Article 7 of the European Water Frame Directive (Pesticide Forum, 2012).

The model was first set up for a standard soil used in previous studies (Brockhurst series; Brown et al. (2004)). Meteorological parameters from stations near the catchment were used along with daily rainfall from Mannington Hall to verify the proper performance of the model. Then, individual model runs were generated for each soil association as described below.

3.3.6.1 Soil parameters

Soil profiles for each simulation were divided into 60 layers. The only soils requiring tile drainage systems were Beccles, Burlingham and Isleham (Hodge et al., 1984). Initial moisture content in the different horizons at the start of the simulations was set to field capacity. The tile drainage designs are summarized in Table 3-3. A constant hydraulic gradient was used as the bottom boundary condition in the model. Hydraulic gradient values controlling the flow from the bottom boundary (GRAD) were adjusted for some of the soils such as for Barrow where a high GRAD value was used to account for high permeability in coarse-textured soils; initial GRAD values were taken from previous studies (Brown et al., 2004) and were then modified by a "trial-and-error" calibration to allow free soil drainage so as to avoid ponding at the base of the soil layer. Final GRAD values are shown in Table 3-3. Table 3-4 and

Table 3-5 provide the soil properties and the physical soil hydraulic parameters used in the model. Input values were established from a combination of guidance on how to parameterise MACRO (Beulke et al., 2002b; FOCUS, 2000) as follows: the boundary water tension for each horizon between micropores and macropores (CTEN) was established by expert judgement and then, their respective water content values (XMPOR) were derived from the water release curves; the boundary conductivity (KSM) was calculated from CTEN and XMPOR using the equation proposed by Laliberte et al. (1968) and Jarvis et al. (1997) and the pore size distribution factor for macropores (ZN) was also estimated by expert judgement.

Table 3-3 Tile drainage system design and GRAD values used in the model.

Soil	DRAINDEP (m)	SPACE (m)	GRAD (unitless)
Isleham	NA	NA	0.0005
Newport	NA	NA	0.002
Barrow	NA	NA	0.1
Beccles	0.55	20	0.002
Burlingham	0.80	20	0.0005

NA: Not applicable; DRAINDEP: Drain depth (primary drainage system); SPACE: Drain spacing (m). Source: (Hodge et al., 1984).

Table 3-4 Soil properties used in the model.

Soil association	Depth (cm)	Clay %	Silt %	Sand %	pH	Bulk density (g/cm^3)	Organic carbon %
Beccles							
A	25	25	29	46	7.4	1.35	1.7
E	45	22	32	46	7.5	1.55	0.4
B	70	44	32	24	8	1.47	0.5
BC	150	42	37	18	8	1.56	0.2
Burlingham							
A	25	22	34	44	7.5	1.4	1.4
E	45	22	32	46	8	1.52	0.5
B	60	33	33	34	8.3	1.54	0.4
B’	80	30	33	37	8.3	1.55	0.4
BC	150	28	34	38	8.4	1.65	0.2
Newport							
A	25	8	19	73	7	1.5	1.1
B	55	5	8	87	7.1	1.43	0.5
BC	100	4	9	87	7.6	1.38	0.4
C	150	3	4	93	6.9	1.42	0.3
Barrow							
A	30	12	20	68	7	1.5	0.8
B	55	14	23	63	7.1	1.43	0.4
B’	95	36	30	34	7.6	1.38	0.3
BC	150	29	45	26	6.9	1.42	0.2
Isleham							
A	30	20	13	67	6.4	1.03	6.2
E	50	3	7	90	6	1.45	0.4
B	75	3	6	91	5.5	1.54	0.3
C	150	1	4	95	4.9	1.47	0.1

(Hallett et al., 1995)

Table 3-5 Soil hydraulic properties used in the model.

Soil association	Depth (cm)	TPORV*	XMPOR	WILT	CTEN	N*	KSATMIN*	KSM	ZN	ASCALE	ALPHA*
Beccles											
A	25	48.5	41.0	16.1	18	1.248	42.8	0.160	4.0	10	0.0590
E	45	41.4	37.2	15.1	18	1.242	23.5	0.147	4.0	20	0.0601
B	70	44.4	41.0	22.7	25	1.207	3.4	0.068	3.0	75	0.0450
BC	150	41.1	33.0	21.5	25	1.200	4.9	0.055	3.0	50	0.0421
Burlingham											
A	30	46.7	42.5	15.2	15	1.252	40.2	0.285	4.0	5	0.0576
E	50	42.5	38.2	15.2	15	1.224	26.8	0.256	4.0	50	0.0600
B	75	41.7	39.1	19.2	20	1.219	7.9	0.125	3.0	100	0.0510
B’	100	41.4	38.5	18.1	20	1.224	10.5	0.123	3.0	100	0.0530
BC	150	37.7	35.0	17.0	20	1.222	6.5	0.112	3.0	100	0.0543
Newport											
A	25	43.0	38.1	8.1	10	1.356	102.5	0.634	4.0	5	0.0927
B	55	45.9	40.0	4.2	10	1.440	258.1	0.665	4.0	5	0.1237
BC	100	47.8	41.1	3.8	10	1.444	203.1	0.684	4.0	6	0.1250
C	150	46.3	33.5	2.0	10	1.574	292.6	0.799	4.0	6	0.1580

TPORV: Saturated water content (%); XMPOR: Boundary water content (%); WILT: Wilting point (%); CTEN: Boundary soil water tension (cm); N: van Genuchten’s N (unitless); KSATMIN: Saturated hydraulic conductivity (mm h^{-1}); KSM: Boundary hydraulic conductivity (mm h^{-1}); ZN: Tortuosity/Pore size distribution factor for macropores (unitless); ASCALE: Effective diffusion pathlenght (mm); ALPHA: van Genuchten’s alpha (1/cm). *Hallett et al. (1995)

Table 3-5 Soil hydraulic properties used in the model (cont.)

Soil association	Depth (cm)	TPORV*	XMPOR	WILT	CTEN	N*	KSATMIN*	KSM	ZN	ASCALE	ALPHA*
Barrow											
A	30	40.5	34.1	9.5	12	1.317	64.6	0.394	4.0	10	0.0841
B	55	45.9	40.0	11.5	12	1.279	76.2	0.462	4.0	10	0.0768
B’	95	49.0	45.0	22.3	20	1.205	12.3	0.144	3.0	25	0.0504
BC	150	41.8	39.2	19.1	20	1.213	4.7	0.125	3.0	25	0.0454
Isleham											
A	30	59.6	35.4	14.7	12	1.294	149.4	0.314	4.0	5	0.0819
E	50	45.1	38.7	2.8	12	1.500	221.2	0.641	4.0	5	0.1386
B	75	41.8	46.0	2.6	12	1.516	192.8	0.762	4.0	6	0.1433
C	150	44.5	39.8	2.0	12	1.557	256.9	0.660	4.0	6	0.1583

TPORV: Saturated water content (%); XMPOR: Boundary water content (%); WILT: Wilting point (%); CTEN: Boundary soil water tension (cm); N: van Genuchten’s N (unitless); KSATMIN: Saturated hydraulic conductivity (mm h^{-1}); KSM: Boundary hydraulic conductivity (mm h^{-1}); ZN: Tortuosity/Pore size distribution factor for macropores (unitless); ASCALE: Effective diffusion pathlenght (mm); ALPHA: van Genuchten’s alpha (1/cm). *(Hallett et al., 1995).

3.3.6.2 Crop parameters

The simulated pesticides were all herbicides, mainly used in agriculture so no application to urban areas was expected. The simulated crops were cereals and oilseed rape (OSR) because they are the main crops present in the catchment and they are also common to all the pesticides simulated. Generic crop parameters were taken from FOCUS (2000) Châteaudun scenario (Table 3-6); except for cereal dates which were modified to agree with typical growing information for the UK.

Table 3-6 Crop parameters used in the model (FOCUS, 2000).

Parameter	Parameter description	Crop Cereals	 OSR
IDSTART	Day of crop emergence	294*	250
ZDATEMIN	Day number for intermediate crop development stage between emergence and maximum leaf area	60	90
IDMAX	Day of maximum leaf area/rood depth	166*	110
IHARV	Day of harvest	212*	191
CFORM	Form factor that controls the rate of increase of leaf area between emergence and maximum leaf area (unitless)	2	2
RPIN	Root distribution (%)	80	60
FAWC	Root adaptability factor (unitless)	0.65	0.5
CRITAIR	Critical soil air content for root water uptake (%)	5	5
CANCAP	Canopy interception capacity (mm)	2	3
ATTEN	Attenuation factor for solar radiation in a crop canopy	0.6	0.6
RI50	The solar radiation that reduces stomatal conductance by 50%	55	55
ROOTINIT	Root depth at ZDATEMIN (m)	0.25	0.2
ROOTMAX	Maximum root depth (m)	0.8	0.8
LAIMIN	Leaf area index at ZDATEMIN (unitless)	1	1
LAIMAX	Maximum leaf area index (unitless)	5	4
LAIHAR	Leaf area of harvest (unitless)	1	2
ZHMIN	Crop height at ZDATEMIN (m)	0.15	0.2
HMAX	Maximum crop height (m)	0.8	1.5

OSR: Oilseed rape. *Dates modified to typical UK crop data

The crops to which the pesticides are usually applied in the UK are shown in Table 3–7. Clopyralid and MCPA are applied to more than one crop but just one crop was simulated for each of them, OSR and cereals, respectively. However, the amount of pesticide used in the other crops was also taken into account in the model by adding the application rates for all the crops to the model and then using the total crop area treated with the pesticide for the scale-up process.

Table 3-7 Crops to which the target pesticides can be applied (Netherton and Brown, 2010).

Pesticide	Crops
Chlorotoluron	Cereals
Carbetamide	OSR
Clopyralid	ORS; cereals; beet; grass
MCPA	Cereals; grass
Mecoprop	Cereals
Propyzamide	OSR

OSR: Oilseed rape

Reported crop areas for the Eastern region (Table 3-8) were also used to determine the percentage of crop area treated with pesticides in the scale-up process as explained in Section 3.3.9. The removal of set-aside in 2007 resulted in an increase in the area of individual arable crops (Table 3-8), in particular wheat (Garthwaite et al., 2009) and in the area treated with pesticide (Table 3-10). Set-aside was a scheme implemented in the European Economic Community from 1992 to 2007 (Council of the European Communities, 1993). Set-aside refers to land that farmers were not allowed to use for any agricultural purpose to prevent over-production and to allow land regeneration and ecosystems to develop. All relevant crops showed a substantial increase in crop area without significant changes in the total arable land during the studied period in the Eastern region. The most significant increases in crop area between 2006 and 2012 were observed for OSR (62.6%), grassland (27.2%), sugar beet (13.3%) and cereals (8.8%). The reports on arable crops in the UK also showed a substantial decrease in other crops such as beans (with a reduction of 58.4%), peas (36.2%) and linseed (16.4%) due to crop rotations, changes in land use (Garthwaite et al., 2013; Garthwaite et al., 2007) due to the increasing demand in the production of wheat and OSR in the country (Spink et al., 2009).

Table 3-8 Crop areas in the Eastern region for target crops and arable land between 2005 and 2013.

	Crop area (ha)			
	2006[a]	**2008**[b]	**2010**[c]	**2012**[d]
Cereals	471,706	534,735	502,081	513,356
OSR	103,488	130,181	140,960	168,241
Beet	72,656	80,732	75,918	82,346
Total arable land	1,017,084*	987,447	967,621	990,137
	2005[e]	**2009**[f]	**2013**[g]	
Grassland	29,137	36,103	37,065	

OSR: Oilseed rape. * Including set-aside

[a]Garthwaite et al. (2007); [b]Garthwaite et al. (2009); [c]Garthwaite et al. (2011); [d]Garthwaite et al. (2013); [e]Garthwaite et al. (2006); [f]Garthwaite et al. (2010); [g]Garthwaite et al. (2014)

3.3.6.3 Pesticide parameters

The physicochemical properties of the pesticides used in the model are presented in Table 3-9. The sorption distribution coefficient (ZKD) for each horizon was calculated from the K_{oc} and soil organic carbon content. Reported mean values of K_{oc} were used in the model (AERU, 2007); the exception was for propyzamide since an initial simulation using the reported average K_{oc} value of 840 ml g^{-1} greatly under-simulated the pesticide concentrations. Pedersen et al. (1995) reported K_d values for various soils with different organic carbon contents. Based on the organic carbon content of Beccles (1.7%) and Burlingham (1.4%), K_d values of 4.96 and 4.09, respectively, were estimated by extrapolation of the reported data. These K_d values correspond to an average K_{oc} value of 292 ml g^{-1} that was then used in the model to improve the simulation of propyzamide.

Table 3-9 Pesticide properties used in the model.

Pesticide	Koc (mL g^{-1})	Half-life soil[a] (days)	TREF (°C)	TRESP (K^{-1})	EXPB (unitless)	Freundlich coefficient (unitless)
Carbetamide	89[b]	10.9	20	0.08	0.7	0.93[b]
Chlorotoluron	184[b]	59	20	0.08	0.7	0.90[b]
Clopyralid	4.9[b]	11*	10	0.001	0.01	0.76[b]
MCPA	74[b]	24	20	0.08	0.7	0.68[b]
Mecoprop	20[b]	8.2	20	0.08	0.7	0.90[b]
Propyzamide	292[c]	47	20	0.08	0.7	0.90[c]

[a]AERU (2007), [b]Netherton and Brown (2010), [c]Pedersen et al. (1995)
*Field-based degradation rate. TREF: Reference temperature. TRESP: Exponent in the temperature response function. EXPB: Exponent in the degradation water response function.

Degradation rates for liquid and solid phases in the macropores and micropores (DEGMAL, DEGMIL, DEGMAS and DEGMIS) were assumed identical and calculated from soil half-lives assuming first-order kinetics. Degradation rates varied with temperature and moisture content for laboratory-based studies using the exponent in the temperature response function (TRESP) and the exponent in the degradation water response function (EXPB). The recommended values from FOCUS (2000) for TRESP and EXPB when using laboratory-based degradation data were used in the model (0.08 K^{-1} and 0.7, respectively); the exception was clopyralid where the half-life was a field value. Degradation values were supplied for the top soil (0-30 cm); the model calculated variation in degradation with depth by assuming a degradation rate of 50, 30 and 0% of that in topsoil at depths of 30 – 60, 60 – 100 and >100 cm, respectively (FOCUS, 2000).

Information about the total area treated with pesticide and the total weight applied was used in order to calculate annual pesticide application rates (Table 3-10). This information is usually reported by the Department for Food, Environment and Rural Affairs (Defra) every two years for arable crops and every four year for grassland. Pesticide usage for the missing years was estimated by linear interpolation between data from the previous and the following year for arable crops, whilst for grassland it was assumed to remain constant between reported values.

Table 3-10 Pesticide usage information for the Eastern region of the UK.

Pesticide / Crop / Year	Total area treated with pesticide (ha)	Total pesticide weight applied (kg)	Pesticide / Crop / Year	Total area treated with pesticide (ha)	Total pesticide weight applied (kg)
Chlorotoluron	**Cereals**		**Carbetamide**	**OSR**	
2006[a]	19,548	32,607	2006[a]	12,121	25,086
2008[b]	44,697	96,841	2008[b]	30,383	61,725
2010[c]	101,014	178,711	2010[c]	26,066	49,453
2012[d]	58,293	84,938	2012[d]	27,229	45,596
Clopyralid	**Cereals**		**Clopyralid**	**Beet**	
2006[a]	811	151	2006[a]	65,273	4,810
2008[b]	1,964	175	2008[b]	64,532	4,856
2010[c]	7,797	255	2010[c]	107,283	7,835
2012[d]	12,152	830	2012[d]	58,830	4,673
Clopyralid	**Grassland**		**MCPA**	**Grassland**	
2005[e]	9,233	1,311	2005[e]	103,504	131,101
2009[f]	23,988	4,597	2009[f]	20,997	20,469
Clopyralid	**ORS**		**MCPA**	**Cereals**	
2006[a]	34,848	2,767	2006[a]	19,977	14,910
2008[b]	94,076	7,729	2008[b]	9,826	5,867
2010[c]	98,711	7,794	2010[c]	21,980	13,016
2012[d]	137,486	11,781	2012[d]	17,575	16,128
Mecoprop	**Cereals**		**Propyzamide**	**OSR**	
2006[a]	167,289	98,793	2006[a]	81,144	60,493
2008[b]	187,286	102,590	2008[b]	110,357	83,970
2010[c]	180,532	95,611	2010[c]	161,367	125,987
2012[d]	135,446	77,745	2012[d]	215,375	171,889

[a]Garthwaite et al. (2007); [b]Garthwaite et al. (2009); [c]Garthwaite et al. (2011); [d]Garthwaite et al. (2013); [e]Garthwaite et al. (2006); [f]Garthwaite et al. (2010)

Note that the area treated with pesticide for a crop may exceed the area grown. For example, the OSR area treated with propyzamide in 2012 (Table 3-8) was 1.3 times larger than OSR area grown in the Eastern region (Table 3-10). This is because the reported area treated with pesticide is the sum of all applications made to that crop during the year (Thomas, 2009). Table 3-11 shows the resulting pesticide application rates used in the model and the pesticide application dates as well as the percentage of the total application rate are shown in Table 3-12.

Table 3-11 Pesticide application rates used in the MACRO.

Year	Chlorotoluron (kg/ha)	Carbetamide (kg/ha)	Clopyralid (kg/ha)	MCPA (kg/ha)	Mecoprop (kg/ha)	Propyzamide (kg/ha)
2006	1.67	2.07	0.07	1.18	0.59	0.75
2007	1.92	2.05	0.08	1.19	0.57	0.75
2008	2.17	2.03	0.08	1.21	0.55	0.76
2009	1.90	1.94	0.09	0.99	0.54	0.77
2010	1.77	1.86	0.09	0.78	0.53	0.78
2011	1.61	1.76	0.10	0.86	0.55	0.79

Interpolated values appear highlighted on the table

Table 3-12 Pesticide application dates and percentage of usage used in the MACRO.

Pesticide	**Application date/ Percentage of usage**
Chlorotoluron	25-Oct
Carbetamide	1-Nov
Clopyralid	25-Feb (39%), 25-May (61%)
MCPA	25-Apr (31%), 20-Jun (52%), 15-Oct (17%)
Mecoprop	25-Oct
Propyzamide	30-Nov

3.3.7 Modelling pesticide surface runoff

The models RZWQM2 and PRZM were used to calculate surface runoff and associated pesticide loss from each soil association. The models were not applied to Isleham soils since it is unlikely that runoff would be generated from a peaty soil with artificial drains.

3.3.7.1 Modelling pesticide loss via surface runoff using RZWQM2

The input parameters used in RZWQM2 were the same as those used for MACRO. In addition, water content values at -33 and -1500 kPa were supplied to the model to estimate the full Brooks–Corey (BC) parameters (Table 3-13).

Table 3-13 Brooks–Corey parameters used in RZWQM (Hallett et al., 1995).

Soil	Saturated water content	Water content at 33 kPa	Water content at 1500 kPa	Residual water content
Beccles				
A	0.485	0.2590	0.1611	0.0241
E	0.414	0.2319	0.1509	0.0226
B	0.444	0.3120	0.2271	0.0340
BC	0.411	0.2870	0.2150	0.0322
Burlingham				
A	0.467	0.2470	0.1520	0.0228
E	0.425	0.2350	0.1520	0.0228
B	0.417	0.2730	0.1921	0.0288
B’	0.414	0.2610	0.1810	0.0271
BC	0.377	0.2430	0.1700	0.0255
Newport				
A	0.430	0.1510	0.081	0.0121
B	0.459	0.0950	0.042	0.0063
BC	0.478	0.0930	0.038	0.0057
C	0.463	0.0510	0.020	0.0030
Barrow				
A	0.405	0.0995	0.0392	0.0142
B	0.459	0.1074	0.0437	0.0172
B’	0.490	0.1722	0.0997	0.0334
BC	0.418	0.2282	0.1612	0.0286

3.3.7.2 Modelling pesticide loss via surface run off using PRZM

PRZM was also used to calculate pesticide runoff in the catchment. Input values such as cropping, pesticide application data and soil properties were the same as those used for the MACRO model. Soil erosion was turned off in the model because eroded sediment is not a significant route of transport for the pesticide simulated. Runoff curve numbers were supplied according to the hydrologic soil groups estimated for each soil association (Table 3-14). Runoff curve numbers describe the interaction of soil types and land use to identify the average soil moisture condition for three physical stages of the soil: fallow, cropping and residue remaining following harvest (Suárez, 2006). Curve numbers used in the model corresponded to poorly drained conditions and cropping values to small grain crop in straight row.

Table 3-14 Hydrological soil group classification and initial runoff curve numbers used in PRZM (USDA, 1986).

Soil association	Hydrological group	Soil description	Fallow	Cropping	Residue
Beccles	C	Poorly drained soils	91	83	88
Burlingham	C	Poorly drained soils	91	83	88
Barrow	B	Moderately well drained soils	86	75	83
Newport	B	Moderately well drained soils	86	75	83

3.3.8 Runoff from developed areas

Urban areas are reported to account for approximately 2% of the Wensum catchment (Sear et al., 2006); however, this information refers to major urban areas, not taking into account roads, farms and small villages. For modelling purposes it was estimated that the total developed areas would be about 4% of the catchment. In the model, it is considered that 50% of the rainfall from hard surfaces will end in the river network as rapid runoff. Surface runoff was the only source of flow considered from the development areas.

3.3.9 Scale-up of model results

Modelling results were scaled-up for the entire catchment area since all models accounted for only 1 ha of land.

3.3.9.1 Scale-up of water flow results

Individual sources of water flow simulated by the models include tile drainage (MACRO), percolation (MACRO), run-off (PRZM and RZWQM) and urban runoff (50% of rainfall falling on these areas). Simulated water percolation was added to the groundwater mixing model to estimate the river baseflow. Individual water flow results were scaled-up by taking into account the size of catchment, soil associations and urban areas. All the resulting flows were then added together to estimate the total water flow at the catchment outlet. It was assumed that there was no delay (larger than a day) between flow leaving the field and arriving at the catchment outlet (i.e. to simplify the simulation the travel time was ignored).

3.3.9.2 Scale-up of pesticide concentration results

The pesticide loss simulated by MACRO corresponded to daily pesticide rate (mg/m^2/h) through leaching and tile drainage. In order to scale up these results information about the pesticide usage in the catchment was required. As there were no reported detailed land use data specific to the Wensum catchment, it was necessary to use information for the Eastern region of England and assume that pesticide usage in the Wensum was proportional to these data. The annual percentage of crop area treated with each pesticide (p) in the Eastern region ($\%CATE$) was calculated using reported information about the annual crop area treated with each pesticide ($CATE$) (Table 3-10) and the annual crop area in this region (CAE), both in hectares (Table 3-8), using Equation 3-2. The results are shown in Table 3-15.

Equation 3-2 $$\%CATE_p = (CATE_p\ /CAE)\ \times 100\%$$

Table 3-15 Percentage of crop treated with a specific pesticide in the Eastern region.

Year	Chlorotoluron	Carbetamide	Clopyralid	MCPA	Mecoprop	Propyzamide
2006	4.14	11.7	11.9	16.5	35.5	78.4
2007	6.38	18.2	14.5	15.2	35.2	82.0
2008	8.36	23.3	16.9	3.70	35.0	84.8
2009	14.0	21.0	18.9	4.52	35.5	100
2010	20.1	18.9	23.3	5.37	35.6	114
2011	15.7	23.0	19.0	5.06	35.4	121

Interpolated values in the table appear highlighted

The resulting %CATE were then used together with information about the crop areas in the Wensum (CAW, in ha) (Table 3-16) to calculate the crop area treated with pesticide in the catchment ($CATW$, in ha) using Equation 3-3.

Equation 3-3 $$CATW = CAW \times \%CATE_p$$

Table 3-16 Crop areas in the Wensum catchment (Farrow, 2013).

Year	Cereals (ha)	OSR (ha)	Beet (ha)	Grass (ha)
2005	21,646	3,534	5,406	6,263
2007	20,616	4,162	4,829	6,269
2008	19,606	4,067	4,699	6,300

Then, the daily pesticide loads (L, in mg/day) for each soil association were calculated using Equation 3-4, where PR is the simulated pesticide loss rate (mg/m$^{2/}$h), and SA is the proportion of each soil association (Table 3-1).

Equation 3-4 $$L = CATW \times PR \times SA \times 24h\ d^{-1}$$

Finally, these results were divided by the predicted water flow (F, in m^3/day) to calculate the pesticide concentration at the Wensum outlet (PC, in μg/l) using Equation 3-5.

Equation 3-5 $$PC = L/F$$

3.3.10 Model evaluation

Model evaluation was applied to the results from all models for both water flow and pesticide simulations. The simulated runoff from PRZM and RZWQM2 was also evaluated to determine which model better simulated this emission route. LOQ for most of the pesticides varied during the simulation period as shown in Table 3-17.

Table 3-17 LOQ reported in the monitoring data (CSF, 2012).

Pesticide	LOQ (μg/l) 2006 – Oct 2009	LOQ (μg/l) Nov 2009 – 2011
Chlorotoluron	0.04	0.01
Carbetamide	0.04	0.01
Clopyralid	0.04	0.01
MCPA	0.04	0.001
Mecoprop	0.04	0.001
Propyzamide	0.005	0.005

The first analysis was carried out by visual comparison of the simulated and measured data; concentrations was set to LOQ values in the measured data for monitoring days when pesticide concentration were below the LOQ. Goodness-of-fit and model efficiency were calculated for a quantitative evaluation of the simulations.. The residuals (e) were calculated for each data point over the simulation period by calculating the difference between the observed (Q_0) and predicted daily flow (Q_m) (Equation 3-6). The results were represented in a residual plot to evaluate their pattern over time.

Equation 3-6 $$e = Q_o - Q_m$$

A hydrological year corresponds to the period between September 1st and August 31st. Model efficiency was evaluated for each hydrological year and for the overall period of time, i.e. from January 1st 2006 to December 15th 2011. The Nash-Sutcliffe model efficiency coefficients (Nash and Sutcliffe, 1970) were calculated on a daily time-step (t) for each hydrological year, for periods of high and low flows, and for the entire simulation period using Equation 3-7.

Equation 3-7 $$E = 1 - \frac{\sum_{t=1}^{T}\left(Q_o^t - Q_m^t\right)^2}{\sum_{t=1}^{T}\left(Q_o^t - \bar{Q}_o\right)^2}$$

where Q_o^t and Q_m^t are the observed and modelled flow at time t, respectively; and $\bar{Q}_o$is the observed mean value. Model efficiencies values can range from -∞ to 1. An efficiency of E

= 1 corresponds to a perfect match between the model and the observed data. A model efficiency of E = 0 indicates that the simulation is as accurate as the mean of the observed data, whereas simulations with E <0 occur when the observed mean is a better predictor than the model. Therefore, the best simulation results would have positive efficiency values near to one.

3.3.11 Model calibration

3.3.11.1 MACRO calibration

The main aim of the model calibration was to improve the behaviour of the hydrograph simulation from MACRO at the end of the low flow periods. Discrepancies between the simulated and observed water flow indicated the need for calibration of cereals and OSR crop parameters as well as for the soil parameters of the most influential soils in the simulation, Beccles and Burlingham. Root parameters were changed to reduce the amount of water uptake by plants. For both crops the root distribution (RPIN) was increased to 90; the root depth at ZDATEMIN (ROOTINIT) and the maximum root depth (ROOTMAX) were reduced to 0.05 and 0.7, respectively. Finally, for cereals the root adaptability factor (FAWC) was reduced to 0.5. Table 3-18 summarized these parameters.

Table 3-18 Uncalibrated and calibrated crop parameters.

Parameter	**Parameter description**	**Crop** **Cereals uncalibrated**	**Cereals calibrated**	**OSR uncalibrated**	**OSR calibrated**
RPIN	Root distribution (%)	80	90	60	90
FAWC	Root adaptability factor (unitless)	0.65	0.5	0.5	0.5
ROOTINIT	Root depth at ZDATEMIN (m)	0.25	0.05	0.2	0.05
ROOTMAX	Maximum root depth (m)	0.8	0.7	0.8	0.7

OSR: Oilseed rape

Since Beccles and Burlingham are the main soils in the area and also they are the ones contributing to pesticide loss through tile drainage, calibration was applied to increase water flow infiltration capacity by facilitating the movement of water in the soil profile. The modified parameters were the tortuosity/pore size distribution factor for macropores (ZN), the effective diffusion path length (ASCALE) and the fraction of sorption sites (FRACMAC). ZN is very sensitive value influencing preferential flow which cannot be measured directly and systematic calibration is normally required (Beulke et al., 2002b). ZN was reduced in a unit for all horizons in Beccles and in 0.5 for the first two horizons in Burlingham. In addition, FRACMAC was changed reduced from 0.2 to 0.1 for Beccles since the original value was too big (common values range between 0.005 and 0.1 (Beulke et al., 2002b)). For Burlingham, ASCALE was increased to 10 since the original value of 5 was too small (common values range between 10 and 40). Calibrated values appear in Table 3-19. In addition, a calibrated value of 1% was use as the outflow rate from the deep aquifer to the river network in the groundwater mixing model.

Table 3-19 Uncalibrated and calibrated ZN and ASCALE parameters for Beccles and Burlingham.

Soil association	ZN Uncalibrated	ZN calibrated	ASCALE uncalibrated	ASCALE calibrated
Beccles				
A	4.0	3.0		
E	4.0	3.0		
B	3.0	2.0		
BC	3.0	2.0		
Burlingham				
A	4.0	3.5	5	10
E	4.0	3.5		

3.3.11.2 PRZM calibration

Runoff curve numbers were calibrated in PRZM to reduce the over-estimation of runoff by the model. Runoff from Beccles and Burlingham was considered to be non-significant as these soils include tile drainage systems, a practice that is expected to greatly reduce surface runoff from these soils but is not simulated by PRZM. Thus, any runoff from arable lands was considered to come from Newport and Barrow. Therefore, the first step of the calibration was to remove the predicted runoff from Beccles and Burlingham. The evaluation of the calibration effect was initially carried out by visual comparison between the observed hydrograph and the predicted runoff from PRZM; subsequently, model efficiency was applied to facilitate the calibration process. Since considerable over-estimation of the flow was still observed; the hydrologic soil group for Newport and Barrow was changed from B to A. Further calibration of the curve numbers was required, so their values were reduced by 2% until an optimal value of a reduction of the curve number by 10% was determined. Table 3-20 shows initial and calibrated curve numbers used in the model.

Table 3-20 Uncalibrated and calibrated runoff curve numbers for PRZM.

Uncalibrated			Calibrated		
Fallow	**Cropping**	**Residue**	**Fallow**	**Cropping**	**Residue**
86	75	83	69	57	67

3.4 Results

3.4.1 Water flow simulation using MACRO

3.4.1.1 Tile drainage and percolating flow simulation

MACRO was used to simulate tile drainage and percolating flow within the Wensum catchment. Figure 3-6 shows the hydrograph from the initial uncalibrated simulation. Results showed over-estimation of the flow in periods of high flow. The largest over-estimation was observed from November 2006 to March 2007 (up to a factor of 2.1) whereas for the remainder of the period only a few peaks were over-estimated but to a lesser degree (up to a factor of 1.3). The simulated hydrograph had a smooth behaviour in periods of low flow compared to the observed data. The simulation suggested that most of the peaks in periods of high flow corresponded to drain and percolating flow. Table 3-21 shows the simulated drain and percolating volume for each hydrological year and for the whole simulation period, together with observed and total simulated volume from MACRO at the catchment outlet. Similar proportions for drain flow and percolating volumes were simulated between years but percolation was simulated in larger amounts for all periods, ranging between 54.2 and 64.0% year of the total flow from MACRO. The simulated flow between 2006 and 2011 from MACRO accounted for 85.9% of the total observed volume; however, the model matched observed volume in 2006-2007, exceeding the observed volume by 0.6%.

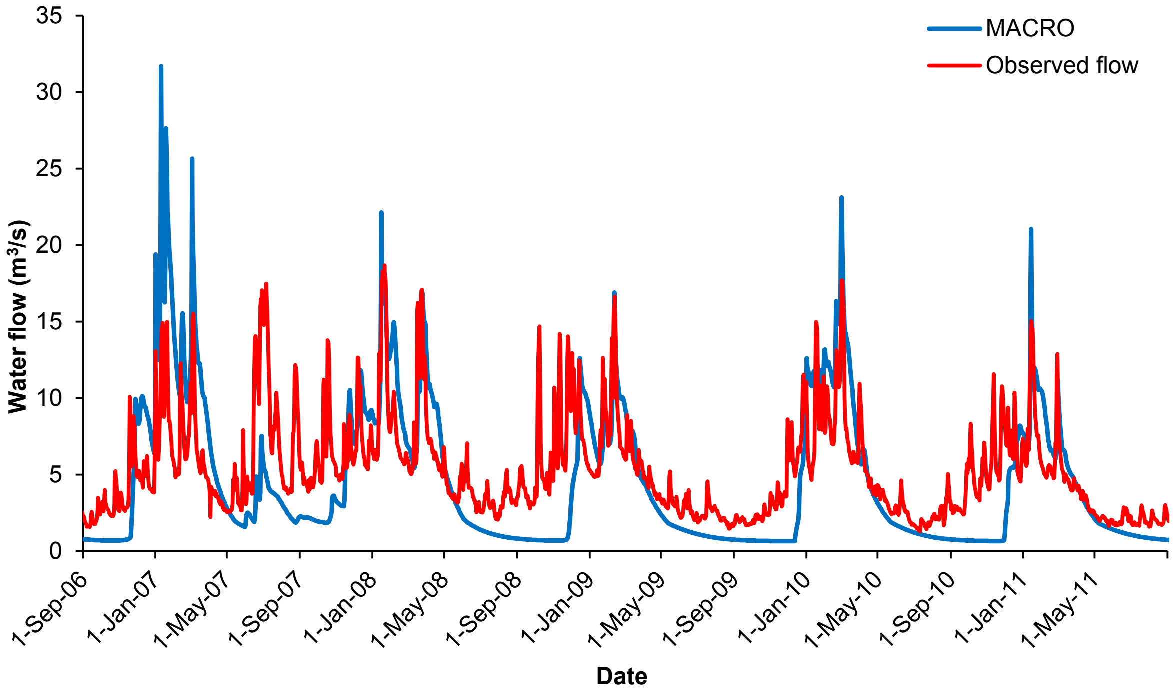


Figure 3-6 Observed and simulated flow using MACRO.

Table 3-21 Observed water volume and simulated drainage, leaching volume from MACRO and including the runoff from the development areas (MACRO + Urban runoff) together with the estimated runoff from the development areas (Urban runoff) and its percentage simulated from the observed volume from each hydrological year.

Hydrological year	**MACRO drainage (10^6 m^3)**	**MACRO percolation (10^6 m^3)**	**Urban runoff (10^6 m^3)**	**Observed flow (10^6 m^3)**	**Total simulated flow (10^6 m^3)**	**Total simulated flow MACRO + Urban runoff (% of the observed)**
2006 – 2007	84.2	107.3	12.7	190.5	204.3	107.2
2007 – 2008	83.1	98.5	8.6	198.1	190.3	96.0
2008 – 2009	43.7	70.6	7.0	168.0	121.2	72.2
2009 – 2010	55.7	79.9	7.6	150.9	143.3	94.9
2010 – 2011	37.7	67.1	7.5	140.0	112.3	80.2
2006 – 2011	304.4	423.4	43.5	847.5	771.3	91.0

3.4.1.2 Runoff from developed areas

Runoff coming from developed areas (urban runoff) was calculated and added to the simulation from MACRO. The resulting hydrograph is compared to the initial simulation and the observed flow in Figure 3-7. The runoff added a large number of small peaks to the hydrograph particularly during low flow periods in contrast to the smooth curve of the initial simulation. The runoff peaks also matched the timing and pattern of the observed flow despite the lack of baseflow in the simulation. Over-estimation of the flow was increased for 2006, exceeding the observed flow by 7.2% (Table 3-21). To this point, without including other sources of surface runoff, the simulation accounted for 91.0% of the observed flow. The missing simulated flow compared to the observed data between 2007 and 2011 varied between hydrological years from 4.0% (2007-2008) to 27.8% (2008-2009).

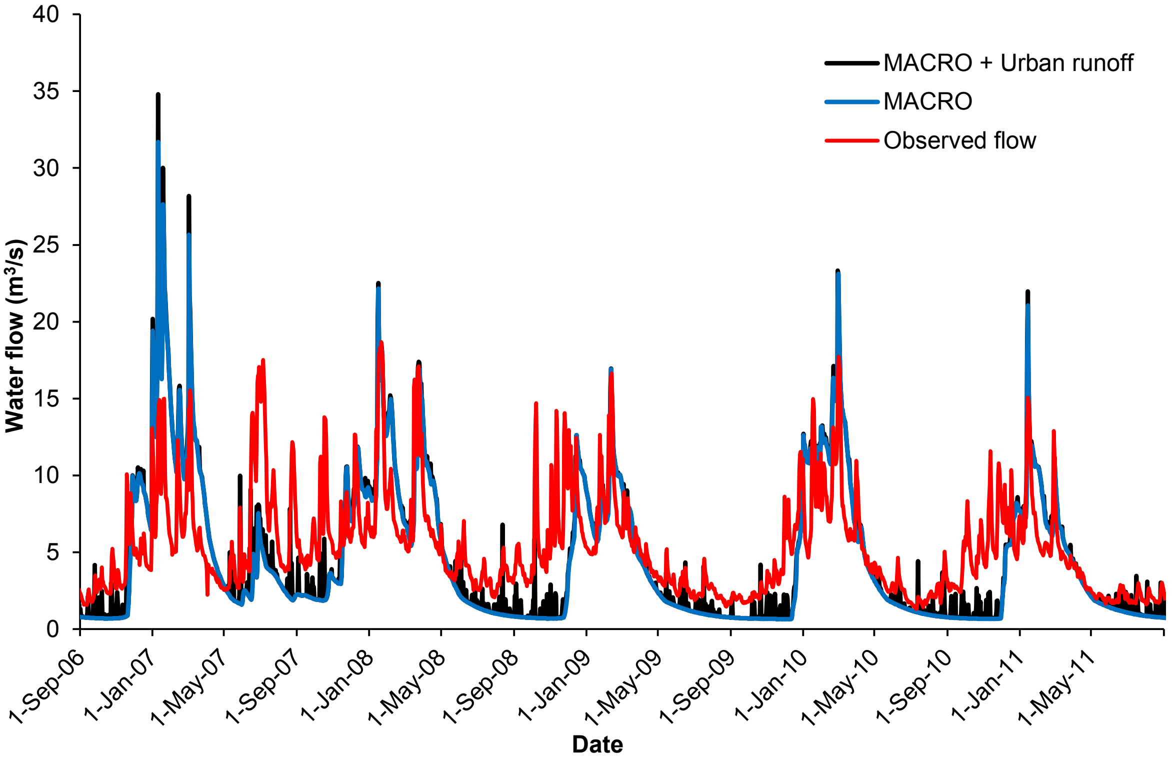


Figure 3-7 Observed and simulated flow from MACRO with (MACRO + Urban runoff) and without (MACRO) the runoff from development areas.

3.4.1.3 Groundwater mixing model simulation

The effect of adding the groundwater mixing (GW) model to the simulation is presented in Figure 3-8; a closer behaviour to a typical hydrograph including baseflow was observed particularly at the beginning of the low flow periods. However, at the end of these periods the flow took a longer time to recover which suggests delays to the normal wetting up of the soil. Instead of the symmetric shape in the hydrograph during low flow periods, a more asymmetrical shape was observed characterized by a gradual decrease in the curve flow until reaching a minimum value and then followed by an under-estimate of flow at the beginning of high flow periods. The GW model also had a varied effect on the total simulated volume for the hydrological years (Table 3-22); the simulated volume in 2006-

2007, 2009-2010 and for the overall simulation period (2006 – 2011) was reduced while for the rest of the hydrological years an increased volume was observed. Over-estimation for 2006-2007 decreased from 7.2 to 1.9% compared to the observed volume. The simulated volume for the period 2006 – 2011 was 89.5% of the observed volume.

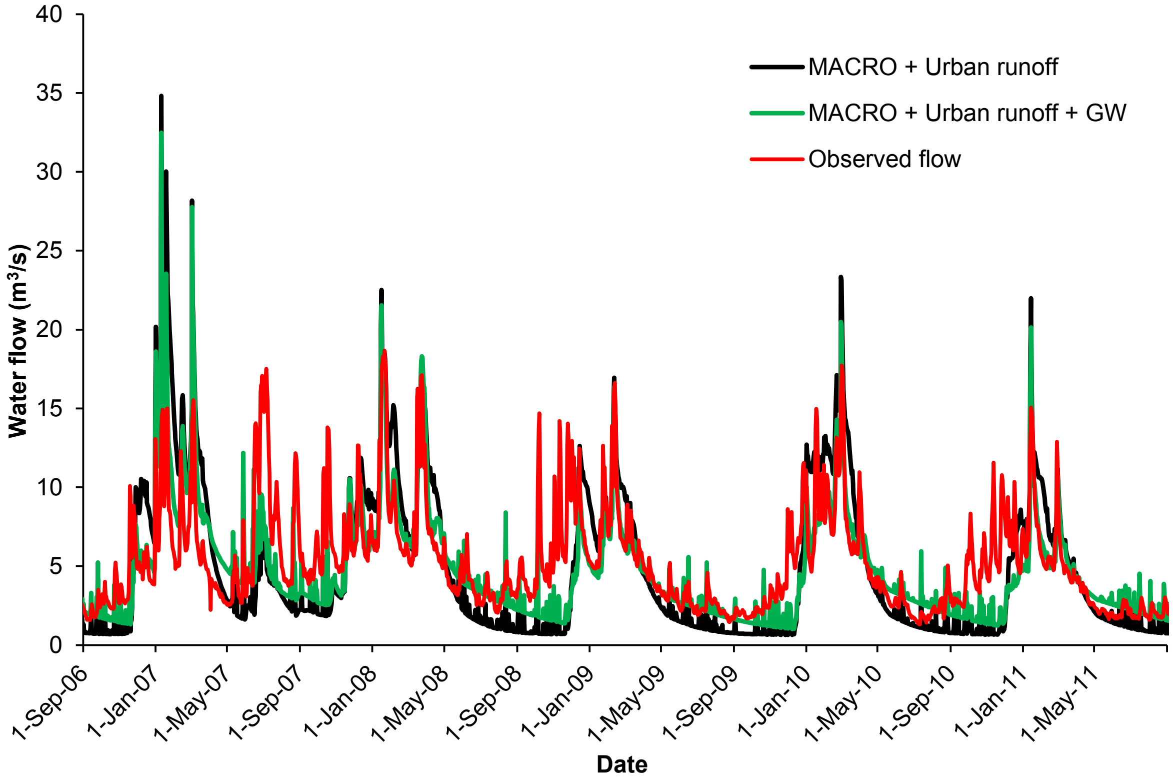


Figure 3-8 Comparison of the simulation from MACRO with (MACRO + urban runoff + GW) and without (MACRO + urban runoff) the groundwater mix model together with the observed flow.

Table 3-22 Observed water volume and that simulated from MACRO including the runoff from the development areas (MACRO + urban runoff) together with the simulation including the volume from the GW model and its percentage simulated from the observed volume from each hydrological year

Hydrological year	**MACRO + Urban runoff (10^6 m^3)**	**MACRO + Urban runoff + GW (10^6 m^3)**	**Observed (10^6 m^3)**	**Total simulated (% of the observed)**
2006 – 2007	204.3	194.1	190.5	101.9
2007 – 2008	190.3	190.9	198.1	96.3
2008 – 2009	121.2	123.4	168.0	73.5
2009 – 2010	143.3	137.7	150.9	91.2
2010 – 2011	112.3	112.7	140.0	80.5
2006 – 2011	771.3	758.8	847.5	89.5

Figure 3-9 shows the effect of the GW model on the model residuals. The residuals for the initial simulation exhibited a sinusoidal pattern with large positive and negative values due to under-estimation of the flow at the end of low flow periods and over-estimation during periods of great flow, respectively. The GW model showed a great reduction in the magnitude of negative residuals as well as for some large positive ones. However, the large negative values were still observed in 2006-2007. A non-random behaviour in the residuals was also observed for the simulation including the GW model but with a different pattern; the residuals tended to behave with a "U-shape" for each hydrological year due to the sustained under-estimation of flow at the beginning of the winter.

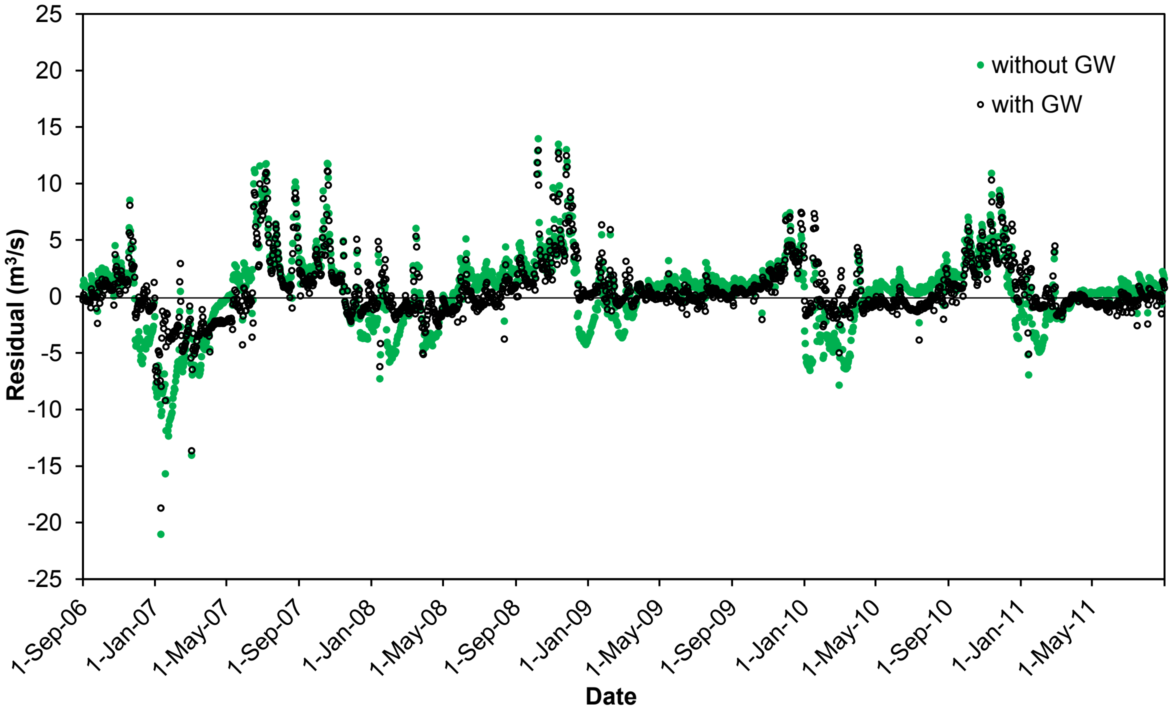


Figure 3-9 Comparison of the residuals from the simulations with and without the GW model.

The Nash-Sutcliffe model efficiency coefficients (*E*) were calculated for individual hydrological years, for the overall simulation (2006 – 2011), and for high (1 November – 30 April) and low flow periods (1 May – 31 October) for both simulations: with and without the GW model (Table 3-23). The simulation without the GW model showed negative values of model efficiency for most of the hydrological years as well as for low and high flow periods. The exceptions were for the hydrological years 2007-2008 and 2009-2010 and for the high flow period 2007-2008 were positive but small values were observed. The use of the GW model greatly improved the simulation; positive values were achieved for the entire simulation period (*E* = 0.35) and for all the hydrological years varying between 0.04 (in 2006-2007) and 0.64 (in 2009-2010). The best model efficiencies were obtained for 2007-2008 and 2009-2010 (*E* = 0.61 and 0.64, respectively). The worst model efficiency was obtained for 2006-2007 due to the over-estimation of the flow. Negative efficiency values were obtained for some high and low flow periods but positive values were achieved for both overall simulations (E = 0.11 and 0.20, respectively). Better results were generally obtained for high than for low flow periods; apart from 2008-2009. The best model efficiency in the simulation was obtained for the high flow period in 2007-2008 (*E* = 0.73).

Table 3-23 Nash-Sutcliffe model efficiency coefficients for the simulated flow with and without the GW model for each hydrological year as well as for the high and low flow periods.

	Simulation without the GW model			**Simulation with the GW model**		
Hydrological year	E hydrological year	E high flow period 1 Nov – 30 Apr	E low flow period 1 May – 31 Oct	E each hydrological year	E high flow period 1 Nov – 30 Apr	E low flow period 1 May – 31 Oct
2006 – 2007	-0.85	-2.29	-3.79	0.04	-0.30	-0.87
2007 – 2008	0.23	0.30	-2.18	0.61	0.73	-0.82
2008 – 2009	-0.23	-0.92	-3.16	0.10	-0.54	0.05
2009 – 2010	0.31	-0.34	-1.71	0.64	0.29	-0.70
2010 – 2011	-0.11	-0.69	-5.70	0.19	-0.29	-3.82
2006 – 2011	-0.12	-0.65	-0.19	0.35	0.11	0.20

3.4.2 Water flow simulation using RZWQM

Table 3-24 shows the simulated runoff for one hectare of each soil association in the Wensum catchment using RZWQM. The simulated runoff had exactly the same values for all the soil associations despite the fact that their physical and hydraulic properties were different. The reason for this behaviour was that for the present catchment and parameter set, the model only predicted surface runoff on days when the temperature was below or close to zero; at such times the model assumed that the soil surface was frozen so precipitation could not infiltrate resulting in a runoff event. The lack of runoff when the soil was not frozen was thought to be due to the high saturated hydraulic conductivity values of the soils which yielded high infiltration capacity for this particular model. Runoff peaks were mostly predicted during high flow periods in 2010-2011 and only a few peaks in 2009 and a single small one in 2007.

Table 3-24 Runoff resulting runoff from 1ha of the different soil associations using RZWQM along with the measured maximum and minimum temperatures.

	Runoff values					
Date	Beccles (cm d^{-1})	Burlingham (cm d^{-1})	Barrow (cm d^{-1})	Newport (cm d^{-1})	T max (°C)	T min (°C)
8/2/2007	0.001	0.001	0.001	0.001	4.6	-7.2
12/1/2009	0.022	0.022	0.022	0.022	8.1	2.2
2/2/2009	0.007	0.007	0.007	0.007	2.0	-2.1
3/2/2009	0.035	0.035	0.035	0.035	3.1	-2.2
4/2/2009	0.016	0.016	0.016	0.016	4.8	-6.1
7/2/2009	0.002	0.002	0.002	0.002	2.2	-2.3
25/12/2009	0.044	0.044	0.044	0.044	3.7	0.3
26/12/2009	0.022	0.022	0.022	0.022	3.9	-1.5
28/12/2009	0.029	0.029	0.029	0.029	5.5	-2.0
29/12/2009	0.036	0.036	0.036	0.036	6.0	-3.1
2/1/2010	0.005	0.005	0.005	0.005	3.5	-4.3
5/1/2010	0.004	0.004	0.004	0.004	2.3	-5.2
7/1/2010	0.023	0.023	0.023	0.023	2.3	-1.7
8/1/2010	0.007	0.007	0.007	0.007	2.8	-6.2
10/1/2010	0.041	0.041	0.041	0.041	2.2	-0.6
27/1/2010	0.006	0.006	0.006	0.006	2.3	-3.9
28/1/2010	0.032	0.032	0.032	0.032	7.1	0.4
21/2/2010	0.018	0.018	0.018	0.018	5.0	-5.5
22/2/2010	0.007	0.007	0.007	0.007	2.3	-3.9
23/2/2010	0.037	0.037	0.037	0.037	3.5	0.0
24/2/2010	0.021	0.021	0.021	0.021	5.3	1.6
29/11/2010	0.005	0.005	0.005	0.005	1.5	-2.4
30/11/2010	0.033	0.033	0.033	0.033	2.8	-1.5
2/12/2010	0.010	0.010	0.010	0.010	1.5	-0.7
9/12/2010	0.031	0.031	0.031	0.031	4.6	-1.6
12/12/2010	0.028	0.028	0.028	0.028	8.0	-0.8
22/12/2010	0.007	0.007	0.007	0.007	1.5	-1.6
25/12/2010	0.010	0.010	0.010	0.010	2.9	-3.7
28/12/2010	0.008	0.008	0.008	0.008	2.9	-4.1
29/12/2010	0.025	0.025	0.025	0.025	3.6	1.7

More detailed hydrographs comparing the observed flow to the runoff simulation from RZWQM added to the uncalibrated simulation from MACRO (MACRO + urban runoff + GW + RZWQM) and the simulation without RZWQM (MACRO + urban runoff + GW) for periods when RZWQM predicted runoff events are shown in Figure 3-10. Hydrographs showed that most of the simulated runoff peaks did not match the observed flow (Figure 3-10 a – c). Simulated runoff events when the behaviour of the flow was under-estimated at the beginning of the high flow periods were difficult to evaluate (e.g. from December 24th to

31st 2009 and from November 28th to December 24th 2010); despite this, the simulation without RZWQM (MACRO + urban runoff + GW) matched the observed data better but even though calibration is required to address the under-estimation of flow.

Table 3-25 shows the Nash-Sutcliffe model efficiency coefficients for the simulations with and without the runoff from RZWQM. A slight reduction in model efficiency values was observed for hydrological years 2008-2009 and 2009-2010 as well as for their respective high flow periods and the overall simulation of high flow (2006 – 2011); the exception was for 2010 when a slightly improvement in model efficiency for the hydrological year and its low flow period occurred likely due to the reduction in the under-estimation of the flow but not because the runoff peaks agreed with the observed data. No effect was observed for periods of high flow since significant improvements were observed during these times. Due to the large disagreement in the simulation of the runoff by RZWQM and as no improvements were made in water flow simulation, it was concluded that the RZWQM model could not predict the real runoff behaviour in the catchment; hence, it was not included in the modelling framework.

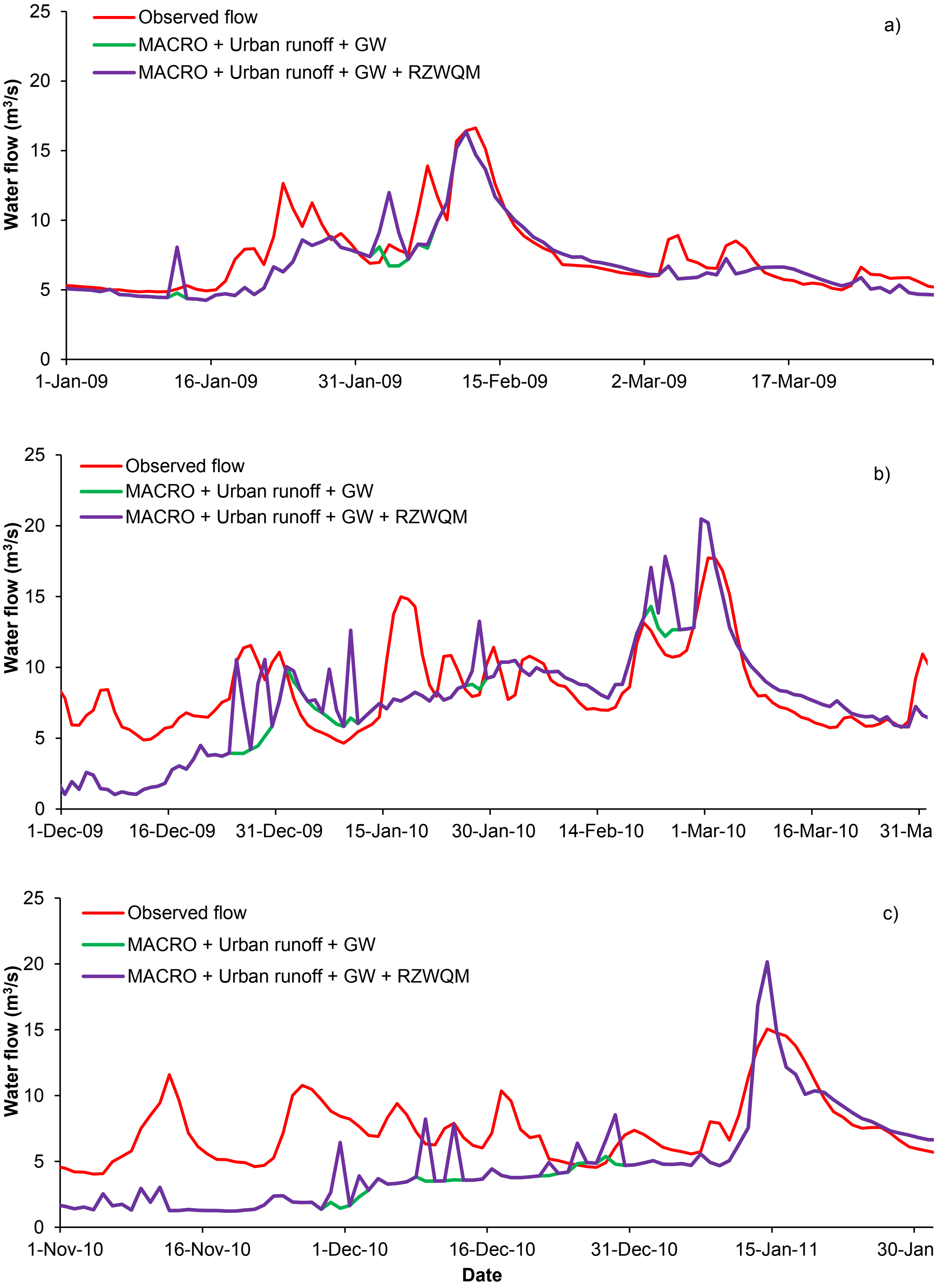


Figure 3-10 Comparison of the measured flow with the simulation from MACRO (MACRO + urban runoff + GW) and including the runoff from RZWQM (MACRO + urban runoff + GW+ RZWQM).

Table 3-25 Nash-Sutcliffe model efficiency coefficients for the simulation with and without RZWQM for each hydrological year as well as for the high and low flow periods.

	Without RZWQM			**Including RZWQM**		
Hydrological year	E each hydrological year	E high flow period 1 Nov – 30 Apr	E low flow period 1 May – 31 Oct	E each hydrological year	E high flow period 1 Nov – 30 Apr	E low flow period 1 May – 31 Oct
2006 – 2007	0.04	-0.30	-0.87	0.04	-0.30	-0.87
2007 – 2008	0.61	0.73	-0.82	0.61	0.73	-0.82
2008 – 2009	0.10	-0.54	0.05	0.09	-0.55	0.05
2009 – 2010	0.64	0.29	-0.70	0.62	0.25	-0.70
2010 – 2011	0.19	-0.29	-3.82	0.23	-0.22	-3.82
2006 – 2011	0.35	0.11	0.20	0.35	0.10	0.20

3.4.3 Water flow simulation using PRZM

PRZM was also used to simulate runoff in the catchment. Table 3-26 shows the simulated runoff for each soil association during the 5-year period (2006 – 2011) before calibration (i.e. including Beccles and Burlingham in the simulation). In contrast to RZWQM, PRZM simulated different runoff values for all soils according to their infiltration capacity. Figure 3-11 shows the resulting flow when adding the simulation from MACRO to the runoff from PRZM (MACRO + urban runoff + GW + PRZM). PRZM was also able to simulate more runoff events than RZWQM with a good match in the timing compared to the observed flow. However, the model greatly over-estimated runoff by up to a factor of nine.

Table 3-26 Simulated runoff using PRZM for each soil association over the period 2006 – 2011 for the uncalibrated simulation.

Newport (cm/5 years)	**Barrow (cm/5 years)**	**Beccles (cm/5 years)**	**Burlingham (cm/5 years)**
5.151	4.725	15.082	16.434

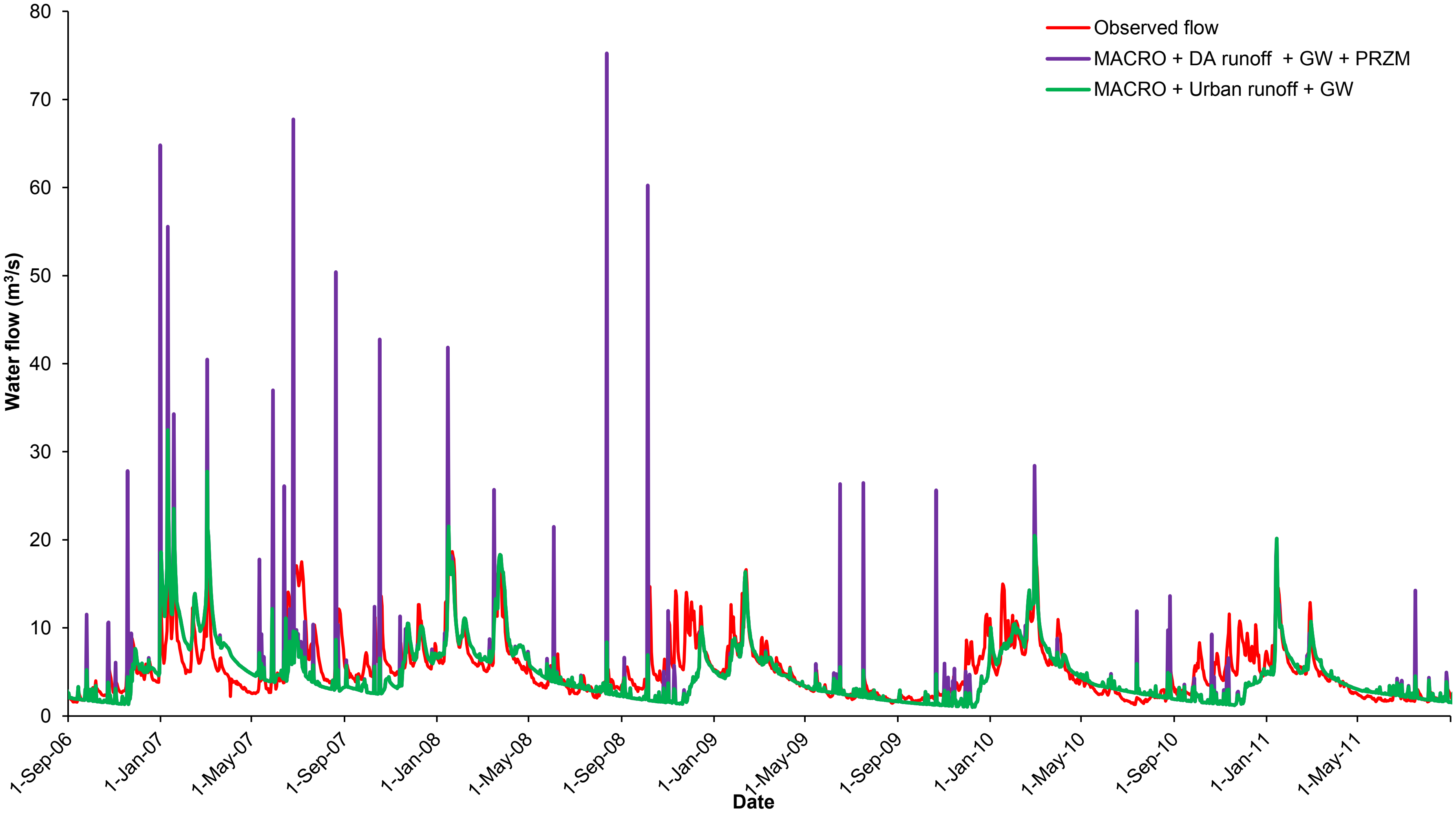


Figure 3-11 Comparison of the measured and the simulated flow from MACRO including the runoff from PRZM **(**MACRO + urban runoff + GW).

Discrepancies in the runoff simulation from PRZM were also reflected in model efficiency which was significantly reduced for all the hydrological years compared to the simulation without PRZM (Table 3-14). The runoff over-estimation may be explained by the fact that PRZM is an empirical model designed for conditions in the USA so the modelling results would differ from UK behaviour. In addition, PRZM does not include the simulation of drainage systems which are present in the area. Drainage systems are able to greatly reduce runoff by improving soil infiltration. Model calibration can improve the runoff simulation from PRZM since the timing of the peaks did agree with the observed flow.

Table 3-27 Nash-Sutcliffe model efficiency coefficients for the simulations with and without PRZM for each hydrological year as well as for the high and low flow periods.

	Without PRZM (MACRO + urban runoff + GW)			**Including PRZM (MACRO + urban runoff + GW + PRZM)**		
Hydrological year	E each hydrological year	E high flow period 1 Nov – 30 Apr	E low flow period 1 May – 31 Oct	E each hydrological year	E high flow period 1 Nov – 30 Apr	E low flow period 1 May – 31 Oct
2006 – 2007	0.04	-0.30	-0.87	-2.26	-3.11	-4.94
2007 – 2008	0.61	0.73	-0.82	-1.1	0.32	-15.12
2008 – 2009	0.10	-0.54	0.05	-0.93	-0.540	-19.65
2009 – 2010	0.64	0.29	-0.70	0.43	0.23	-1.37
2010 – 2011	0.19	-0.29	-3.82	0.16	-0.23	-14.69
2006 – 2011	0.35	0.11	0.20	-0.80	-0.58	-2.45

3.4.4 Model calibration

3.4.4.1 Model calibration for MACRO

The main aim of the model calibration was to improve the behaviour of the flow at the end of the low flow periods. Changes in the root parameters of both crops and in soil parameters for Beccles and Burlingham were applied in order to reduce the amount of water uptake by plants and to increase soil moisture. Figure 3-12 shows the effect in the hydrograph for 2009-2010; the calibrated simulation allowed an increase in the soil moisture at the beginning of the high flow periods earlier than for the uncalibrated simulation. A slight increase in the flow was also observed for the high flow period. Table 3-28 compares the effect in the drainage, percolation and total volume simulation after including the GW model. Volume values for the different sources increased by an average factor of 1.1. The water volume for the simulation period after calibration accounted for 97.4% of the observed volume but with over-estimation in 2006 and 2009, which exceeded the observed volume by 12.5 and 0.7%, respectively. The shortfall in simulated volume for 2007-2008, 2008-2009 and 2010-2011 was by 1.4, 19.0 and 8.9%, respectively, compared to the observed data which was expected to come from other sources of flow such as runoff and/or non-recorded rainfall.

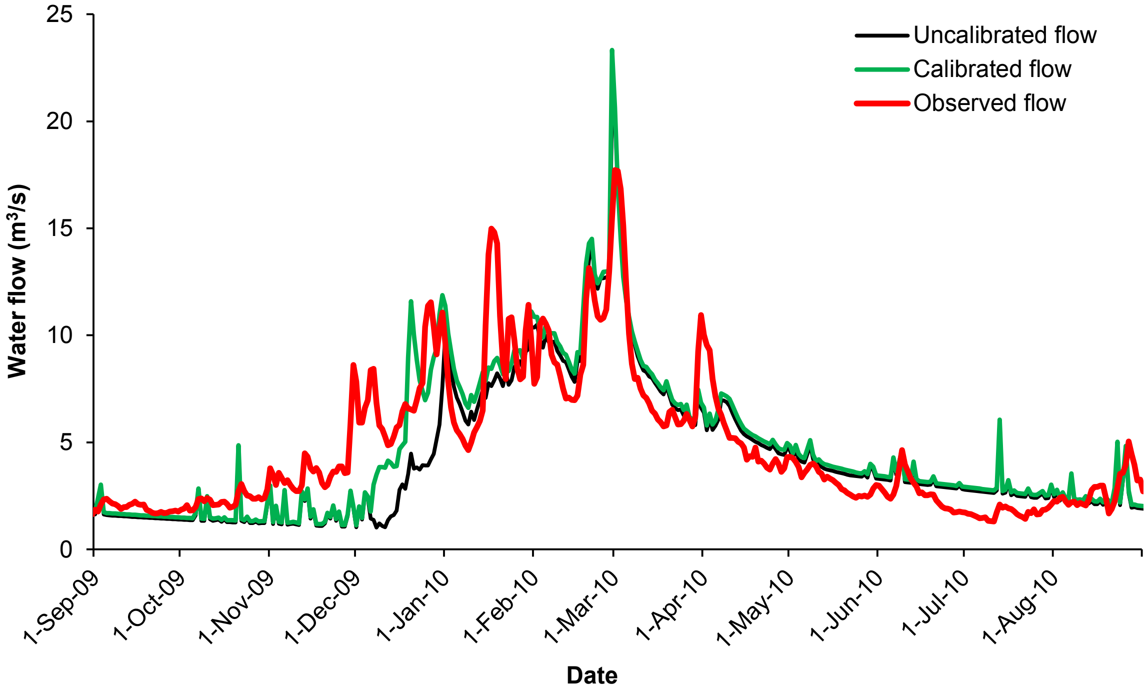


Figure 3-12 Effect of model calibration on the simulated flow for the beginning of the high flow period in 2009. The graph also shows uncalibrated and observed flow.

Table 3-28 Simulated drainage and percolation from the simulation using MACRO with (MACRO + urban runoff + GW) and without (MACRO + urban runoff) the GW model together their percentage simulated from the observed volume from each hydrological year.

	Uncalibrated MACRO + urban runoff + GW				**Calibrated MACRO + urban runoff + GW**			
Hydrological year	Drainage (10^6 m^3)	Percolation (10^6 m^3)	Simulated flow (10^6 m^3)	Total simulated (% of the observed)	Drainage (10^6 m^3)	Percolation (10^6 m^3)	Simulated flow (10^6 m^3)	Total simulated (% of the observed)
2006 – 2007	84.2	107.3	194.1	101.9	97.1	117.4	214.3	112.5
2007 – 2008	83.1	98.5	190.9	96.3	84.0	99.9	195.3	98.6
2008 – 2009	43.7	70.6	123.4	73.5	51.0	76.2	136.1	81.0
2009 – 2010	55.7	79.9	137.7	91.2	64.1	86.2	152.0	100.7
2010 – 2011	37.7	67.1	112.7	80.5	46.3	73.6	127.6	91.1
2006 – 2011	304.4	423.4	758.8	89.5	342.5	453.3	825.4	97.4

The residual plot (Figure 3-13) for the calibrated water flow did not show a significant change; the same non-random behaviour of the residuals was obtained. Only an increase in the magnitude of some of the negative residuals was observed due to the increase in the simulated flow.

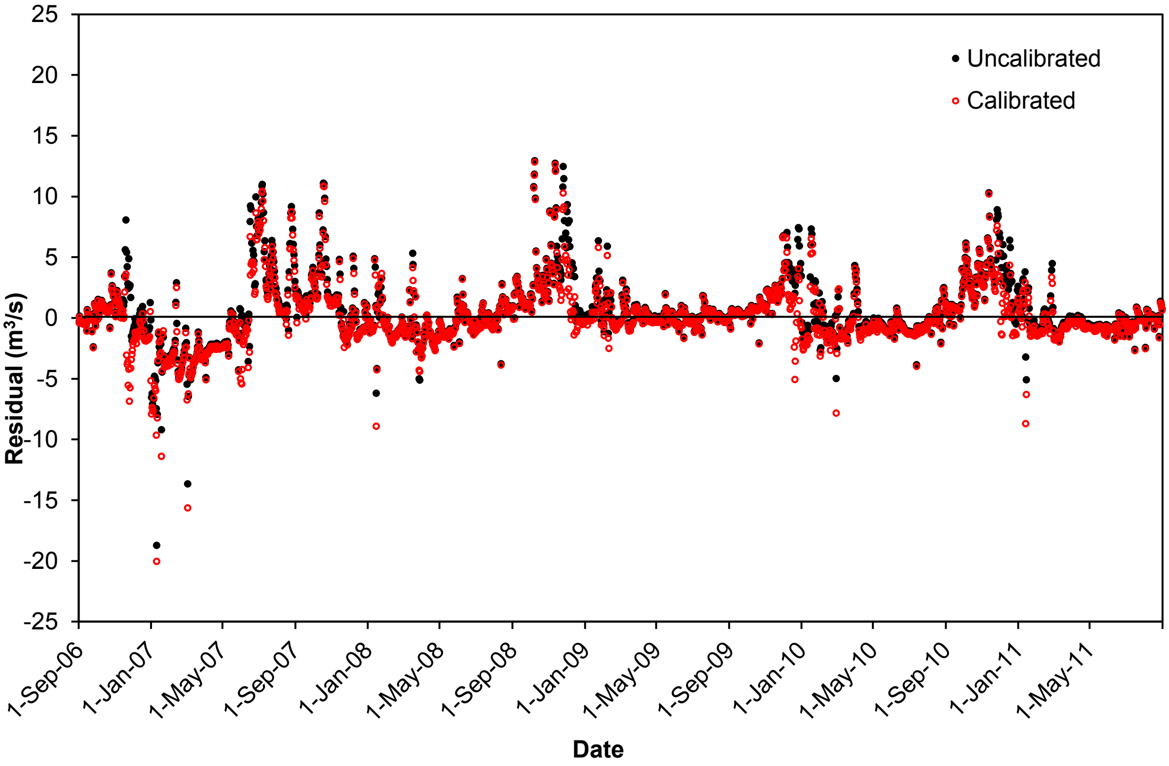


Figure 3-13 Comparison of the residuals from the uncalibrated and calibrated simulations using MACRO.

The model efficiency values for the calibrated simulation confirmed the improvement in the model simulation (Table 3-29), particularly, for individual hydrological years, high flow periods and the overall simulation (*E* = 0.43); the exception was for 2006-2007 where a reduction in the efficiency was obtained for the hydrological year and for the high flow period. For low flow periods a slight improvement in the efficiency values was observed but only by reducing the magnitude of the negative values, except for 2010-2011 when a slightly worse efficiency was obtained. The best simulations were obtained for 2007-2008 (*E* = 0.63) including high flow period (*E* = 0.73) and for 2009-2010 (*E* = 0.72).

Table 3-29 Nash-Sutcliffe model efficiency coefficients for the uncalibrated and calibrated simulations for each hydrological year as well as for the high and low flow periods.

	Uncalibrated MACRO + urban runoff + GW			**Calibrated MACRO + urban runoff + GW**		
Hydrological year	E each hydrological year	E high flow period 1 Nov – 30 Apr	E low flow period 1 May – 31 Oct	E each hydrological year	E high flow period 1 Nov – 30 Apr	E low flow period 1 May – 31 Oct
2006 – 2007	0.04	-0.30	-0.87	0.02	-0.54	-0.73
2007 – 2008	0.61	0.73	-0.82	0.63	0.73	-0.77
2008 – 2009	0.10	-0.54	0.05	0.33	-0.001	0.13
2009 – 2010	0.64	0.29	-0.70	0.72	0.47	-0.67
2010 – 2011	0.19	-0.29	-3.82	0.39	0.12	-4.93
2006 – 2011	0.35	0.11	0.20	0.43	0.23	0.28

3.4.4.2 Model calibration for PRZM

Model calibration was applied to Newport and Barrow simulations using PRZM in order to reduce over-estimation in runoff. The first stage of the calibration was to change the runoff curve numbers (CN) from the hydrologic soil group B to A (PRZM calibrated HG), then curve numbers were reduced by 8 (PRZM calibrated -8%CN) and 10% (PRZM calibrated -10%CN) and the soils with draining systems (Beccles and Burlingham) were removed from the simulation. Figure 3-14 and Table 3-30 show the effect of the calibration on the magnitude and number of runoff events. Each calibration stage greatly reduced the runoff over-estimation as well as the number of runoff events. The uncalibrated simulation predicted 140 runoff events and with each stage of the calibration the events were reduced by 65, 82 and 86%, respectively. Similarly the total simulated runoff volume was reduced by 66, 86 and 90%, respectively.

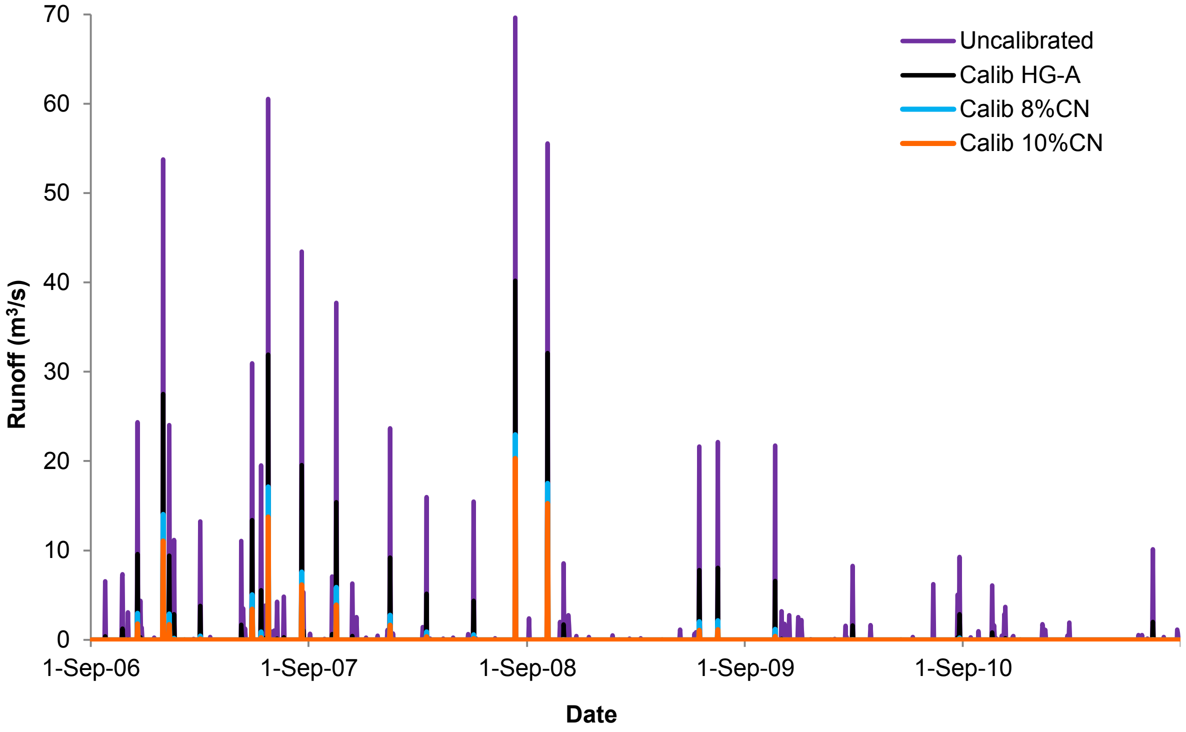


Figure 3-14 Simulated runoff events from the uncalibrated simulation using PRZM (i.e. including Beccles and Burlingham) as well as for each calibration stage: changing the hydrologic soil group to A (Calib HG-A), reducing the curve numbers by 8 and 10% (Calib -8%CN and -10%CN, respectively) and excluding Beccles and Burlingham.

Table 3-30 Simulated runoff volume and number of runoff events from the uncalibrated simulation using PRZM (i.e. including Beccles and Burlingham) as well as for each calibration stage: changing the hydrologic soil group to A (Calibrated HG-A), reducing the curve numbers by 8 and 10% (Calibrated -8%CN and -10%CN, respectively) and excluding Beccles and Burlingham.

	Uncalibrated	**Calibrated HG-A**	**Calibrated -8%CN**	**Calibrated -10%CN**
Runoff (10^6 m^3)	68.6	23.5	9.3	7.1
Number of runoff events	140	49	24	20

Table 3-31 shows the Nash-Sutcliffe model efficiency values for each stage of the calibration and for the uncalibrated simulation with PRZM. An improvement in model efficiency was observed for each stage of the calibration but the values were not better than those obtained for MACRO without PRZM, except for the high flow period in 2006-2007. The calibration was not continued since reducing the curve numbers would also reduce the number of runoff events and no significant improvement in the flow compared to the simulation from MACRO was likely to occur.

Table 3-31 Nash-Sutcliffe model efficiency coefficients for the uncalibrated simulation using PRZM (i.e. including Beccles and Burlingham) as well as for each calibration stage: changing the hydrologic soil group to A (Calibrated HG-A), reducing the curve numbers by 8 and 10% (Calibrated -8%CN and -10%CN, respectively) and excluding Beccles and Burlingham.

Hydrological year	**Uncalibrated PRZM**			**PRZM calibrated HG**		
	E each hydrological year	E high flow period 1 Nov – 30 Apr	E low flow period 1 May – 31 Oct	E each hydrological year	E high flow period 1 Nov – 30 Apr	E low flow period 1 May – 31 Oct
2006 – 2007	-2.48	-3.83	-4.90	-0.56	-1.37	-0.71
2007 – 2008	-1.09	0.24	-15.12	0.16	0.64	-5.34
2008 – 2009	-0.70	-0.009	-19.73	0.07	-0.009	-2.50
2009 – 2010	0.49	0.38	-1.36	0.70	0.46	-0.71
2010 – 2011	0.34	0.16	-16.01	0.38	0.11	-5.13
2006 – 2011	-0.79	-0.58	-2.41	0.14	0.03	-0.36
]	**PRZM calibrated -8%CN**			**PRZM calibrated -10%CN**		
2006 – 2007	-0.11	-0.74	-0.69	-0.06	-0.66	-0.69
2007 – 2008	0.48	0.71	-2.22	0.52	0.72	-1.89
2008 – 2009	0.27	-0.01	-0.08	0.29	-0.011	0.09
2009 – 2010	0.72	0.47	-0.68	0.72	0.47	-0.68
2010 – 2011	0.38	0.10	-4.26	0.38	0.10	-4.26
2006 – 2011	0.35	0.18	0.12	0.38	0.20	0.16

The evaluation of the runoff simulation from PRZM showed that the model was able to simulate runoff events with good timing but over-estimation was a problem in the simulation; no significant improvement was expected from further calibration. Results from MACRO showed that most of the water contributing to the water flow in the catchment is likely to come from drainage and percolation. For this reason, it was decided not to include other sources of runoff apart from the ones coming from the development areas and to estimate the pesticide loss based only on drainage and percolation.

3.4.5 Pesticide modelling results

None of the models used to calculate surface runoff was able to provide good predictions for the catchment and there is no evidence to suggest that significant amounts of runoff can occur in the catchment. Hence, it was decided that only MACRO would be used to estimate the pesticide loss in the Wensum catchment.

3.4.5.1 Pesticide concentrations

The simulated pesticide concentrations at the Wensum outlet from the modelling framework using MACRO are compared to the measured data in Figure 3-15 to Figure 3-20 for hydrological years 2006 – 2011. The results are presented in application date order during the crop year starting from autumn. The LOQ values were used in the graphs for the monitoring days when no pesticide concentrations were detected. The model simulates daily pesticide concentrations even below the LOQ and these data were included in the graphs even though they cannot be evaluated. There was variability in simulations for the different pesticides; the model generally simulated autumn and winter applications better than those occurring during spring and summer. Concentration results for each pesticide are described below.

The simulation of pesticide concentration for chlorotoluron (Figure 3-15) showed a good prediction of the pattern of the peaks for each hydrological year though there were some discrepancies in the timing and magnitude of some of the peaks. The model tended to miss the first emission peaks in autumn and early winter periods for the hydrological years 2008-2009 to 2010-2011. Under-estimation of the concentrations was observed by factors of 2.9 and 2.5 when the first and second maximum observed concentrations took place on December 2nd 2009 and November 26th 2010, respectively. Over-estimation of the concentrations was mostly observed throughout the simulation by up to one order of magnitude.

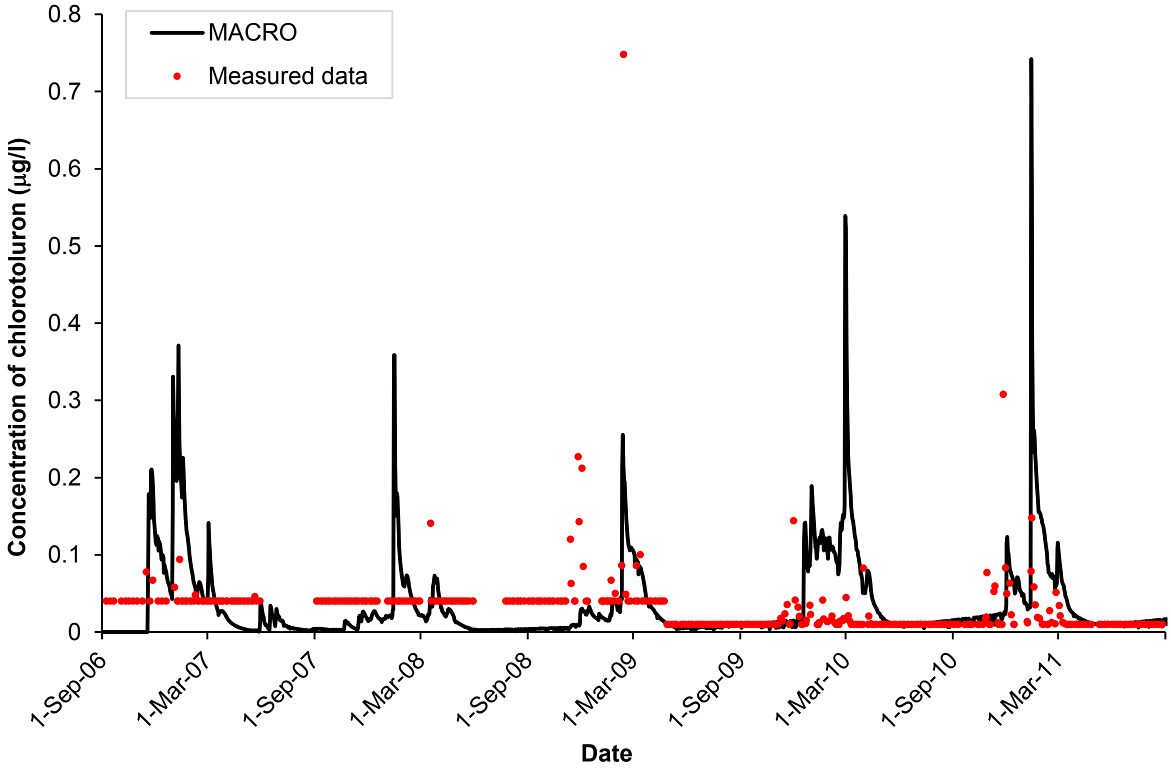


Figure 3-15 Comparison of measured concentrations of chlorotoluron with those simulated by the model framework using MACRO.

Concentrations for mecoprop (Figure 3-16) were generally simulated within the same order of magnitude as the observed data but with some disagreements in the timing of the peaks; the model simulated peaks occurring two months earlier than observed in spring 2007 and 2008 and two months later, than observed in early winter 2008. The model did not simulate peaks occurring in autumn and early winter 2007 or in summer 2009.

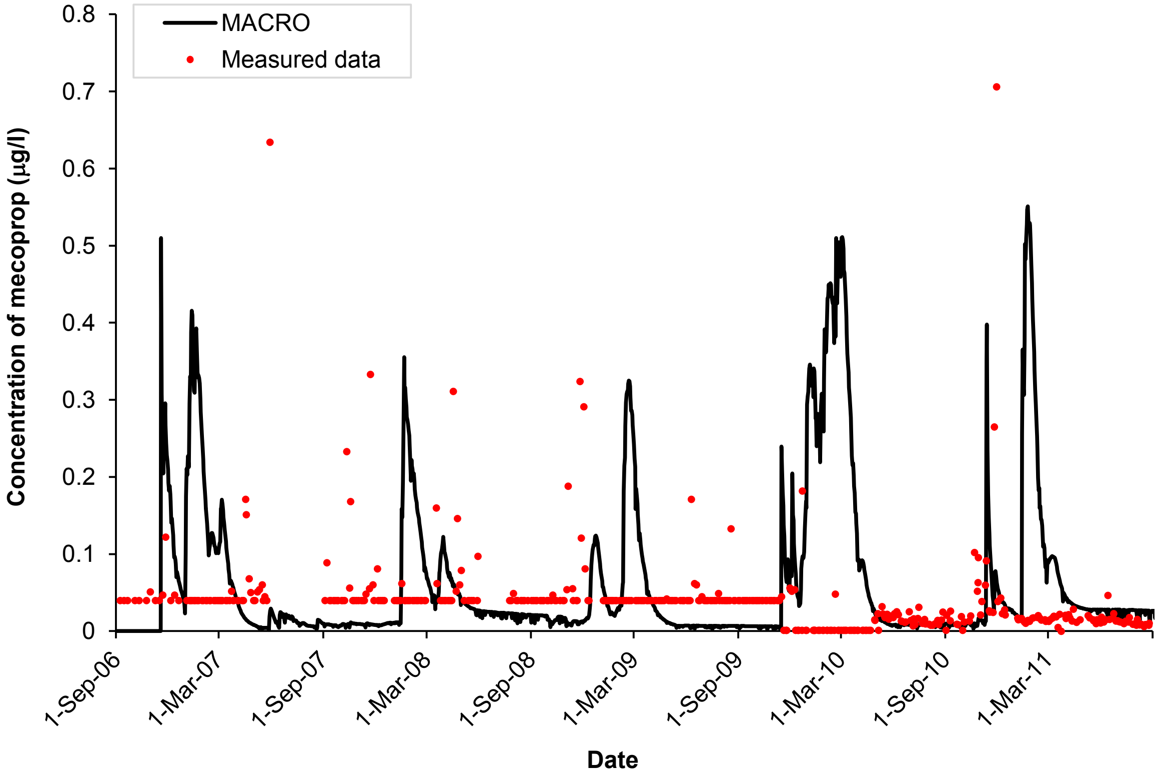


Figure 3-16 Comparison of measured concentrations of mecoprop with those simulated by the model framework using MACRO.

In the case of carbetamide and propyzamide (Figure 3-17 and Figure 3-18, respectively), the model achieved a good simulation of the patterns of the peaks but greatly under-estimated the concentrations by up to one order of magnitude for some hydrological years. For carbetamide, less under-estimation was obtained for the hydrological years 2006 and 2010 by up to factors of 2.4 and 1.4, respectively. In the case of propyzamide the model under-estimated concentrations for 2008-2009 and 2009-2010 but over-estimation was observed for the rest of the hydrological years. In 2006 over-estimation occurred by up to a factor of 9.3 and in 2009-2010 and 2010-2011 by factors of 2.4 and 1.8, respectively although the model matched the timing of the maximum observed concentrations.

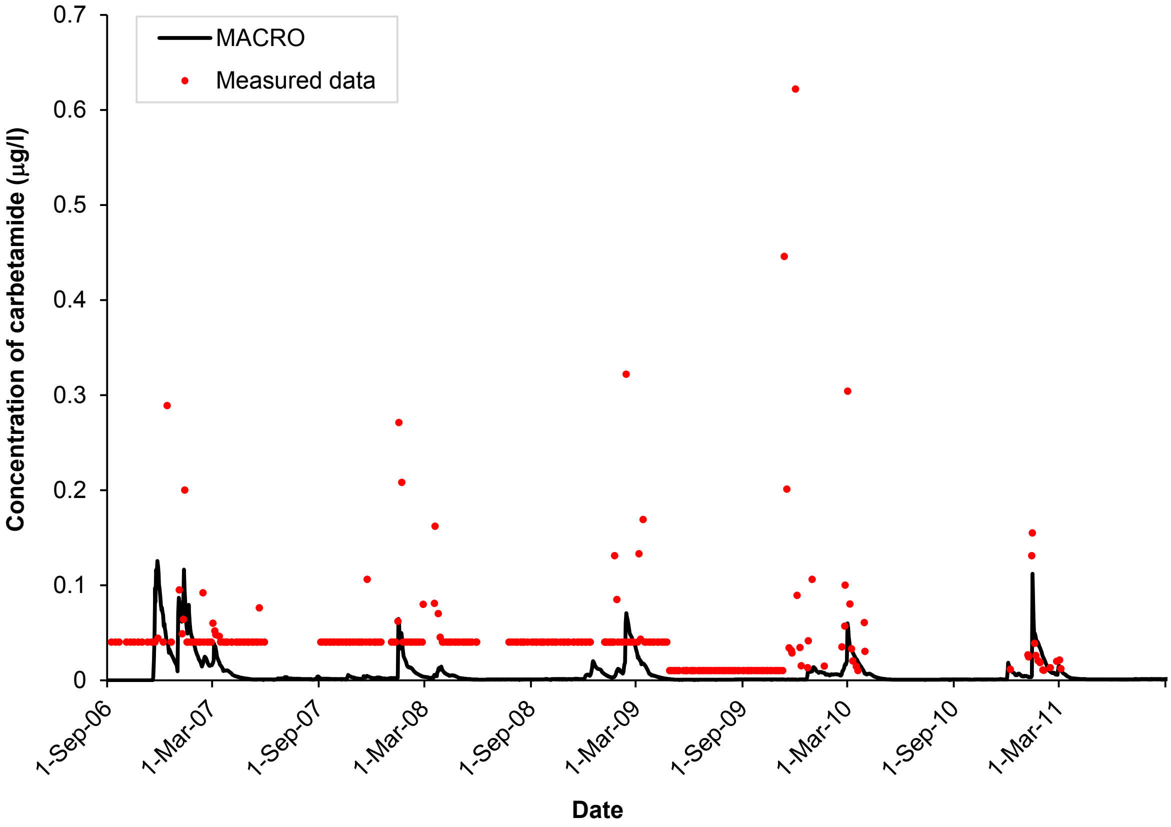


Figure 3-17 Comparison of measured concentrations of carbetamide with those simulated by the model framework using MACRO.

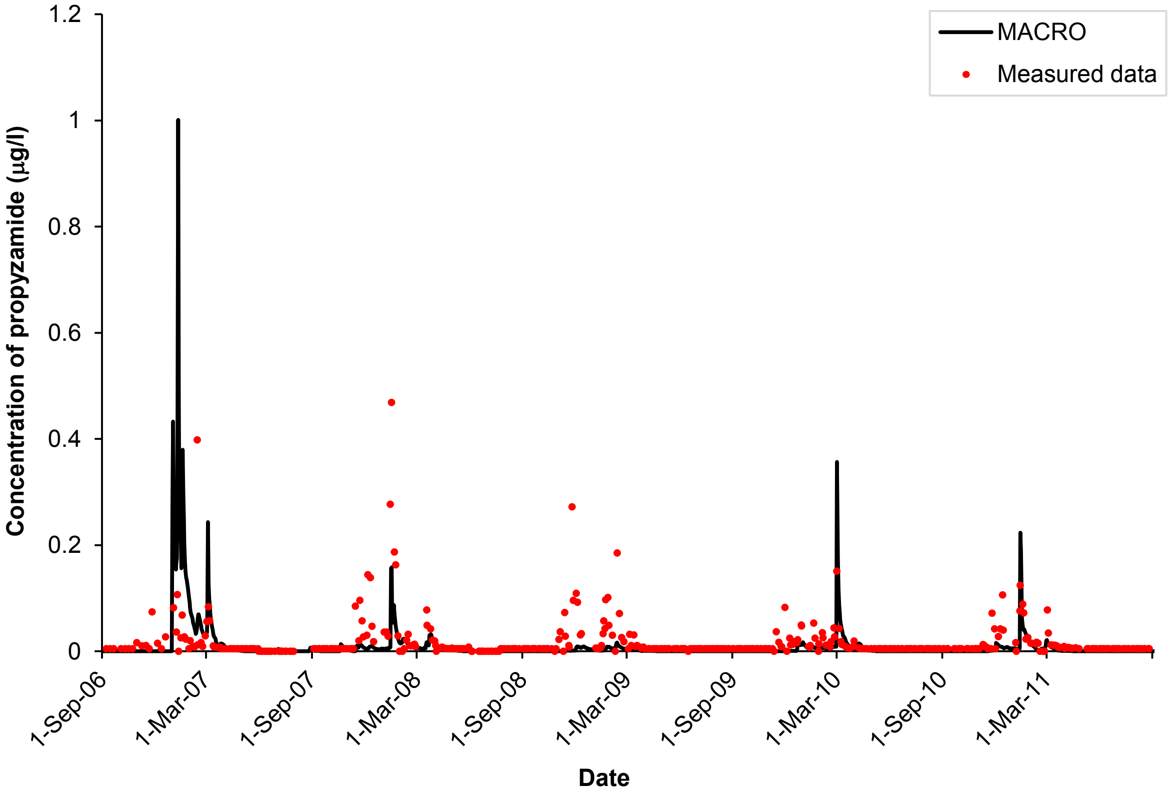


Figure 3-18 Comparison of measured concentrations of propyzamide with those simulated by the model framework using MACRO.

Poor simulations were obtained for clopyralid and MCPA (Figure 3-19 and Figure 3-20, respectively). For clopyralid, two peaks were simulated above the LOQ and differing in the timing while 13 emissions were observed in the measured data. Quantifiable residues were generally detected during the late spring and summer periods with a couple of observations during early spring (in March 2008 and April 2011) and autumn (September and November 2010). The first simulated peak occurred in March 2007 but the first measured concentration took place in May 2007. Similarly behaviour was seen for the second simulated peak above the LOQ that occurred in March 2010 and the measured in May of the same year. A small peak was simulated at the same time that an observed emission but the simulated concentrations were below the LOQ.

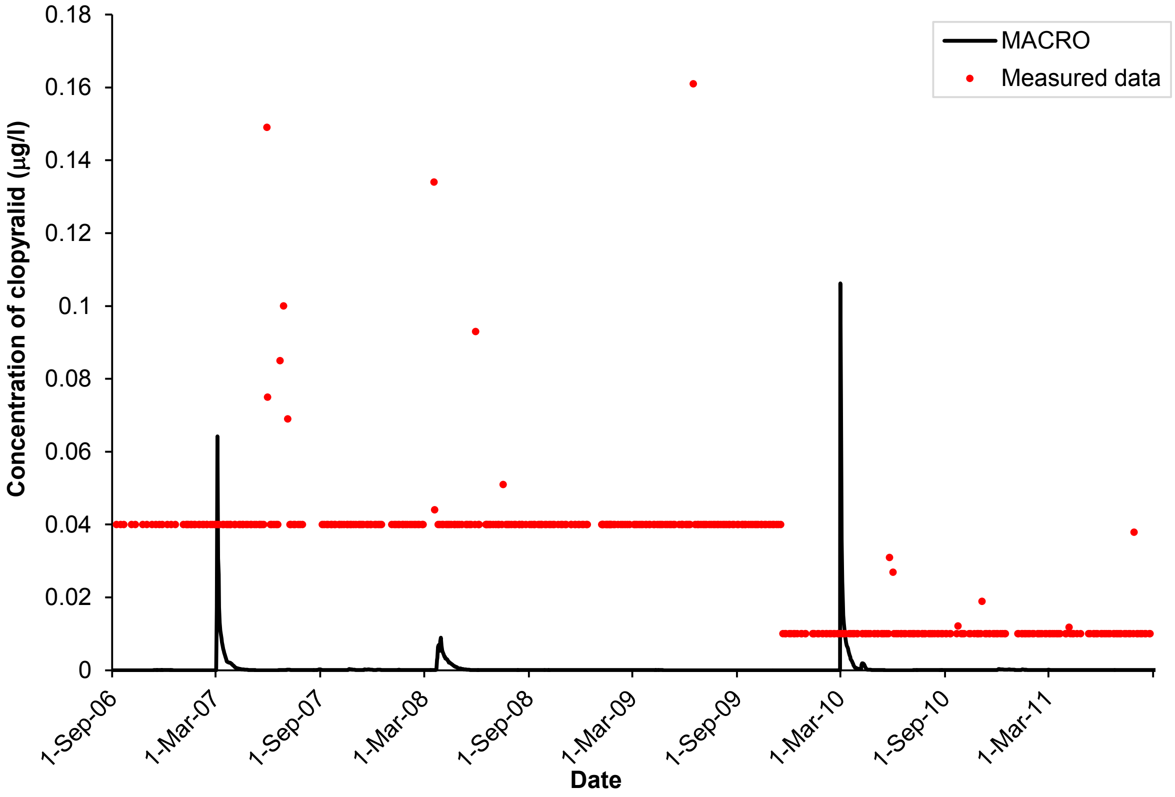


Figure 3-19 Comparison of measured concentrations of clopyralid with those simulated by the model framework using MACRO.

For MCPA (Figure 3-20), the model could not simulate peaks for most of the simulation period; the exception was for 2006-2007 when the model simulated well both the magnitude and the timing of emission that took place from May to beginning of July 2007; however, the model missed peaks during the rest of the summer period. Some simulated peaks during the late autumn and winter 2006 were not detected in the measured samples and the rest of the simulated peaks were below the limit of detection and disagreed with the timing of the measured data.

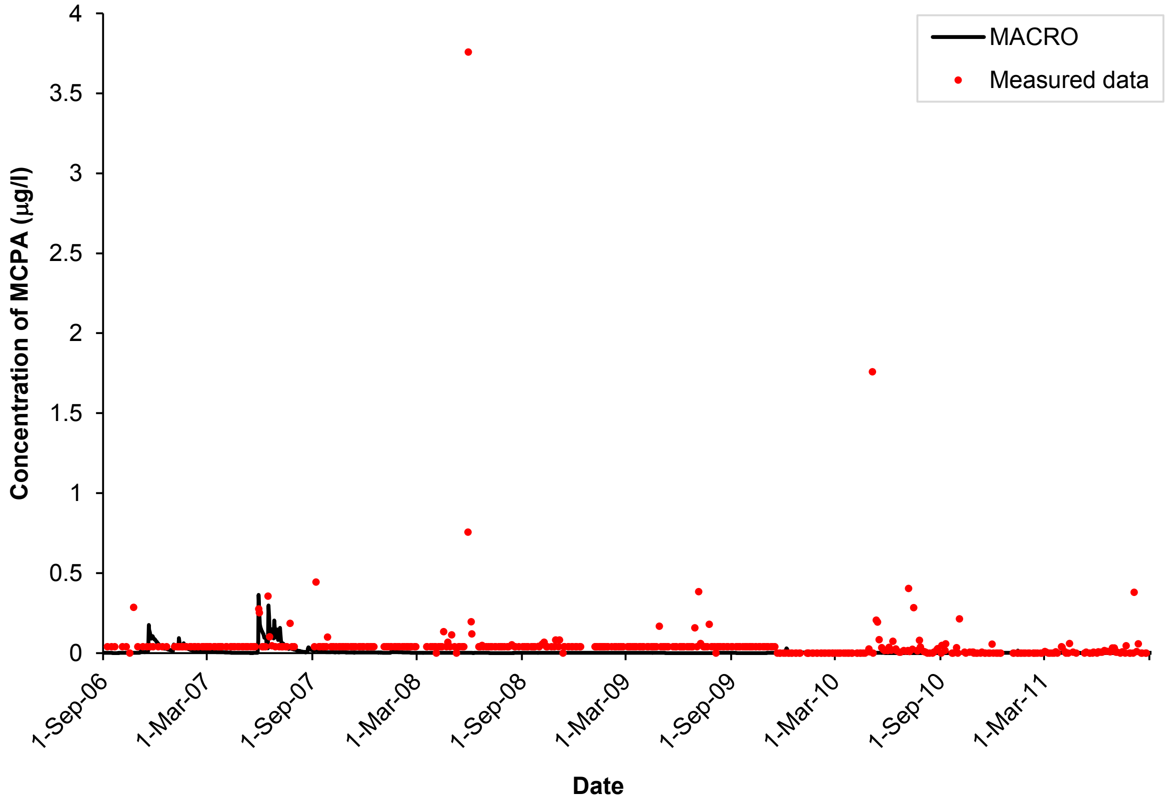


Figure 3-20 Comparison of measured concentrations of MCPA with those simulated by the model framework using MACRO.

3.5 Discussion

3.5.1 Development of the modelling framework

Coupling fate models consists in combining more than one model in order to address limitations of individual models by setting a modelling framework (Zhu et al., 2013; Li et al., 2007; Yakirevich et al., 1998; Rabbani and Warner, 1997; Kool et al., 1994). In this study a modelling framework was developed by combining a series of hydrological and fate models in an attempt to simulate various sources of water flow and their associated pesticide losses in the Wensum catchment. Sources of water flow that were thought to be important contributors to the Wensum included tile drainage, percolation, river baseflow and runoff from both developed and arable areas; other inflow and outflow sources (such as water abstraction, irrigation and sewage discharge) were assumed to have little impact on the hydrograph.

3.5.1.1 Tile draining and percolation simulation

MACRO was the core model of the framework since preferential flow was known to be an important contributor to hydrology and pesticide loss in the catchment. The initial uncalibrated simulation from MACRO also suggested that the most important input to the river network is tile drainage. About 57% of the soils in the catchment are clay loams with artificial drainage systems. No surface runoff water was predicted by MACRO for the Wensum which showed that the tile drainage systems might be working properly since the infiltration capacity of the soil was not exceeded during the simulation period. From this result, it was expected that surface runoff generated from the crop lands would be small. A similar behaviour was observed for a modelling study using MACRO in an agricultural field with heavy clay soils and artificial drainage systems in Oxfordshire, UK (Besien et al., 1997); during the simulation period the model did not predicted surface runoff and the observed data showed that drain flow accounted for 98% of the total flow (drain flow + runoff) demonstrating that surface runoff was a minor process in the area.

The uncalibrated flow from MACRO represented 86% of the observed flow for the simulation period (2006 – 2011). A match in the flow was only obtained for the hydrological year 2006 with a small over-estimation of 0.6% due to high over-estimation of the flow in January 2007. Flow under-estimation was the main issue throughout the remainder of the simulation and this was thought to come for other sources of flow such as from surface runoff from developed areas and crop land.

3.5.1.2 Runoff from developed areas

Surface runoff generated from rainfall was considered the only significant source of water flow from developed areas to the river network. It was assumed that 50% of the rainfall would enter the river system by surface runoff which agrees with findings from runoff studies in urban landscapes. For example, Pataki et al. (2011) reported that impermeable paving covers in urban areas can generate between 40 and 83% surface runoff from a given rainfall event. This source of flow only added 5% of the observed flow to simulation but the major impact was observed in the shape of the simulated hydrograph from MACRO. The predicted smooth behaviour of the flow was transformed to a noisier curve in agreement with the timing and magnitude of the peaks in the observed hydrograph.

3.5.1.3 Groundwater mixing model

An important aspect of flow estimation is the calculation and incorporation of the baseflow component to the hydrograph. Baseflow is primarily generated from groundwater discharge into the river network which depends on regional hydrological conditions. A simple groundwater mixing model was developed to simulate the baseflow in the Wensum catchment and the transfer of pesticide that could reach the groundwater by leaching. The model performs a complete water mass balance of the simulated water and pesticide recharge from MACRO and the estimated groundwater volume which is considered in the model as a tank with the base area of the catchment and 3m deep. An outflow factor of 1% discharge from the groundwater to the river was estimated by model calibration. The recession periods were generally well simulated at the beginning of the low flow periods but a poor baseflow recovery was obtained at the end of these periods. An asymmetric behaviour of the baseflow was observed at the end of the low flow periods for every hydrological year causing under-estimation of the flow at these times.

Tediosi et al. (2013) also used a coupled model using MACRO and a simple groundwater model to simulate the water flow in a 199-km^2 catchment located in central England. The groundwater model was developed based on a variation of the saturated thickness (Rushton and Youngs, 2010) using typical values of hydraulic conductivity and specific yield for the study area. According to the authors, this approach showed a good representation of the recession periods in the hydrographs and the simulation of the water flow which increased model efficiency from 0.02 to 0.56 and the hydrograph was only affected by under-estimation of the flow at periods of snow presence and low precipitation. In the present study, despite inaccuracies in the simulation of the flow recovery at the end of low-flow periods, the incorporation of the baseflow component to the uncalibrated flow from MACRO (including the runoff from developed areas) increased model efficiency from -3.25 to 0.35 for the overall simulation period. Model efficiency for both periods of great and low flow also changed from negative to positive values (0.11 and 0.20, respectively). In addition, the GW model had a regulation effect in the flow by significantly reducing the over-estimation of the flow during 2006, from 7.2 to 1.9% of the observed flow, slightly reducing the flow for 2009-2010 and increasing the flow for the rest of the hydrological years.

3.5.1.4 Runoff simulation using RZWQM

RZWQM was used to simulate overland flow and the associated pesticide loss in the Wensum catchment. Runoff is calculated in the model as the difference between rainfall and infiltration/macropore flow by using the Green–Ampt equation for infiltration and Richards' equation during redistribution. A poor simulation of the runoff was obtained for the Wensum catchment which did not match the timing of the observed flow. In addition, runoff from each soil association was predicted to occur in the same amount and on the same days when temperature was close or below to zero (i.e. when the model assumes that the soil surface is frozen). Other studies have found poor runoff simulation using RZWQM. For instance, Ghidey et al. (1999) related bad results to deficiencies in the simulation of cracks in the model for clay soils which could not be modified. Malone et al. (2004) reviewed the use of RZWQM for pesticide modelling and attributed the negative results from Ghidey et al. (1999) to bad parameterization by the user instead of a model limitation. Studies have found that flow predictions from RZWQM can be improved by simulating macropores and after calibration of macroporosity parameters (Bakhsh et al., 1999; Kumar et al., 1998; Singh et al., 1996), particularly, for runoff simulation (Malone et al., 2004; Singh et al., 1996). Malone et al. (2004) simulated metribuzin transport in runoff and percolation in two fields near Frankfort, Kentucky (USA) using RZWQM and compared results for the three different sorption models included in RZWQM. Metribuzin runoff was simulated within a factor of two after calibration of the macropore radius and the crusted saturated hydraulic conductivity using the equilibrium-kinetic sorption models in RZWQM but pesticide percolation was under-estimated by more than an order of magnitude with any sorption model (Malone et al., 2004). In the present study, an equilibrium-kinetic sorption approach was used for all pesticides but surface soil crusting (typical from sub-humid to semi-arid tropic regions) was not modelled since this phenomena is not likely to occur on clay and loam soils in the UK. However, no calibration of the macroporosity was attempted since none real runoff events were simulated for the different soil associations with the initial parameterization and the most likely explanation continued to be that runoff in the area is minimal due to the presence of tile drains.

3.5.1.5 Runoff simulation using PRZM

A second attempt to investigate the occurrence of runoff in the Wensum was carried out using PRZM. The US EPA uses PRZM to estimate pesticide losses via runoff from agricultural fields. The model has been used in several studies (Farenhorst et al., 2009; Young and Carleton, 2006; Trevisan et al., 2000; Brown et al., 1996; Mueller, 1994; Nicholls, 1994; Loague, 1992; Loague et al., 1989a; Loague et al., 1989b; Carsel et al., 1985) providing both satisfactory and inaccurate results (Young and Carleton, 2006; Trevisan et al., 2000; Loague, 1992; Banton and Villeneuve, 1989). The uncalibrated simulation using PRZM showed a good agreement in the timing of the peaks with the observed data but a great over-estimation of the flow by up to a factor of 9. Intense calibration of the curve numbers resulted in unrealistic values for the simulated crops and hydrological conditions in the catchment. In addition, no significant improvements to the simulation of flow from MACRO were obtained. Consequently, the model was not included in the framework and runoff was concluded to be minimal based on the simulation from MACRO. However, the model framework MACRO–PRZM has shown a good potential for describing runoff and drain flow in catchments where drain flow and runoff are important but calibration of the curve numbers in PRZM might be necessary to tackle differences between USA and European conditions due to the use of an empirical model.

3.5.1.6 MACRO calibration

Calibration of MACRO was carried out to improve the simulated hydrograph at the end of low flow periods. Calibration of soil and crop parameters was necessary to allow a more rapid increase of soil moisture at the end of low flow periods. The root depth and the root distribution were selected based on reported parameters but then changed to reduce evapotranspiration. Water transpired through leaves comes from the roots so plants with deep reaching roots can transpire water more constantly. Other authors calibrated crop and soil parameters to improve the hydrology of the simulation (Besien, 1997; Cameira, 2005). Cameria (2005) observed a decrease in the simulation error of 17 and 20% by adjusting LAI and root parameters. The authors stated that root extraction and evapotranspiration which correspond to the sink term in the Richards' equation have a great impact on the quality of the simulation of soil moisture profiles. The macropore parameters such as ZN and ASCALE were calibrated in the model. A sensitivity analysis for MACRO showed apart from degradation and sorption input data, parameters related to the soil structure such as ZN have great impact on the hydrology of the model (Dubus et al., 2003a). These parameters initially received values based on the description of the soil structure but were then changed within the ranges found in the literature (Beulke et al., 2002b).

Model calibration increased the simulated flow for all the hydrological years. The calibrated flow represented 97.4% of the observed flow in the catchment and improved model efficiency for most of them as well as for the overall simulation (from $E = 0.35$ to $E = 0.43$). Improvements in both overall low and high flow periods were also achieved. Negative impacts on model efficiency were only observed for 2006-2007 and 2010-2011, particularly for the high flow period and overall simulation of 2006-2007, due to an increase in the over-estimation of the flow from 1.9 to 12.5% compared to the observed flow, and for the low-flow period in 2010-2011. Model calibration slightly improved the behaviour of the low-flow periods but disagreements in the hydrograph shape and under-estimation of the flow were still observed.

The River Wensum has a groundwater dominated flow regime coming from the chalk aquifer. The river has a high baseflow index varying from 0.82 to 0.73 from the top of the catchment at Fakenham to downstream at Costessey, respectively (Sear et al., 2006); this means that between 82 and 73% of the flow arises from the underlying aquifer. The modified flow regime (not natural) is consequential of the field drainage systems and other modifications of the drainage schemes (such as gravity and pumped drainage). The maximum flow is usually reached in March and April. Periods of low flows in the catchment are a consequence of low autumn precipitations, aquifer recharge during autumn as well as minimal discharges during the summer. Different authors have attributed disagreements in water flow simulation from MACRO during low flow periods to over-estimation of the evapotranspiration (Tediosi et al., 2013; Roulier and Jarvis, 2003; Besien et al., 1997). Besien et al. (1997) found that the over-estimation of evapotranspiration causes the model to miss small drain discharges when there is low rainfall after long dry periods in the early spring; this generates errors in the simulation of the drain flow as well as failure to simulate pesticide peaks. It is possible that the same phenomena could be affecting the hydrograph by delaying the normal increase of soil moisture at the end of low flow periods when small drain flow and low rainfall events are the main sources of flow recovery. This possibility is assessed further in Chapter 4 (Section 4.5.1.1).

3.5.2 Pesticide simulation

The modelling framework used the field-scale model MACRO and assumed that the catchment system could be simulated as the sum of multiple field-scales processes; this has also been assumed in other studies (Renaud et al., 2008; Lindahl et al., 2005). The developed modelling framework was concentrated on the simulation of pesticide emissions from field drains since pesticide transport from fine-textured soils takes place principally via preferential flow pathways (Beulke et al., 2001a; Harris and Catt, 1999; Besien et al., 1997; Johnson et al., 1996; Brown et al., 1995a; Brown et al., 1995b; Haria et al., 1994; Harris et al., 1994). Modelling results showed field drains to be the most important emission pathway to surface water in the Wensum catchment since the model simulated most of the emission peaks. Other studies in the UK have also found drain flow to be the most important emission pathway in different areas of the England when tile drainage is present (Tediosi et al., 2013; Tediosi et al., 2012; Besien et al., 1997; Johnson et al., 1996). For instance, Johnson et al. (1996) found that between 75 and 90% of the total isoproturon loss from a field in Oxfordshire, UK was removed via artificial drains, even when following best management practices in the application; in contrast, pesticide loss by runoff only accounted for 0.7% of the total loss.

In contrast, Holvoet et al. (2007b) considered that in-stream processes (e.g. microbial activity, dissolved oxygen concentration, pH, sedimentation, re-suspension) have a significant impact on modelling pesticide at the catchment-scale. This was addressed by combining the watershed model SWAT (Arnold et al., 1998) with a modified version of the river water quality model RWQM1 (Reichert et al., 2001) to study the fate of pesticide in the river Nil in Belgium and provide a better description of the river processes. However, in the present study, the modelling framework was able to satisfactorily simulate water flow from a relatively big catchment like the Wensum and predict reasonably well the pattern of pesticide concentrations even though the framework ignored in-stream processes.

Modelling results for pesticide concentrations varied between pesticides. The calibrated model generally provided reasonable order-of-magnitude simulations of pesticide concentrations and a good simulation of the timing of the peaks. Pesticide concentrations occurring in the early autumn were generally missed by the model because flow was under-estimated at the end of the low flow periods. Better simulations were observed for pesticides that are normally applied in late autumn such as chlorotoluron, mecoprop, carbetamide and propyzamide. These pesticides are mainly applied to a single crop therefore uncertainty in their usage patterns (i.e. application date and amount) is small. For instance, chlorotoluron is exclusively applied as a pre- or early post-emergence herbicide to winter cereals to control annual grasses and broad leaved weeds (CSF, 2012). In addition, the relatively large degradation rate (59 days) means that differences in the application date will have relatively little impact on the timing and magnitude of emission peaks simulated by MACRO.

Propyzamide and carbetamide showed a good agreement between the pattern of the simulated concentrations with the measured data but with some disagreements in the magnitude of the peaks. The simulation for carbetamide showed under-estimation of the pesticide concentrations by up to one order of magnitude. Propyzamide showed both under- and over-estimation of the peaks for some hydrological years. These herbicides are mainly applied to winter OSR but carbetamide may also be applied to brassicas, field beans and fodder crops and propyzamide to field beans, fruit, amenity vegetation and forestry; however, these crops are not significantly present in the Wensum. In OSR, these pesticides are mainly used to control broadleaved weeds and blackgrass resistant to other herbicides (CSF, 2012). Pesticide application takes place from October to the end of January depending on soil moisture and temperature. Good soil moisture and low temperatures (equal to or less than 8ºC) are needed to allow the herbicides to penetrate the top layers of the soil profile and persist for a longer time. Farmers need to check for the appropriate soil conditions before the application (HGCA, 2014). The relatively wide window of time for application and the specific environmental conditions required mean that the use of a uniform and fixed application date would generate uncertainty that will mainly affect the magnitude of the peaks. However, the uncertainty in the application date appeared to have a greater impact on the simulation of carbetamide than propyzamide losses. The moderately large soil sorption of propyzamide (292 ml/g) and half-life (47 days) allow the pesticide to bind strongly to soils and persist for a longer time. In contrast, carbetamide has both a smaller soil sorption (89 ml/g) and half-life (10.9 days) so if there is a delay between application date and a storm flow event, under-estimation can occur due to pesticide degradation. Boithias et al. (2014) showed that the effect of the uncertainty in the application date on pesticide simulations would depend on pesticide specific factors including sorption and degradation.

Application date is a major source of uncertainty in the simulation of pesticide emissions (Boithias et al., 2014; Gericke et al., 2010; Holvoet et al., 2005; Dubus et al., 2003b). Pesticide labels only provide guidance of the crop stage at which the herbicide can be applied. Therefore, most model users estimate this parameter from field studies or from typical application dates (Gericke et al., 2010). However, field studies give only a snap-shot of pesticide usage under the environmental conditions at that time. Pesticide application dates vary from year to year and depend on many factors such as farmers, weather and land use conditions (Gericke et al., 2010; Campbell, 2004; Commission of the European Communities, 1999). On the other hand, undergoing large-scale surveys with farmers would not always provide sufficient and accurate information about pesticide usage at a daily time-step in a catchment (Boithias et al., 2011); however, this information can be useful to identify application patterns such as preferred dates and times for application. For instance, a survey on pesticide usage with farmers in the SK grid tile of the UK found that most of the farmers tend to apply pesticides on Sundays or during the evening (ADAS, 2005).

Mecoprop simulation showed a good agreement in the magnitude of the peaks but with discrepancies in the timing of the events particularly for emissions observed during spring. Mecoprop has a complex usage pattern since it is applied to a variety of crops including cereals, grassland and amenity grass/lawns (CSF, 2012). Therefore, it is unlikely that the regional pesticide usage statistics give a sufficiently accurate representation of its use within the catchment. Mecoprop is mainly applied during autumn and spring. Spring emissions could be due to application to grassland which was not included in the model. In addition, since 2009 this herbicide was withdrawn from single use in cereals during autumn and winter so only a co-formulated product could be applied during this period. This change in usage would have reduced emissions from cereals in autumn and increased emissions from grassland since reduction in the application amount was observed in the statistics by DEFRA (2009) and was also mentioned by the CSF (2012) report.

Boithias et al. (2014) studied the impact of uncertainty in application date on pesticide concentration patterns for two contrasting pre-emergence herbicides (metolachlor and aclonifen) in a 1,110-km^2 agricultural watershed in south-western France using SWAT (Arnold et al., 1998). Improvements in pesticide simulation were found by adjusting the application date; however, in some cases improvements were not good enough which suggested that other sources of uncertainty could have also affected the simulations. The authors suggested that uncertainty in pesticide usage could be included as part of the calibration process (i.e. application date and amount) when modelling pesticide emissions at the catchment-scale (Boithias et al., 2014).

Poor simulations were observed for spring- and summer-applied compounds, which is the case for clopyralid and MCPA when the peaks were completely missed or disagreement in their timing was observed. The complex usage pattern of these herbicides is difficult to simulate. Clopyralid is applied to a wide range of crops including cereals, grassland, amenity grass/lawns, OSR, brassicas and maize to control broadleaved weeds and MCPA is used on cereals, grassland and amenity grass/lawn (CSF, 2012). These post-emergence herbicides are mainly applied during spring when weeds start to grow. In the model, two and three application dates during the crop year were simulated for clopyralid and MCPA, respectively; however, since these herbicides can be applied during a very wide window of time and it is not possible to predict when weeds would grow, the uncertainty generated by the use of fixed application dates can greatly affect the simulation. Different authors have suggested supplying application date input as a probability distribution in fate models (Gevaert et al., 2008; Holvoet et al., 2005; Lindahl et al., 2005). However, this approach also requires knowledge of the distribution of application dates along the catchment. On the other hand, Gericke et al. (2010) used phenological data for different crops collected by the German weather services since 1951 along with climate data to estimate application dates in Germany and the Czech Republic; satisfactory results were obtained when comparing estimated to actual application dates. This approach can provide a broader amount of information to estimate application dates but the methodology requires further development and validation under different environmental conditions.

The quality of the monitoring data is an important part of the evaluation of both river quality evaluation and modelling results (Holvoet et al., 2007b; Dubus et al., 2003b, 2001; Addiscott et al., 1995). Model evaluation was in some cases affected by the resolution of the measured pesticide concentrations. Some important emissions predicted by the models could not be evaluated due to the absence of monitoring data for those days. Monitoring frequency varies within hydrological years and a large proportion of none detections was observed for most herbicides. For instance in the Wensum, between September 2006 and November 2011, 453 samples were analysed for chlorotoluron from which only 79 detections were observed; however, during this period MACRO predicted 660 days with emissions on days when samples were not taken. The CSF monitoring programme has a high sampling frequency (an average of one sample every four days) and this information is useful to analyse pesticide trends and to undertake model evaluation; however, modelling results show that the monitoring programme can be improved by applying a variable sampling frequency during the year. A report from the CSF (2012) explains that the monitoring design has been based on the major crop types present in the catchment and highlights that a large proportion of the analysed pesticides are not detected in the samples. This report highlights that predicting the likelihood of occurrence of pesticide is a complex task that is influenced by many factors such as pesticide properties, soil types, and pesticide usage and drainage systems (CSF, 2012). Pesticide fate modelling takes into account all these factors and helps avoid bias and speculative methodologies. Fate models have been shown to be a useful tool to improve the design of the monitoring programme in the CSF (e.g. by focusing sampling collection on days when pesticides are more likely to be present) and can be easily incorporated into the programme without a big financial investment.

Based on the available monitoring data and modelling results, discrepancies in pesticide simulations showed that the modelling framework by its own cannot be used to fill the gaps between measured monitoring data. Different sources of uncertainty could be causing disagreements in pesticide simulations which need to be studied in order to understand the behaviour of modelling outputs. Data filling is a difficult aspect of fate modelling due to the impact of model error and sources of uncertainty. Uncertainty analysis is undertaken in Chapter 4 to identify both the sources of uncertainty and their impact in the simulation.

3.6 Conclusion

A modelling framework was developed to simulate the main sources of water flow contributing to the river network in the Wensum catchment and their associated pesticide emissions. This framework included the preferential flow model MACRO to simulate drain flow and leaching, an approach to estimate the runoff from developed areas and baseflow from a simple groundwater mixing model. The approach used to estimate runoff from developing areas provided a good agreement in the timing and magnitude of the peaks with the observed hydrograph. The groundwater mixing model was able to simulate the recession periods at the beginning of low-flow periods but discrepancies in the results were observed in the recovery of the flow at the end of these periods throughout the simulation. This type of discrepancy is reported very frequently in the literature. RZWQM and PRZM were tested in the framework to evaluate their capacity to simulate runoff in the catchment. RZWQM was unable to simulate the runoff and PRZM showed better model performance after intensive calibration of the curve numbers but no significant improvement when added to the hydrology simulation from MACRO. In addition, modelling results from MACRO and information from the area suggested that runoff was not an important contributor to the water flow so the runoff simulation was not included in the model framework. Field drains were shown to be the most important source of water flow as well as of pesticide loss via preferential flow in the catchment. Despite discrepancies in the baseflow simulation at the end of low flow periods, the modelling framework showed a fairly good performance in the simulation of the water flow at the catchment outlet after calibration of crop root and macropore related parameters. However, less accurate results were obtained for the simulation of pesticide concentrations.

Large variation in the simulation of pesticide concentrations was observed between pesticides. The model showed a better performance for pesticide losses coming from pre- or early post-emergence herbicides normally applied during autumn because of their less complex usage patterns (i.e. pesticides applied mainly to one crop such as chlorotoluron, carbetamide and propyzamide). Post-emergence herbicides usually applied during spring and summer could not be accurately simulated by the model which is very likely to be due to complex usage patterns and uncertainty in the application date. The pesticide modelling results generally showed good simulation of the pattern and a reasonable order-of-magnitude match to pesticide concentrations at the catchment outlet; however, simulated pesticide concentrations were not accurate enough to fill the gaps between measured monitoring data due to discrepancies either in the timing or magnitude of some of the peak emissions. Different sources of uncertainty should be analysed to understand discrepancies in model outputs. The next step will be to compare modelling results against a catchment-scale model to study the impact due to the spatial distribution of soils in the catchment and from the incorporation of a river network in the results. So far, modelling results for a relatively big catchment like the Wensum showed that the fate of pesticides at the catchment level was mainly driven by field-scale processes; in-stream processes were less important as reasonable simulations were obtained by a modelling framework that ignored these processes. The present study demonstrated that field-scale models can be used to describe the hydrology and understand the dynamics of non-point source pollution by pesticide at the catchment level.

Modelling results showed that the monitoring programme currently in place as part of the CSF could be improved when used in combination with models. A variable monitoring frequency focused on days when pesticides are more likely to be present would be a better approach to avoid missing pesticide peaks important for the evaluation of the impact of the programme.

4 Modelling pesticides in the Wensum catchment using SPIDER

4.1 Introduction

Modelling the fate of pesticides at the catchment-scale is an important tool for pesticide management. It provides a bigger picture of what occurs with pesticides at the catchment level that could then be used to evaluate pesticide usage and management practices. On a catchment-scale the simulation of pesticide fate involves modelling spatially distributed hydrological processes and pesticide losses over an entire catchment. Spatially distributed characteristics include climate, soil type, surface-groundwater interactions, land use, slope, pesticide-soil interactions and pesticide usage.

Catchment-scale models such us SWAT (Arnold et al., 1998) and AnnAGNPS (USDA ARS, 2006) have shown good results in modelling pesticide runoff at the catchment-scale but the description of tile drainage is oversimplified. SPIDER (simulating pesticides in ditches to assess ecological risk) is a preferential flow model that simulates hydrological flow and pesticide fate at the field-scale or at small catchment levels (Renaud et al., 2008). The model provides high flexibility to represent the spatial variability of the catchment. For example, SPIDER simulation of the flow in the ditch is simpler that in a river network in a catchment. In contrast to field-scale models like MACRO, SPIDER enables spatial variability in the catchment to simulate the effect of the transport and sorption of pesticides in the river network.

The increasing demand for the use of modelling to target management issues has also lead to an increased need for assessing the impact of uncertainty on the simulations (Larsbo and Jarvis, 2005; Dubus et al., 2003b; Dubus and Brown, 2002; Sohrabi et al., 2002; Dubus et al., 2001). Physically-based hydrologic and pesticide transport models require a large amount of input data from the study area that are not always known with certainty (Sohrabi et al., 2002). Sources of uncertainty in the input parameters usually involve the inherent uncertainty in the physical measurements or the use of average data that do not describe the spatial variability of the study area. These uncertainties are responsible for reducing the predictive capacity of the simulation causing errors in the output data (Haan et al., 1995b). In addition, different sources of uncertainty can magnify the overall uncertainty of the outputs (Zhang et al, 1993).

Despite the importance of uncertainty analyses, very few modelling studies include them in their results. In addition, there is no agreed established procedure for these analyses; authors use a range of different methods. The most widely used method is the Monte Carlo analysis (Cibin et al., 2014; Xie and Lian, 2013; Migliaccio and Chaubey, 2008; Shen et al., 2008; Shirmohammadi et al., 2008; Yang et al., 2008; Carbone et al., 2002; Dubus and Brown, 2002; Pollock et al., 2002; Sohrabi et al., 2002; Warren-Hicks et al., 2002; Trevisan et al., 2001; Ma et al., 2000; Zacharias et al., 1999; Soutter and Musy, 1998; Soutter and Pannatier, 1996; Nofziger et al., 1994; Zhang et al., 1993) which is a probabilistic approach that requires an understanding of the distribution of the different input parameters in the area of study. Other techniques of uncertainty analysis used in fate modelling include differential analysis (Diaz-Diaz et al., 1999; Freissinet et al., 1999; Li et al., 1998; Loague et al., 1996; Loague and Green, 1991), Fourier amplitude sensitivity test (Fontaine et al., 1992), and fuzzy logic (Freissinet et al., 1999; Freissinet, 1998). Pesticide fate modelling using SPIDER and MACRO in this study included key uncertainties in the input data to study the effect approaches and assumptions used to simplify the modelling process of a complex system such as the Wensum catchment.

4.1.1 Aim and objectives

The aim of this chapter was to investigate further the processes controlling pesticide contamination of surface water in the Wensum by application of a distributed catchment model and comparison to the field-scale simulations presented in Chapter 3. The specific objectives to meet this aim were to:

1. Generate a catchment modelling methodology using SPIDER and evaluate the simulations using measured data from the catchment
2. Compare the simulated water flow and pesticide losses from SPIDER with the ones obtained using MACRO in Chapter 3 in order to study the differences in the simulations between models
3. Incorporate key sources of uncertainty in the input parameters to assess their effect in model simulations
4. Evaluate whether the models can be used to study the progress of the Catchment Sensitive Farming programme in reducing pesticide emissions

4.2 Background information

4.2.1 SPIDER model

The SPIDER model simulates pesticide loss into surface water from the most important routes of pesticide entry which are spray drift, drain flow, surface runoff and interlayer flow (lateral transport within the soil profile) (Renaud et al., 2008). The catchment is described in the model as a series of fields and ditch/stream blocks interconnected according to the possible pesticide entry pathways which may be specified by the user. The model enables the representation of the spatial variability of the catchment; the user can provide the model with a maximum of 99 fields and streams for any period of time. Each field will have its own soil properties, pesticide application and crop definition. Likewise, each ditch/stream in the model should be provided with its individual dimension and hydrological parameters. In order to simulate pesticide transport in the soil profile in SPIDER, the soil porosity is divided into two pore domains using a similar approach to MACRO, but simplified to enable a reasonable simulation time at an hourly resolution and with a multi-field approach, and also to simplify the parameterisation process. The soil is divided into macropores and micropores allowing preferential flow to occur above drains. Vertical and lateral movement of water is triggered by soil moisture exceeding field capacity and the water balance (all in mm) at an hourly time step *t* is calculated from Equation 4-1.

Equation 4-1 $$\theta_t = \theta_{t-1} + R_{soil,t} + Ir_t - ETa_t - P_t - LM_t - D_t - Ru_t$$

where θ is the soil water content, R_{soil} and Ir are the amount of rainfall and irrigation, respectively, ETa is actual evapotranspiration, P is percolation, LM is lateral movement, D is drainage, and Ru is runoff. And the general equation of the soil pesticide balance to calculate the pesticide load (all in mg) for each layer is given by Equation 4-2.

Equation 4-2 $$PestL_t = PestL_{t-1} + IL_t + PL_t - SDL_t - RL_t - DrL_t - LFL_t$$

Where *PestL* is the pesticide load in the layer, *IL* is the load from either application or a layer above, *PL* is load from percolation, *SDL* is the pesticide degraded in the soil, *RL* is the load from runoff, *DrL* is load from drainage, and *LFL* is load from lateral flow. When a pesticide is simulated to be transferred from a field into a ditch/stream, it is then transported with water flow into consecutive ditches up to the end of the final ditch outlet using the Muskingum method. Simulation results are provided on an hourly basis so a detailed description of pesticide loss is available for the users from a reasonable set of input data requirements and relatively short simulation time (Renaud et al., 2008).

4.3 Methodology

SPIDER was used to simulate the fate of six pesticides in the Wensum catchment. A detailed description of the study area is presented in Chapter 3. The details about the modelling methodology and model evaluation are provided below. Simulated pesticides included carbetamide, chlorotoluron, clopyralid, mecoprop and MCPA. Information about their chemical properties and usage in the catchment are presented in Chapter 3. Simulations were carried out separately for each pesticide for a particular crop.

4.3.1 Conceptual model

The Wensum catchment was described in SPIDER as follows. The river network was divided into 24 sections and the catchment area into 44 fields according to their soil association and their location relative to the river sections (Figure 4-1). To simplify simulations, small fields with the same soil type that are hydrologically connected to the same river section were combined as one field. The resulting SPIDER conceptual model for the catchment is shown in Figure 4-2. Since Isleham association consists of peaty soils with high moisture content, located on the floodplain and banks of the river network only grass is usually cultivated in this area and for these reasons no pesticide application was included in these fields. Hence, in order to simplify the complexity of the model, Isleham soils were described in the model as two square fields, one was hydrologically connected to the River Wensum and the River Tud (Figure 4-2 fields 26 and 44, respectively). Fields and ditch/stream blocks were connected according to the flow direction. Field connecting arrows were set to the main hydrological connections in the catchment: drain flow, runoff and lateral flow. The slope for each field was calculated from a digital elevation model (METI and NASA, 2011) using the highest and the lowest altitude in the proximity of the river. Slopes ranged between 0.4 and 3.4°. Field areas were represented in the model as rectangles; their length and width dimensions were established by measuring the field length parallel to the river; then, the block width was calculated from this value along with the field area. The groundwater mixing model was also applied to include the baseflow component in the hydrograph following the same procedure undertaken in the model framework using MACRO (Chapter 3) and a daily output factor of 1%.

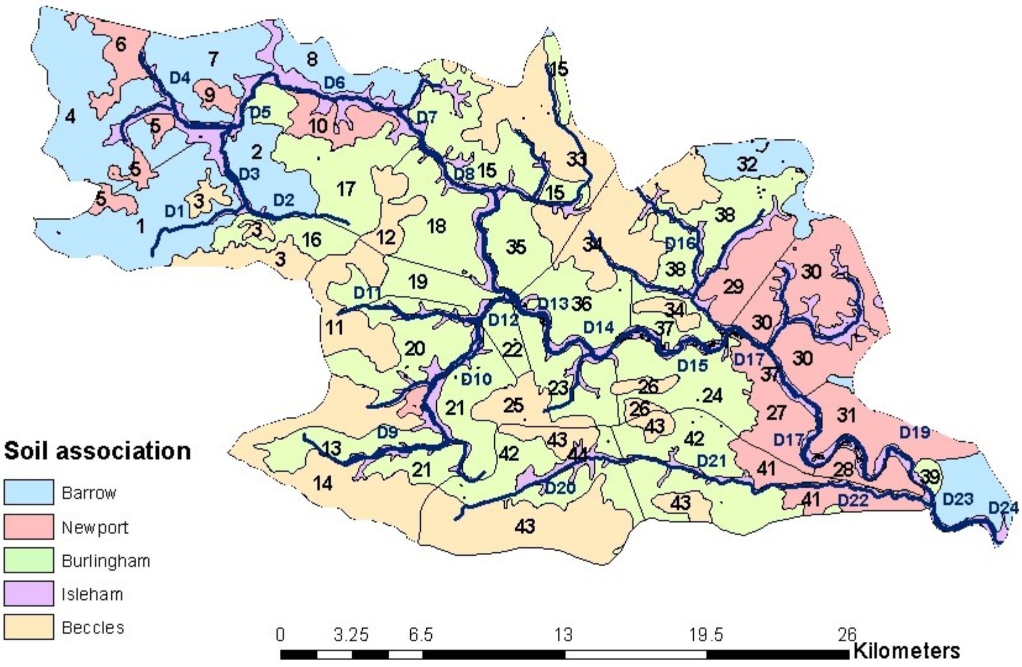


Figure 4-1 Division of the Wensum catchment into 44 fields and 24 ditch/streams segments

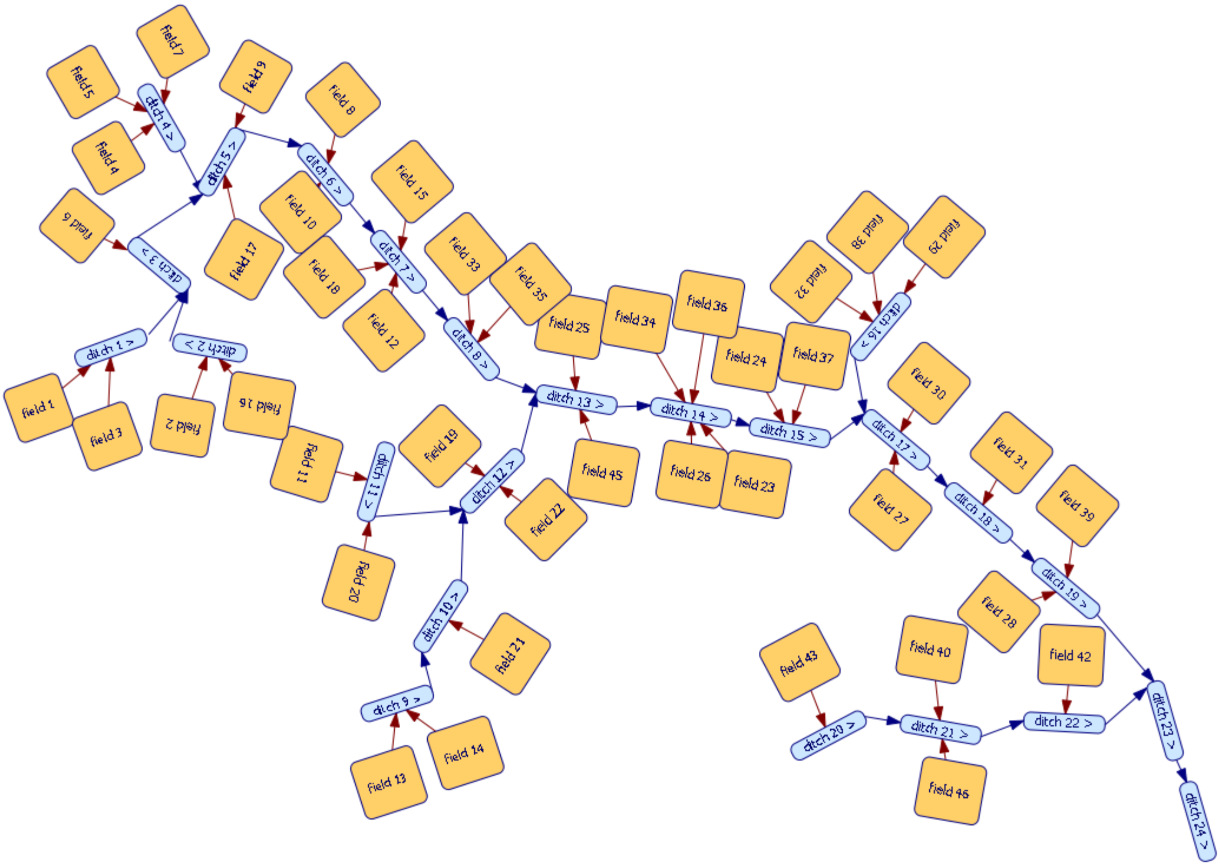


Figure 4-2 Conceptual model for the Wensum catchment.

4.3.2 Model parameterization

4.3.2.1 Soil parameters

Soil properties used in the SPIDER model were the same as those selected for MACRO (Section 3.3.6.1). Additional soil parameters used in SPIDER are shown in Table 4-1 and Table 4-2. The boundary water tension (TenMac) for all the soils was the same as used for the topsoil horizon in MACRO (Table 4-1). The groundwater recharge at the bottom of the soil profile was set to the values calibrated within MACRO for the different soil types (Table 4-1). The saturated vertical and lateral hydraulic conductivities of the soil as well as the hydraulic conductivity at field capacity were set to be calculated by the pedotransfer functions in SPIDER. Pedotransfer functions used by SPIDER are those reported by Evans et al. (1999).

Table 4-1 Field parameters used in SPIDER model.

Soil association	TenMac[1] (cm)	Recharge[2] (mm/h)
Barrow	12.0	0.470
Beccles	18.0	0.0098
Burlingham	15.0	0.00326
Newport	10.0	0.585
Isleham	12.0	0.177

[1]TenMac: Tension of soil water at which macropore flow is initiated; [2]Recharge: Groundwater recharge at the bottom of the soil profile

Table 4-2 Additional soil parameters used in SPIDER model (Hallett et al., 1995).

Soil association	Depth (cm)	Field capacity (unitless)	Van Genuchten n (unitless)	Van Genuchten α (unitless)
Barrow				
A	30	0.257	1.32	0.0841
B	55	0.301	1.28	0.0768
B’	95	0.410	1.20	0.0504
BC	150	0.358	1.21	0.0454
Beccles				
A	25	0.360	1.25	0.0590
E	45	0.314	1.24	0.0601
B	70	0.388	1.21	0.0450
BC	150	0.350	1.20	0.0421
Burlingham				
A	30	0.345	1.25	0.0576
E	50	0.320	1.24	0.0600
B	75	0.348	1.22	0.0510
B’	100	0.338	1.22	0.0530
BC	150	0.311	1.22	0.0543
Newport				
A	25	0.251	1.35	0.0927
B	55	0.190	1.44	0.124
BC	100	0.194	1.44	0.125
C	150	0.131	1.57	0.158
Isleham				
A	30	0.385	1.29	0.0819
E	50	0.157	1.50	0.139
B	75	0.140	1.52	0.143
C	150	0.131	1.56	0.158

4.3.2.2 Pesticide parameters

Pesticide parameters and application rates were the same as used in MACRO simulations (Section 3.3.6.3). Pesticide application was evenly distributed across the fields and adjusted to take into account the proportion of crop treated with a specific pesticide in the Eastern region using the values presented in Chapter 3 (Table 3-11). Apart from pesticide degradation in the soil, SPIDER also simulates degradation in the river network so degradation values in water and sediment must be supplied to the model (Table 4-3). These are the dominant degradation processes. All pesticides are stable to hydrolysis at pH 7 except for carbetamide that has a hydrolysis half-life of 19 days (Table 4-4); even though chlorotoluron and MCPA have short photolysis half-life values, this is not an important degradation route under UK solar radiation conditions. Freundlich coefficients for clopyralid and MCPA had to be adjusted to avoid sorption conflicts in the model because the original values were very small; these coefficients were increased to 0.85 in the model. The Freundlich sorption coefficient for the sediment for each pesticide was calculated from the K_{oc} and an organic carbon content of 3%.

Table 4-3 Pesticide degradation values in water and sediment and original and adjusted Freundlich coefficients in SPIDER.

Pesticide	DT_{50} water (days)	DT_{50} sediment (days)	Freundlich coefficient (-)	Freundlich coefficient used in SPIDER (-)
Carbetamide	9.1	55.5	0.926	0.926
Chlorotoluron	42	352	0.9	0.9
Clopyralid	148	1000*	0.761	0.85
MCPA	13.5	17	0.68	0.85
Mecoprop	37	50	0.9	0.9
Propyzamide	21	94	0.9	0.9

AERU (2007), *Netherton and Brown (2010)

Table 4-4 Photolysis and hydrolysis degradation values for the pesticides (AERU, 2007).

Pesticide	Photolysis DT_{50} at pH 7 (days)	Hydrolysis DT_{50} at pH 7 (days)
Carbetamide	Stable	19
Chlorotoluron	0.12	Stable
Clopyralid	271	Stable
MCPA	0.05	Stable
Mecoprop	44	Stable
Propyzamide	41	Stable

4.3.2.3 Crop parameters

In the same way as in MACRO simulations, cereals and oilseed rape were the crops simulated in SPIDER. The parameters used in the model are presented in Table 4-5. These crops were evenly distributed in the model field blocks (i.e. for each pesticide simulation all the field blocks in the model were assumed to have the same crop) and in cases when a pesticide is applied to more than one crop, only the main crop was simulated but including the pesticide application to all additional crops.

Table 4-5 Crop parameters used in SPIDER (FOCUS, 2000).

	Winter cereals	**Oilseed rape**
Emergence date	21 Oct	7 Sep
End of slow growth (min. leaf area index)	1 Mar	31 Mar
Date maximum cover reached	10 May	10 Apr
Maturation date (max. leaf area index)	15 Jun	20 Apr
Harvest date	31 Jul	10 Jul
Max. root depth (mm)	700	700
Min. root depth (mm)	50	50
Min. leaf area index	1	1
Max. leaf area index	5	4
Leaf area index at harvest	1	2
Min. fraction cover	0.2	0.1
Max. fraction cover	0.95	0.9
Fraction cover at harvest	0.7	0.3
Shape factor that controls the rate of increase of leaf area between emergence and max. leaf area (CFORM)	2.0	2.0
Shape factor that controls the rate of increase of leaf area between max. leaf area and harvest (DFORM)	0.7	0.2
Reference evapotranspiration at min. leaf area index*	0.7	0.5
Reference evapotranspiration at mature*	1.15	1.15
Reference evapotranspiration at harvest*	0.5	0.5

* Allen (1998)

4.3.2.4 Ditch/stream parameters

Ditch/stream blocks in the model represented the river network in the catchment. In the model the river network was divided into 24 ditch/stream blocks with lengths ranging between 680 and 8,194 m. The divisions were made at the points of confluence or where the river was longer than 8 km in order to reduce the number of fields going to the same ditch block and to allow normal water movement; too long ditches can end in causing high flow rates. River slope calculations were also made using a DEM of the catchment (METI and

NASA, 2011) by calculating the elevation at the top and at the end of the river section. The ditch top width at the top of the catchment was estimated to be 3 m and 15 m at the catchment outlet; for the rest of the ditch blocks this parameter was incrementally adjusted. The ditch base widths were estimated to be 1 m less than the top width. The river depth was set to 1 m at the top of the catchment and then gradually increased to 4 m at the catchment outlet. The Manning's n value was set to 0.03 which corresponds to a normal value for a natural main stream (Chow, 1959); and the Muskingum's weighting factor *x* was set to 0.2 for a medium attenuation effect in the channel flood routing (Cunge, 1969). The saturated hydraulic conductivity of the sediment layer was 0.5 mm/h and the sediment bulk density, 0.8 g/cm^3. Sediment thickness was initially set to 3 mm but then was calibrated to a value of 1 mm to reduce pesticide sorption to the sediment.

4.3.3 Model evaluation

The hydrological response of the model was visually evaluated against the simulated water flow for the Wensum catchment by comparing graphs for the simulation period (2006 – 2011). Statistical evaluation of the water flow simulation was also carried out by plotting the residuals and calculating the Nash–Sutcliffe model efficiency coefficients for each hydrological year and for the entire simulation period.

As previously mentioned in Chapter 3, hourly rainfall data for 2006 – 2007 were estimated from daily rainfall data for Mannington Hall (a station near the catchment) since no data were available from Norwich Airport for this two-year period. Thus, model efficiency was also included for the period 2008 – 2011 to evaluate model performance for the water flow simulation during years with less uncertainty in the rainfall data. A water balance for the water flow from SPIDER was also carried out in the evaluation.

Simulated pesticide concentrations for all of the simulated pesticides were also visually evaluated by plotting concentration graphs for the simulation period and comparing with the measured data. Measured data for days when no pesticide was detected were shown in the graphs as the LOQ value. LOQ values for the simulated pesticides are presented in Chapter 3 (Table 3-17). Due to the nature of the two data series, one discrete and the other continuous data, goodness-of-fit and model efficiency were not calculated, instead an evaluation of the magnitude and timings of the simulated pesticide concentration was carried out for each simulation.

4.3.4 Model calibration

Model calibration was applied to SPIDER in order to improve the simulation of the water flow by adjusting the water balance to increase the predicted flow in the river network (i.e. increasing percolation and drain flow volumes and reducing evapotranspiration). Table 4-6 shows the changes in crop and soil parameters applied for each step of the calibration. Model calibration comprised changes in recharge and evapotranspiration parameters. Recharge values in SPIDER were estimated as the maximum predicted daily recharge from MACRO. MACRO predicted a smaller value for Burlingham than for Beccles even though both soils have similar textures and infiltration behaviour. For this reason, the calibrated recharge value for Burlingham was set to the value estimated by MACRO for Beccles. In addition, evapotranspiration values were reduced according to ranges reported by Allen (1998) since the soil in the Wensum is prone to freezing during the winter. Finally, the output factor from the GW model was adjusted for a better simulation of the recession periods, by reducing its hourly value by 0.05% each time until an optimal value of model efficiency was obtained for the simulation period with less uncertainty in the rainfall data (2008 – 2011). The calibrated daily output factor was 0.35%.

Table 4-6 Uncalibrated and calibrated parameters (including the initial attempted calibration and the final calibrated parameters) used in SPIDER.

Parameters	Uncalibrated	Calibrated
Reference evapotranspiration at min. leaf area index*	0.7	0.4
Reference evapotranspiration at mature*	1.15	1.0
Reference evapotranspiration at harvest*	0.5	0.3
Burlingham recharge (m^3/s)	0.00326	0.0098
Daily outflow factor for the GW model	1%	0.35%

*Allen (1998)

4.3.5 Comparison between SPIDER and MACRO simulations

The calibrated water flow simulations from SPIDER and MACRO were visually compared from their hydrographs and quantitatively assessed by comparing model efficiency values for each hydrological year and for the entire simulation period. Graphs showing pesticide concentrations simulated by SPIDER and MACRO and the measured concentrations were generated for all the pesticides to evaluate model performance. Simulated maximum concentration values for the pesticides were also evaluated against the maximum measured data. These comparisons were made for the whole simulation period and for each hydrological year to evaluate the performance of both models at predicting pesticide maximum concentrations in the catchment. As SPIDER predicts hourly pesticide emissions and measured data were reported on a daily basis without specifying the time at which the sample was collected, both hourly and daily average simulated maximum concentrations from SPIDER were evaluated.

The same methodology applied to calculate pesticide loads for MACRO was used for SPIDER (Equation 3-5). Additional assumptions were made to calculate pesticide loads on days when the pesticide concentration was reported to be below the limit of quantification (LOQ). A limit value of 0.001 μg/l was used to define the minimum pesticide concentration that was taken into account for the calculations. This value is 20% of the smallest LOQ reported for the studied pesticides (i.e. a LOQ of 0.005 μg/l for propyzamide). Then, the assumptions made for calculating the loads for these days were:

1) For days when the models (SPIDER or MACRO) simulated a pesticide concentration below a value of 0.001 μg/l, the measured and the simulated concentrations were assumed to be zero. It was considered that if pesticide was neither detected in the sample nor simulated by the models, it is very unlikely that pesticide was actually present in the water.
2) For days when either of the models simulated a concentration between the LOQ and 0.001 μg/l, the measured concentration was assumed to be 25% of the LOQ. This means that if one of the models predicts a pesticide concentration above the set limit of 0.001 μg/l but it is not analytically quantified in the samples, there is reasonable probability that the pesticide was present in the water at a concentration smaller than the LOQ.

Daily simulated loads were first calculated and then added together to estimate the annual simulated load from SPIDER and MACRO for each hydrological year for the period 2006 – 2011.

4.3.6 Uncertainty analysis for SPIDER and MACRO simulation in the Wensum catchment

Model performance in the simulation of pesticide concentrations can be affected by several sources of uncertainty in the input parameters. Main sources of uncertainty for the present study are thought to come from the use of average input parameters instead of site-specific field data for pesticide sorption and degradation as well as average and uniform pesticide usage along the catchment and typical application dates. The impact of uncertainty in the measured rainfall data on the simulation was also investigated.

4.3.6.1 Uncertainty in the rainfall data

There are different types of rain gauge systems including tipping bucket systems, weighing systems and optical systems. Most of them consist of a circular collector (where the sample is taken) and a funnel that channels the collected sampled into a measuring mechanism or into a reservoir where it can be measured manually. For many years the UK Meteorological Office (2010) has used the tipping-bucket rain gauge for the automatic recording of rainfall rates. This mechanism tips each time that 0.2 mm of rainfall accumulation occurs. Like any other measurement, rainfall data from rain-gauges have a level of uncertainty. Studies have shown that uncertainties from tipping-bucket gauges depend mainly on precipitation intensity (Wang et al., 2008; Ciach, 2003; Nystuen et al., 1996) and timescale (Wang et al., 2008; Ciach, 2003). Ciach (2003) estimated errors in rainfall data using tipping-bucket rain gauges for different timescales applying non-parametric regression tools; for hourly recordings and rainfall intensities similar to the observed in Norwich Airport a standard error of 10% was obtained. The effect of this uncertainty in model outputs was investigated by applying simulations with +/-10% of the measured rainfall data.

4.3.6.2 Uncertainty in the pesticide application date

Although, there are typical application dates reported for pesticides, actual application can vary depending on several factors such as the weather, recommendations in pesticide application and different crop types that it can be applied to. For this reason an uncertainty analysis into the effect of the use of typical application dates in the model was assessed using the simulation of carbetamide. Carbetamide is a post-emergence herbicide with residual action usually applied to oilseed rape from the middle of October until the end of February. The recommendation is not to apply if heavy rain is expected within 48 hours and if drains are flowing or are about to flow. Therefore, SPIDER and MACRO were run varying the application date in intervals of 5 days following these recommendations by looking at rainfall patterns during the crop season.

4.3.6.3 Uncertainty in pesticide sorption and degradation parameters

The effect on pesticide simulations due to uncertainties in the use of average reported pesticide sorption and degradation values was also evaluated by running different simulations for carbetamide and comparing with the original simulation. An evaluation of the extreme parameters was carried out by running four simulations combining maximum and minimum sorption and degradation values (Table 4-7).

Table 4-7 Minimum and maximum sorption and degradation values used in the model (AERU, 2007).

	Koc (ml/g)	**DT_{50} in soil (days)**
Minimum	59.5	4.02
Maximum	118.2	28.9

4.3.7 Analysis of pesticide trends in the catchment

In order to evaluate the trends of pesticide losses and the progress of the Catchment Sensitive Farming programme in the Wensum catchment, the calculated pesticide loads for all pesticides using SPIDER and MACRO were used as well as the estimated observed loads obtained by linear interpolation (Section 4.4.3.4). The percentage of reduction in the loads was calculated between hydrological years and for the entire simulation period. Increases and reductions in pesticides loads were shown as positive and negative values, respectively.

Neither of the models applied in the present study are able to simulate the effect of best management practices that the CSF programme have been conducting in the Wensum since 2006. The models that were applied can only respond to the inherent properties of the catchment (land use and soils), pesticide usage and weather conditions. Therefore, if the level of reduction (or increase) in pesticide load predicted by the models is comparable to the level of reduction (or increase) in the observed data, then that reduction (or increase) can be explained based simply on either a reduction (or increase) in pesticide usage or the effect of weather and flow. However, if differences are observed between load simulations and observed emissions other effects such as BMPs might explain the changes.

4.4 Results

4.4.1 Model evaluation

4.4.1.1 Water flow

The uncalibrated water flow simulation for SPIDER including the use of the groundwater mixing model is compared to the measured flow in Figure 4-3. The hydrograph generally showed a good agreement in the pattern of the peaks with over-estimations in flow usually occurring during periods of greatest flow (e.g. in 2006-2007), and under-estimations at low-flow periods. Disagreements in the flow were considered to be important when a factor of 2 was exceeded. A period of large over-estimation of the flow occurred from September to the end of November 2006, up to a factor of 3.5. In 2007, flow over-estimation was also observed particularly in January and June 2007 when two very large flow events on January 10th and June 25th 2007 were over-estimated by factor of 3.3 and 3.0, respectively. Under-estimation was observed for some of the largest flow peaks in hydrological years 2008-2009, 2009-2010 and 2010-2011. However, under-estimation during low-flow periods has shown to be the main issue in the simulation, particularly in the simulation of flow recession and recovery (i.e. at the beginning and end of low-flow periods, respectively). The simulation of the baseflow greatly disagreed with the response of the observed hydrograph; abrupt changes of flow were simulated at beginning and end of low-flow periods which differs to the more gentle behaviour of the baseflow.

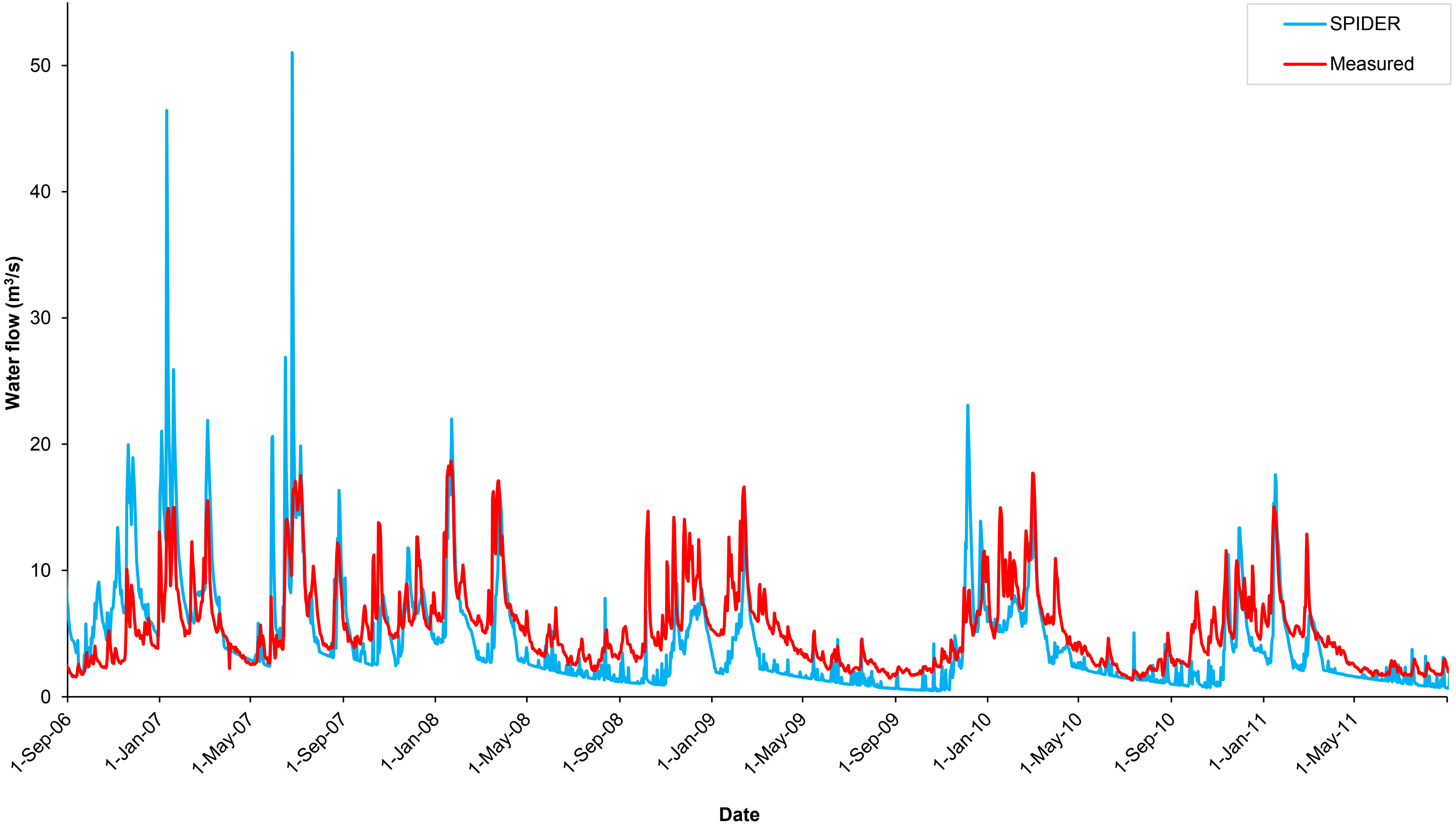


Figure 4-3 Comparison between measured flow and uncalibrated simulation by SPIDER.

Table 4–8 shows the simulated and measured flow values for each hydrological year and for the simulation period. The uncalibrated simulation accounted for 82.5% of the observed flow with variation between years. Under-estimation of the flow was simulated for most of the hydrological years; the exception was for 2006-2007 where over-estimation of the flow was obtained in 35%. Hydrological years 2008-2009 and 2010-2011 showed the largest under-estimations of the flow in 49.8 and 34.3%, respectively.

Table 4-8 Observed water volume and simulated from SPIDER including the baseflow from the GW model and the percentage simulated of the observed volume from each hydrological year and the entire simulation period.

		Uncalibrated		**Calibrated**	
Hydrological year	Observed (10^6 m^3)	SPIDER + GW (10^6 m^3)	Total simulated (% of the observed)	SPIDER + GW (10^6 m^3)	Total simulated (% of the observed)
2006 – 2007	190.5	257.6	135.2	260.9	137.0
2007 – 2008	198.1	148.2	74.8	177.5	89.6
2008 – 2009	168.0	84.3	50.2	115.9	69.0
2009 – 2010	150.9	116.7	77.3	138.7	91.9
2010 – 2011	140.0	92.0	65.7	113.1	80.8
2006 – 2011	847.5	698.8	82.5	806.0	95.1

The Nash-Sutcliffe model efficiency coefficients (*E*) were calculated to evaluate the simulation of the water flow by SPIDER. *E* values were calculated for each hydrological year, for high (1 November – 30 April) and low-flow periods (1 May – 31 October) as well as for the entire simulation (2006 – 2011) and the period with the lowest uncertainty in the rainfall data (2008 – 2011) (Table 4-9). Model performance varied between hydrological years; positive *E* values were observed for 2007-2008, 2009-2010, 2010-2011 and the simulation period 2008 – 2011 but their values was small. Negative *E* values were observed for the hydrological years 2006-2007, 2008-2008 and for the entire simulation period (2006 – 2011). The negative efficiency value for the entire simulation was mainly due to a poor simulation of the flow in 2006-2007. Model performance for the period 2008 – 2011 (E = 0.23) was better than for the entire simulation 2006 – 2011 (E = -0.02) since less over-estimation of the flow was obtained due to the better quality of the rainfall data. On the other hand, *E* values for periods of high-flow were generally better than for low-flow periods but most of them were negative. The best high-flow simulation was in 2007-2008 with a positive value (E = 0.27) which was also the best simulated hydrological year (E = 0.35).

Table 4-9 Nash-Sutcliffe model efficiency coefficients for the uncalibrated and calibrated water flow.

	Uncalibrated flow			**Calibrated flow**		
Hydrological year	E each hydrological year	E high-flow period 1 Nov – 30 Apr	E low-flow period 1 May – 31 Oct	E each hydrological year	E high-flow period 1 Nov – 30 Apr	E low-flow period 1 May – 31 Oct
2006 – 2007	-0.73	-1.86	-0.38	-1.41	-2.14	-1.51
2007 – 2008	0.35	0.27	-1.79	0.59	0.51	-0.39
2008 – 2009	-0.22	-0.98	-4.21	0.22	-0.39	0.13
2009 – 2010	0.33	-0.30	-1.38	0.15	-0.79	-0.24
2010 – 2011	0.15	-0.21	-6.14	0.22	-0.35	-2.46
2006 – 2011	-0.02	-0.51	-0.10	-0.09	-0.53	-0.29
2008 – 2011	0.23	-0.17	-1.11	0.36	-0.12	0.04

The residuals plot in Figure 4-4 showed large negative values for days when the flow was greatly over-estimated by the model in January and June 2007 and December 2009 which resulted in non-random patterns of consecutive negative points. Non-random patterns in the residuals, with a U-shape, were also observed during periods of low flow as a consequence of the under-estimation of the flow at the beginning and end of these periods.

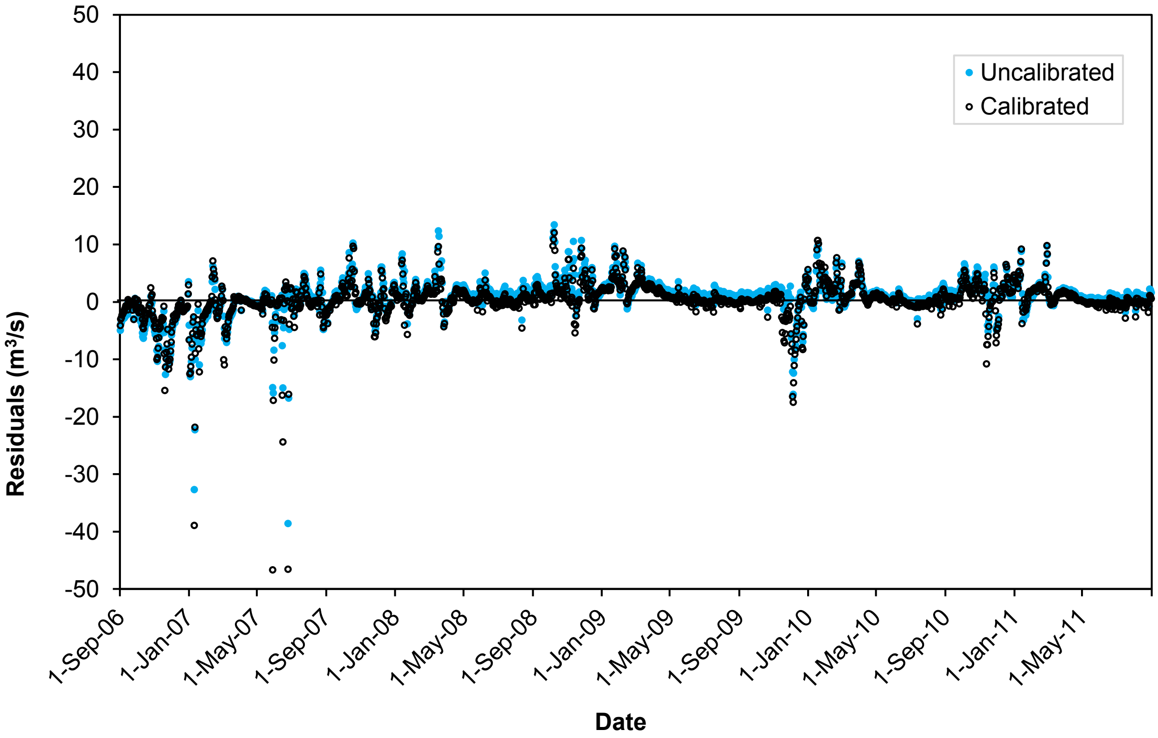


Figure 4-4 Comparison of the residuals from the uncalibrated and calibrated simulations using SPIDER.

A mass balance of the uncalibrated water flow from SPIDER was carried out to assess which routes could be causing under-estimation of the water flow. These results can then be used to decide which parameters should be adjusted in the model calibration. Table 4-10 shows the water balance for the five-year period (2006 – 2011). The total rainfall for this simulation period was 3,958 mm. Evapotranspiration was to be the most important sink term in the under-estimation of the flow. Therefore, evapotranspiration coefficients for the crop should be reconsidered. In addition, percolation from Burlingham was small compared to Beccles although both soil associations have similar hydrological properties; this suggested that the recharge value for Burlingham should be adjusted.

Table 4-10 Mass balance of the uncalibrated water flow from each soil association using SPIDER.

Water budget (mm)	Barrow	Newport	Burlingham	Beccles	Isleham
Drain flow	0	0	1,014	834	0
Percolation	1,276	1,397	171	329	438
Evapotranspiration	2,425	2,390	2,434	2,456	2,521
Interlayer flow	1	116	42	14	988
Soil water storage	106	306	65	36	351
Total	3,808	4,210	3,727	3,669	4,298

4.4.1.2 *Model calibration*

Model calibration was carried out by modifying the evapotranspiration coefficients for each crop stage and the recharge value for Burlingham to reduce flow under-estimation. Table 4-11 shows the water balance for the calibrated simulation. Evapotranspiration and soil water storage showed a reduction in their values; particularly evapotranspiration was reduced by almost 200 mm for all the soils. This resulted in an increase in percolation from all soils; percolation for Burlingham was comparable to Beccles.

Table 4-11 Mass balance of the calibrated water flow from each soil association using SPIDER.

Water budget (mm)	Barrow	Newport	Burlingham	Beccles	Isleham
Drain flow	0	0	911	995	0
Percolation	1,461	1,686	488	358	478
Evapotranspiration	2,238	2,208	2,244	2,262	2,325
Interlayer flow	1	16	44	16	1,147
Soil water storage	85	295	70	15	335
Total	3,786	4,206	3,756	3,646	4,286

The outflow factor from the GW model was calibrated by systematically reducing its value in 0.05% increments from 1% until the optimal value of 0.35% was determine. Figure 4-5 compares the calibrated and uncalibrated simulation of the flow. Model calibration increased the simulated flow in the catchment outlet particularly during low-flow periods. However, the more constant behaviour of the flow during periods of low flow disagreed in the recession and recovery behaviour of the measured flow. In addition, the calibrated simulation could not predict some of the large flow peaks that were also missed by the uncalibrated simulation such as those occurring in August 2008, January 2009, March 2009, January 2010, April 2010 and February 2011. Over-estimation of the flow also affected the simulation particularly during periods of great flow in 2006 – 2007 and in November 2010. For example, for the high flow peaks on January 10th, May 29th and June 25th 2007 with initial over-estimation of the flow by factors of 3.3, 2.7 and 3.1, respectively, increased to 3.5, 6.6 and 3.5, respectively. In addition, the simulation of the peak on November 12th 2010 before model calibration was satisfactorily simulated but after calibration was over-estimated by a factor of 1.9.

Model calibration increased the simulated flow for the entire period in 12.6% which accounts for 95% of the observed flow (Table 4–8). The largest increased in the flow was observed in 2008-2009 in 18.8%; however, this year continues to have the largest under-estimation of the flow in 31%. The over-estimation of the flow in 2006-2007 only increased in 1.8% compared to the uncalibrated simulation.

Model calibration did not improved model efficiency for the entire simulation period (2006 – 2011) but no significant changes were observed (Table 4-9). Model efficiency for the period 2008 – 2011 did show improvement after model calibration from 0.23 to 0.36. Model efficiency values for most of the hydrological years were better after calibration; the exceptions were for 2006-2007 and 2009-2010 due to disagreements due to over-estimation of the flow and bad simulation of the low-flow periods, respectively. The simulation of the high-flow periods did not showed significant improvements after calibration, except for 2007-2008 which increased its model performance and also continued to be the best simulated hydrological year (E = 0.59). Model efficiency for periods of low flow showed better results after calibration even though most of the values continued to be negative; however, two positive coefficients were obtained for 2008-2009 and the simulation period 2008 – 2011.

The plot of the residuals for the calibrated and uncalibrated simulations showed a decrease in the under-estimation of the flow throughout the simulation (Figure 4-4). An increase in the large negative numbers due to flow over-estimation was observed in 2006-2007 and 2009-2010.

4.4.2 Pesticide concentrations simulated by SPIDER

The simulated pesticide concentrations at the catchment outlet using SPIDER are compared with the measured data in Figure 4-6 to Figure 4-11, organized in order of application during the crop season. The patterns and timings of all pesticide simulations generally have a good match to the measured pattern over the whole simulation period with some differences in the magnitude and timing of the peaks.

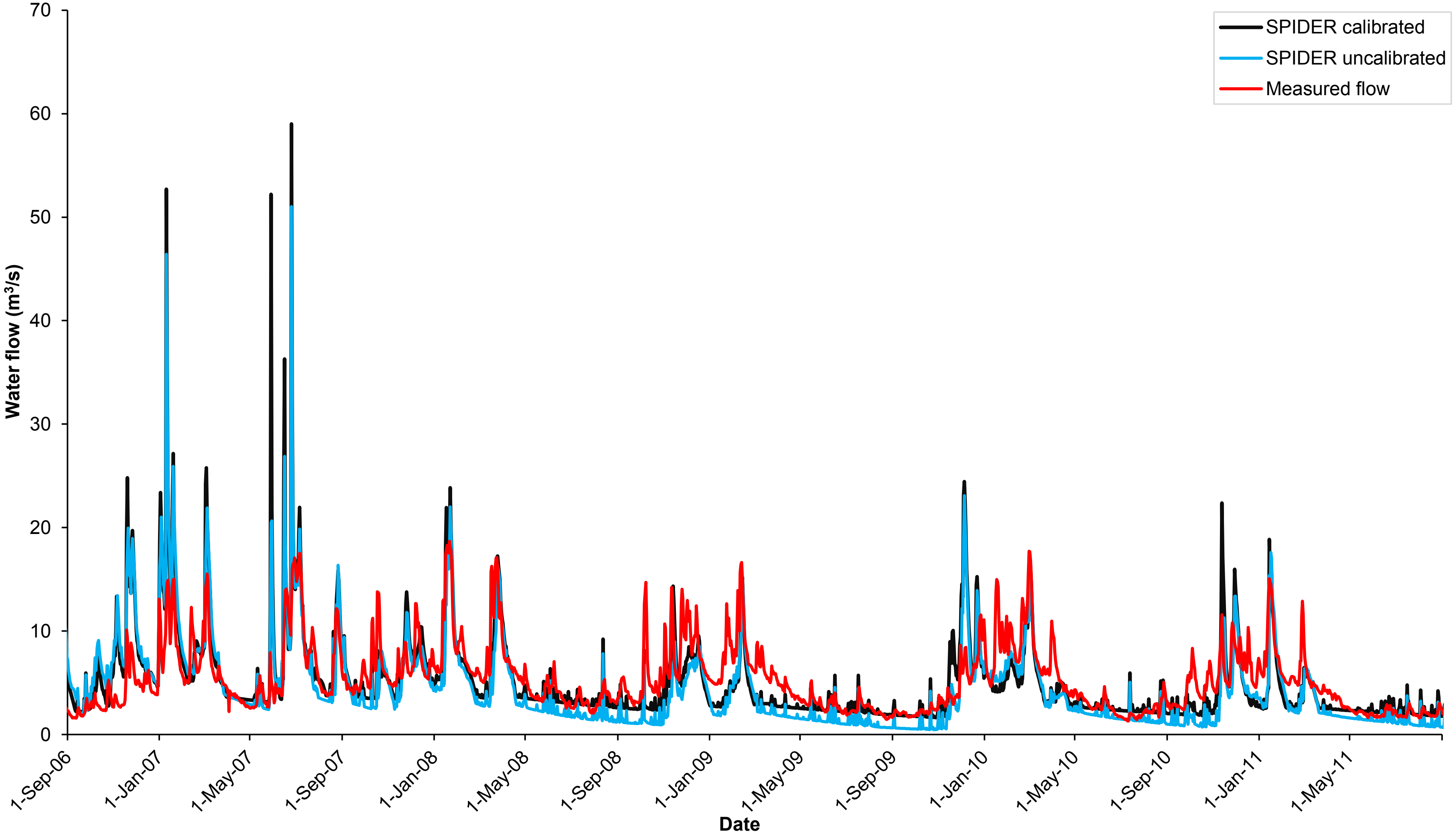


Figure 4-5 Comparison of the uncalibrated and calibrated simulation of the water flow using SPIDER with the observed flow in the Wensum catchment.

Good simulations were achieved for chlorotoluron and mecoprop concentrations (Figure 4-6 and Figure 4-7, respectively). Pesticide concentrations for chlorotoluron showed a good simulation in the pattern, timing and magnitude of the peaks, particularly in 2006-2007, 2009-2010 and 2010-2011 where most of the peaks matched the observed concentrations (Figure 4-6); the exception was the large observed emission on November 26th 2010 which was missed by the model. Large under-estimations in the concentrations were observed in 2008-2009 (up to a factor of 5.7) including the maximum observed concentration on December 12th 2009 where the model matched the timing but under-estimated the concentration by one order of magnitude. The model also missed a peak measured on March 18th 2008 (which was also the only observed concentration during that year). Emission peaks occurring in November 20th 2006 and January 16th 2010 seemed to have been missed by measurements since no sampling was carried out on those days but previous and latter peaks did match the measured data. For peaks occurring in May and June 2007, no evaluation can be carried out since no samples were taken in those months to compare with.

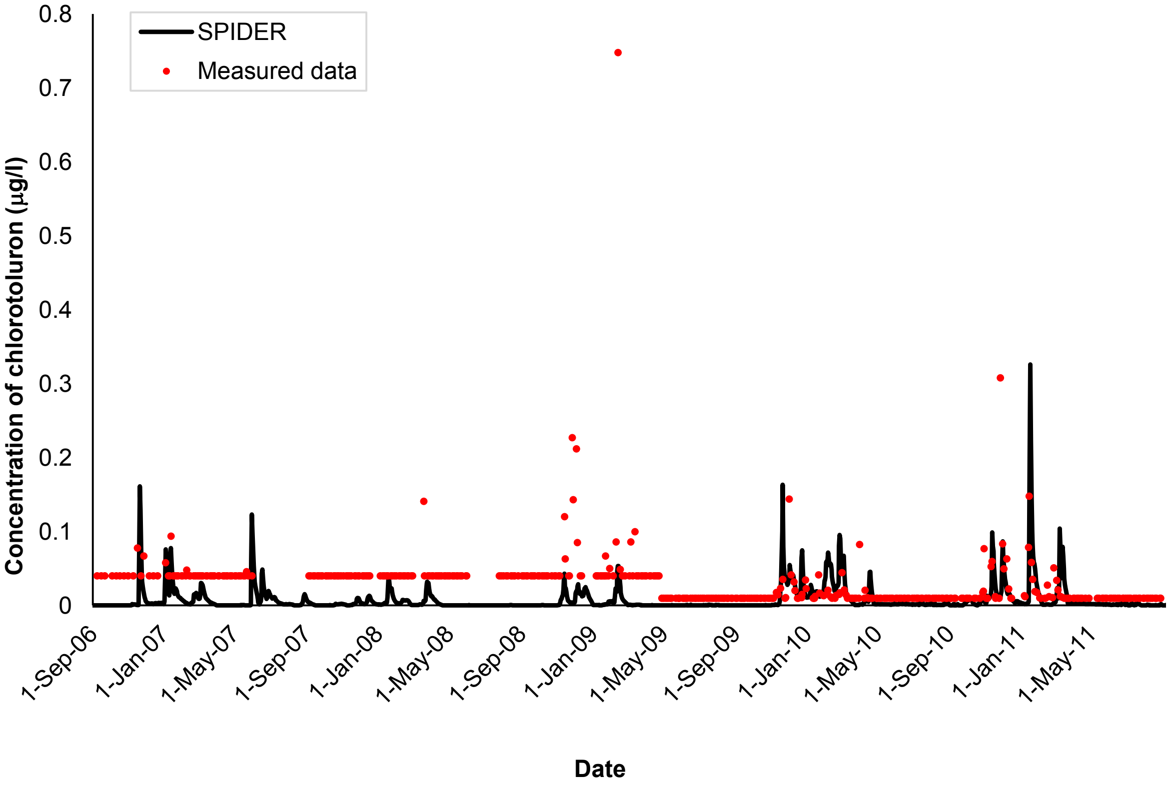


Figure 4-6 Comparison of measured concentrations of chlorotoluron with those simulated by SPIDER.

Mecoprop simulations using SPIDER matched the order of magnitude of the peaks and the patterns of the concentrations for some hydrological years at the catchment outlet (Figure 4-7). Discrepancies were mainly observed in the timing of events. SPIDER did not simulate peaks occurring during spring and summer periods in 2007, 2008 and 2009; instead simulated concentrations during winter periods for those years. Good matches in the timing and magnitude of some of the simulated peaks were observed in November 2006, December 2007, March to April 2008, November to December 2008 and October to November 2010.

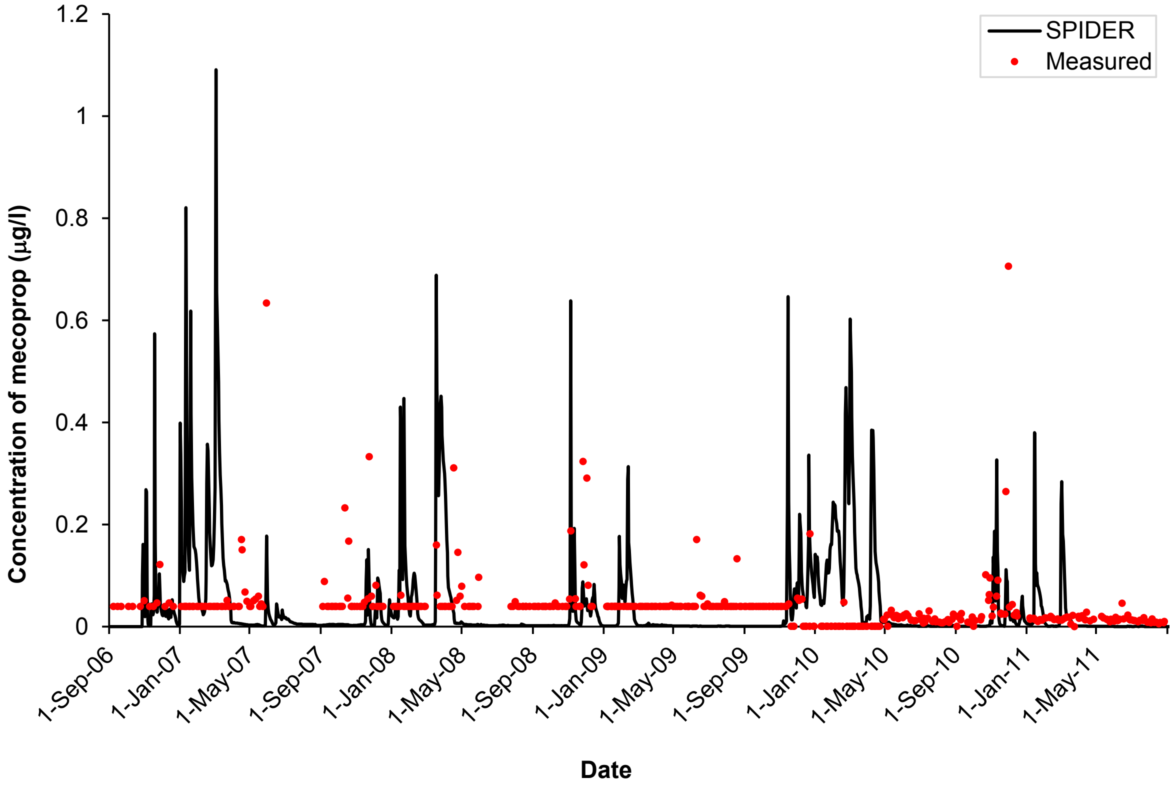


Figure 4-7 Comparison of measured concentrations of mecoprop with those simulated by SPIDER.

Simulations for carbetamide and propyzamide showed a good simulation of the pattern and timing of the peaks but under-estimation of measured concentrations was observed for some hydrological years (Figure 4-8 and Figure 4-9, respectively). Under-estimation in the concentrations occurred by up to one order of magnitude for both pesticides in hydrological years 2007, 2008 and 2009; except for the peak on March 25th 2008 for propyzamide which matched the measured data. A good simulation of the magnitude of the peaks for both herbicides was observed in hydrological years 2006-2007 and 2010-2011. Similarly to chlorotoluron, the simulated concentrations for propyzamide occurring in May and June 2007 could not be evaluated since no samples were taken in those periods.

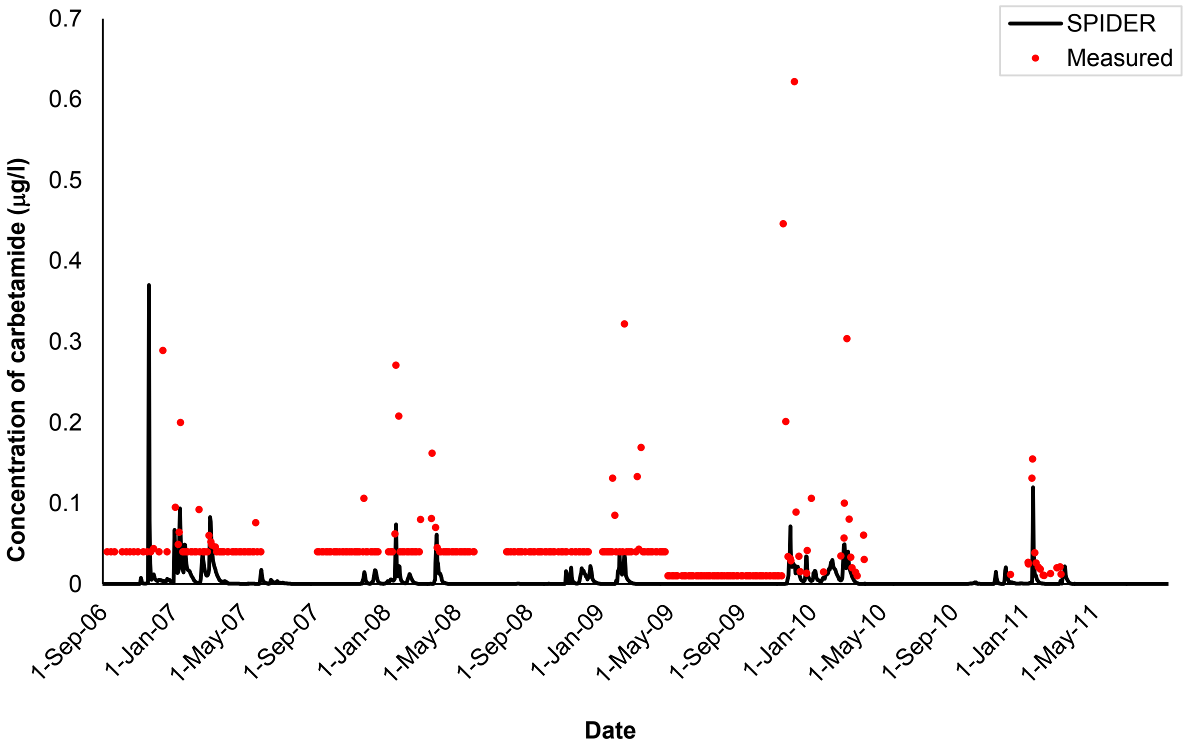


Figure 4-8 Comparison of measured concentrations of carbetamide with those simulated by SPIDER.

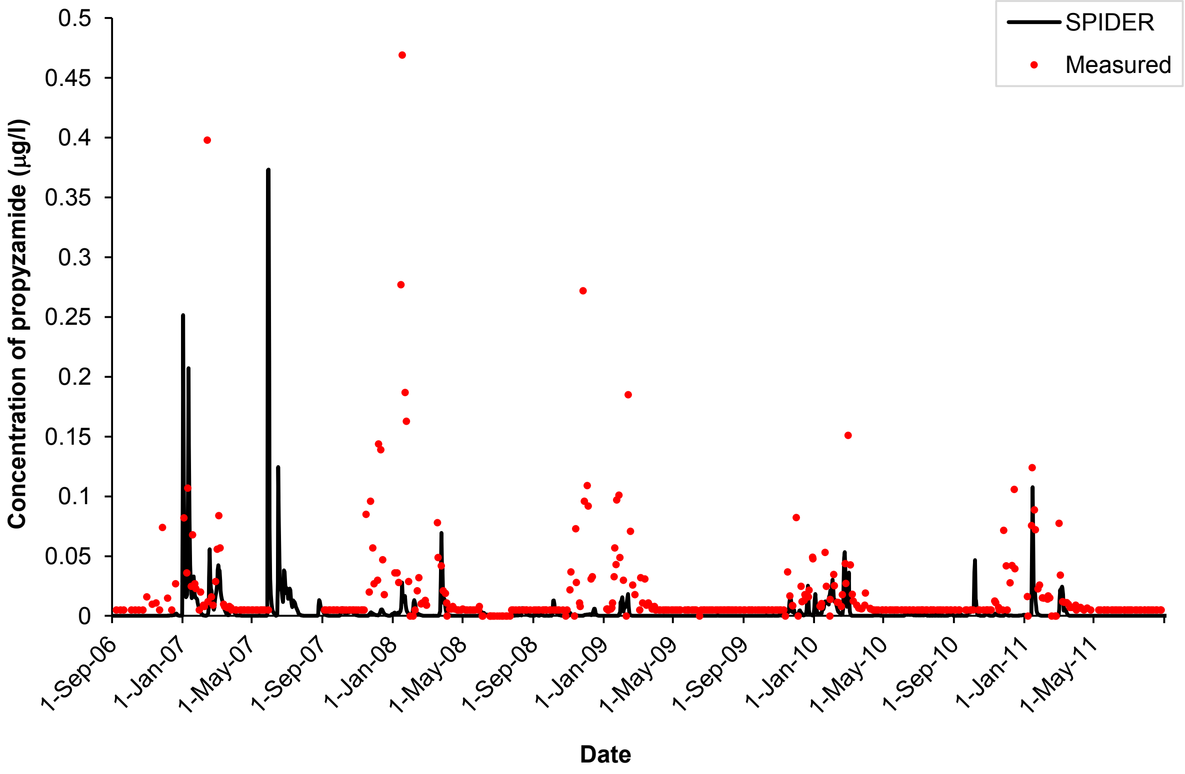


Figure 4-9 Comparison of measured concentrations of propyzamide with those simulated by SPIDER.

Most of the monitoring data for clopyralid were below the LOQ; only a few detections were observed during the simulation period (16 detections out of 480 samples) (Figure 4-10). A few peaks were also simulated, most of them in the same order of magnitude and agreed with the timing of the observed data. Over-estimation in the concentrations was observed in 2006-2007 by up to a factor of 3.1. The observed concentrations in May 2008 and June 2011 were simulated well by the model in both timing and magnitude. Under-estimation in pesticide concentrations was observed in 2009-2010 and 2010-2011.

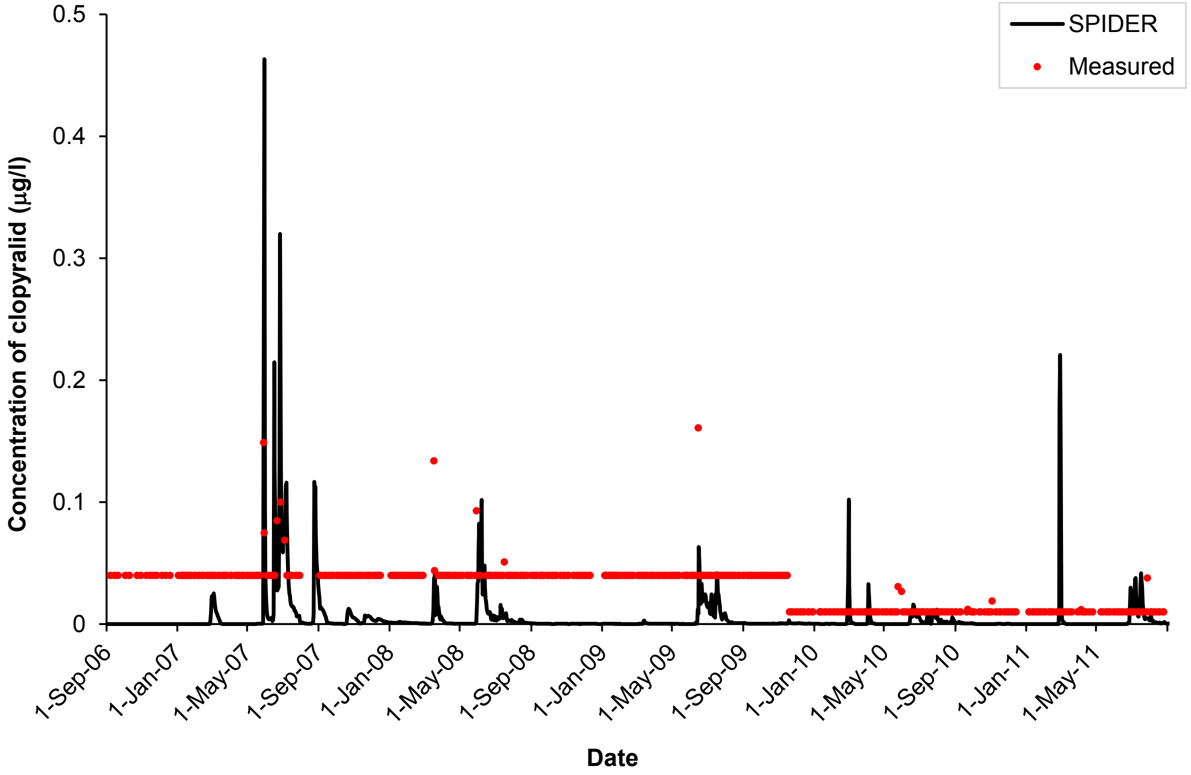


Figure 4-10 Comparison of measured concentrations for clopyralid with those simulated by SPIDER.

A poor simulation was observed for MCPA (Figure 4-11), the model only simulated peaks for the hydrological year 2006 but missed the emissions observed for the rest of the simulation period. Large concentrations were simulated in 2006-2007, with an apparent over-estimation of up to one order of magnitude for the simulated peak on June 26th 2007; however, this peak could not be evaluated since no measured data were available to compare with for the exact day. A good simulation was only observed for the peak occurring on May 29th 2007 by a factor of 1.8.

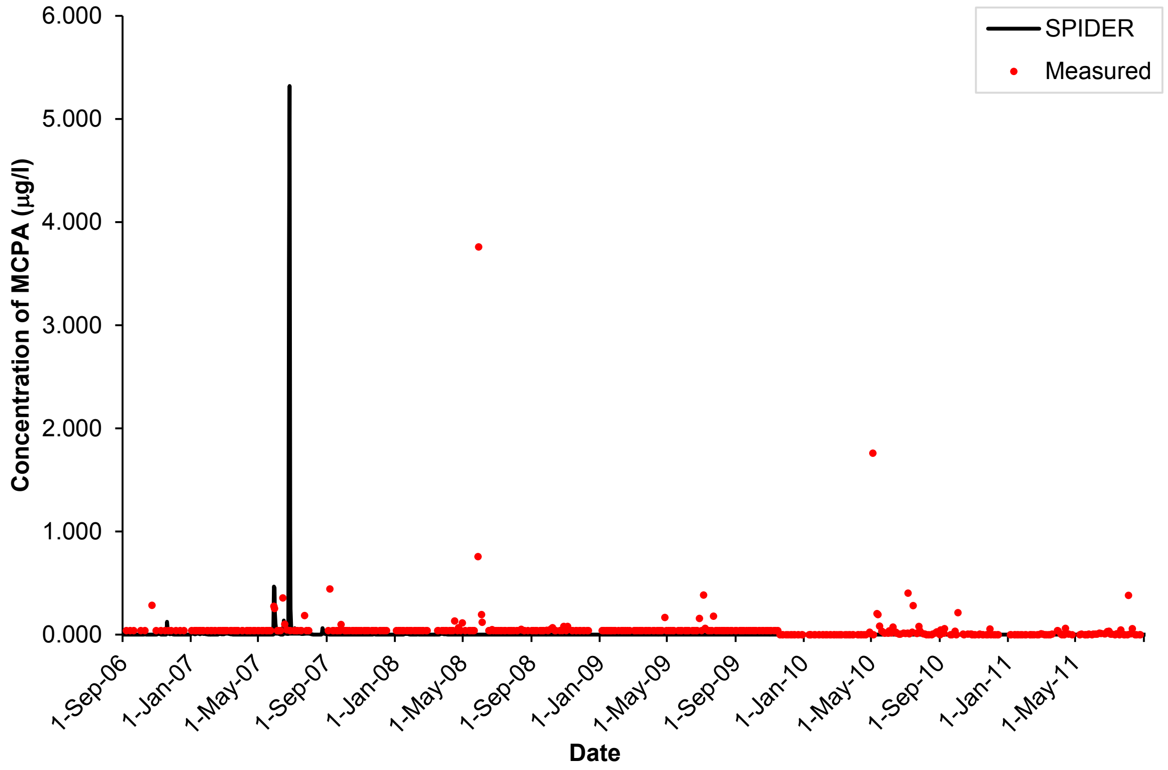


Figure 4-11 Comparison of measured concentrations of MCPA with those simulated by SPIDER.

4.4.3 Comparison between SPIDER and MACRO simulations

4.4.3.1 Water flow

Water flow simulations from MACRO and SPIDER including the use of the GW model are compared to the measured flow in Figure 4-12. Both models showed good simulation of the pattern of the water flow. However, there was a trend for both models to over-estimate flow during periods of greatest flow and under-estimate concentrations during periods of low flow. For the hydrological year 2006-2007, more over-estimation was observed for SPIDER than for MACRO, particularly, for the three large flow peaks predicted by SPIDER in May and June 2007 where MACRO only slightly over-estimated peak flow and under-estimated the others. Similarly over-estimation of the flow by SPIDER was also observed for December 2010 and 2011 whereas MACRO under-estimated peak flow. For both models the level of under-estimation throughout the simulation was more significant issue than over-estimation, particularly during low-flow periods. A better simulation of the recession periods was achieved for MACRO while the simulated flow from SPIDER was significantly smaller than the observed flow. In contrast, during periods of flow recovery (i.e. at the end of low-flow periods) MACRO took more time to increase the flow than SPIDER.

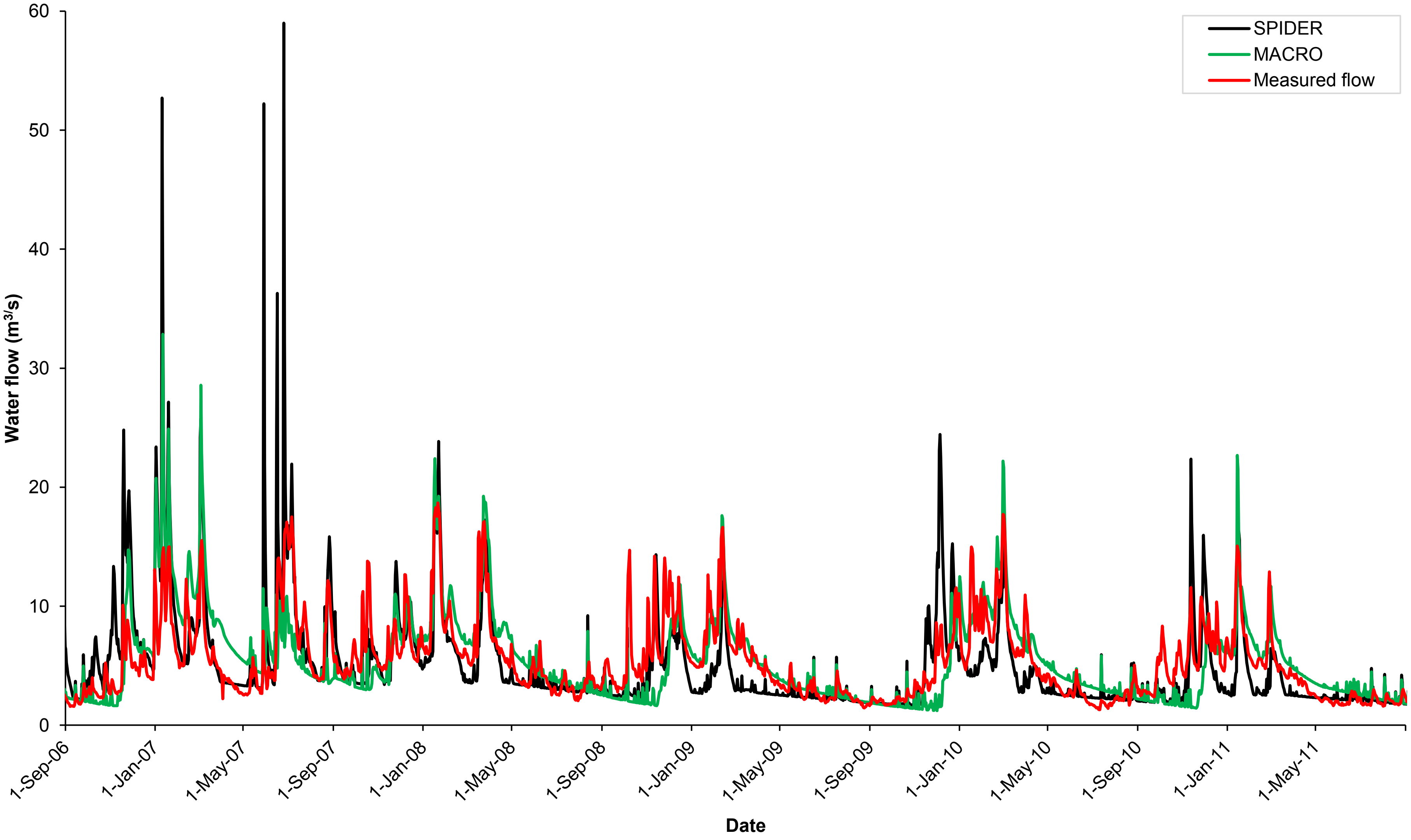


Figure 4-12 Comparison of the measured and simulated water flow (calibrated simulations) by SPIDER and MACRO.

The simulated flow for each hydrological year and for the simulation period is shown in Table 4-12. The models had very similar estimation of the flow for the entire simulated period (95.1 and 97.4% for SPIDER and MACRO, respectively). In addition the simulated flow showed similar behaviour for the hydrological years between models. For both models, 2008 was the hydrological year with most under-estimation of the flow followed by 2010; and flow was over-estimated in 2006 in both simulations. In general, MACRO was closer in the simulation of the observed water flow than SPIDER.

Table 4-12 Observed water volume and simulated from SPIDER including the baseflow from the GW model and the percentage simulated of the observed volume from each hydrological year and the entire simulation period.

		SPIDER		**MACRO**	
Hydrological year	Observed (10^6 m^3)	Simulated flow (10^6 m^3)	Total simulated (% of the observed)	Simulated flow (10^6 m^3)	Total simulated (% of the observed)
2006 – 2007	190.5	260.9	137.0	214.3	112.5
2007 – 2008	198.1	177.5	89.6	195.3	98.6
2008 – 2009	168.0	115.9	69.0	136.1	81.0
2009 – 2010	150.9	138.7	91.9	152.0	100.7
2010 – 2011	140.0	113.1	80.8	127.6	91.1
2006 – 2011	847.5	806.0	95.1	825.4	97.4

The residuals for both models showed similar patterns, particularly in the U-shape during periods of low flow (Figure 4-13). Differences in the behaviour of the residuals were observed for periods of over-estimation of the flow from SPIDER, reflected in the residuals with consecutive large negative residuals (e.g. January and June 2007 and December 2009). In contrast, positive residuals for MACRO showed periods of under-estimation of the flow due to the delay in flow recovery in this model at the end of low-flow periods.

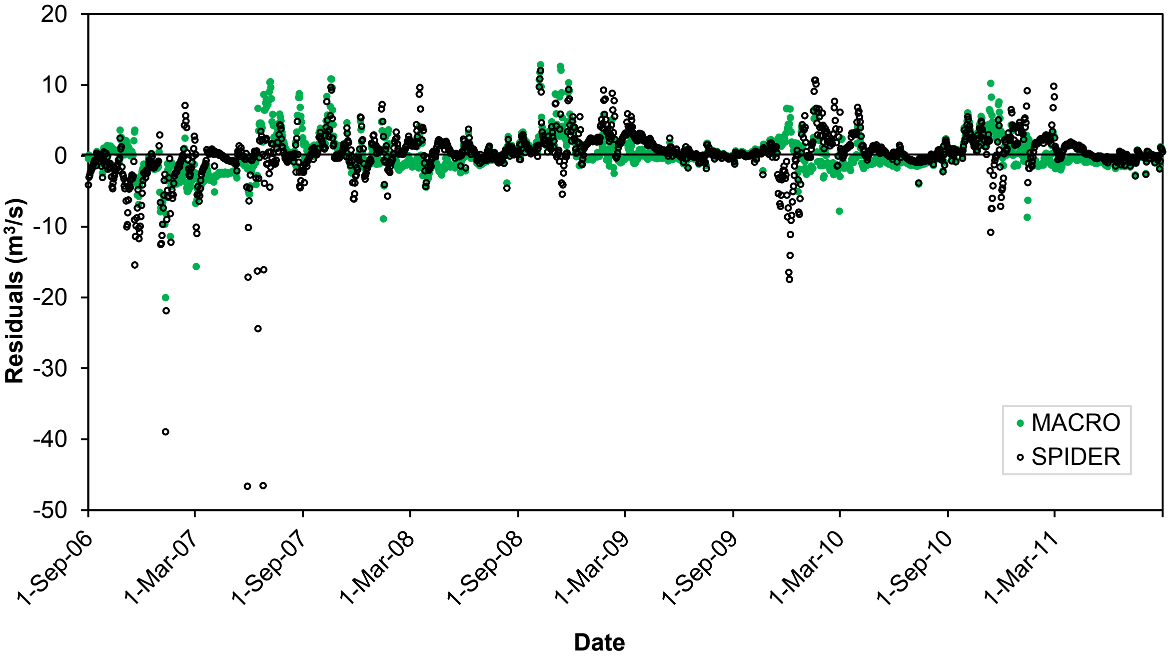


Figure 4-13 Comparison of the water flow residuals from SPIDER and MACRO.

The calculated Nash-Sutcliffe model efficiency coefficients for the water flow simulations from both models are shown in Table 4–13. Best coefficients were generally achieved for MACRO. MACRO achieved positive efficiency values for all hydrological years and for most of the high-flow periods, except for 2006-2007 and 2008-2009. SPIDER showed negative coefficients for 2006-2007 and for the simulation period (2006 – 2011) and for most of the high-flow periods, except for 2007 when a fairly good simulation was achieved (*E* = 0.51). The best simulated year for SPIDER was 2007-2008 and for MACRO was 2009-2010 while the worst simulation for both models was in 2006-2007. Periods of low flow had similar results between models; most of the coefficients were negative and the same positive efficiency value was obtained for 2008 (*E* = 0.13). The exceptions were for the simulation periods 2006 – 2011 and 2008 – 2011 where the models obtained opposite results; MACRO obtained a positive value for the first coefficient and SPIDER for the latter.

Periods of low flow had similar results between models; most of the coefficients were negative and the same positive efficiency value was obtained for 2008 (*E* = 0.13). The exceptions were for the simulation periods 2006 – 2011 and 2008 – 2011 where the models obtained opposite results; MACRO obtained a positive value for the first coefficient and SPIDER for the latter.

Table 4-13 Nash-Sutcliffe model efficiency coefficients for each hydrological year of the calibrated flow simulations from SPIDER and MACRO as well as for the periods of high and low flow, for the overall simulation (2006 – 2007) and for the period of less rainfall uncertainty (2008 – 2011).

	Hydrological year		**High-flow period 1 Nov - 30 Apr**		**Low-flow period 1 May - 31 Oct**	
	SPIDER	**MACRO**	**SPIDER**	**MACRO**	**SPIDER**	**MACRO**
2006 – 2007	-1.41	0.02	-2.14	-0.54	-1.51	-0.73
2007 – 2008	0.59	0.63	0.51	0.73	-0.39	-0.77
2008 – 2009	0.22	0.33	-0.39	-0.001	0.13	0.13
2009 – 2010	0.15	0.72	-0.79	0.47	-0.24	-0.67
2010 – 2011	0.22	0.39	-0.35	0.12	-2.46	-4.93
2006 – 2011	-0.09	0.43	-0.53	0.23	-0.29	0.28
2008 – 2011	0.36	0.60	-0.12	0.42	0.04	-0.25

4.4.3.2 Pesticide concentrations

Comparisons between simulations of pesticide concentration from SPIDER and MACRO with the measured data are presented in Figure 4-14 to Figure 4-19. Most of the simulations showed that the models were able to simulate the overall pattern of pesticide emission at the catchment outlet, except for pesticides applied during summer and spring periods.

Both models achieved good simulations of pesticide concentrations for chlorotoluron and mecoprop (Figure 4-14 and Figure 4-15, respectively). For chlorotoluron, MACRO tended to considerably over-estimate concentrations for most of the years by up to one order of magnitude whereas SPIDER had a better match in the magnitude of the peaks, for example, for peaks on February 28th 2010 and January 13th 2011. In addition, SPIDER simulated chlorotoluron peaks earlier than MACRO; SPIDER generally simulated peaks from November but MACRO from December, except for 2006 when both models simulated peaks at the same time.

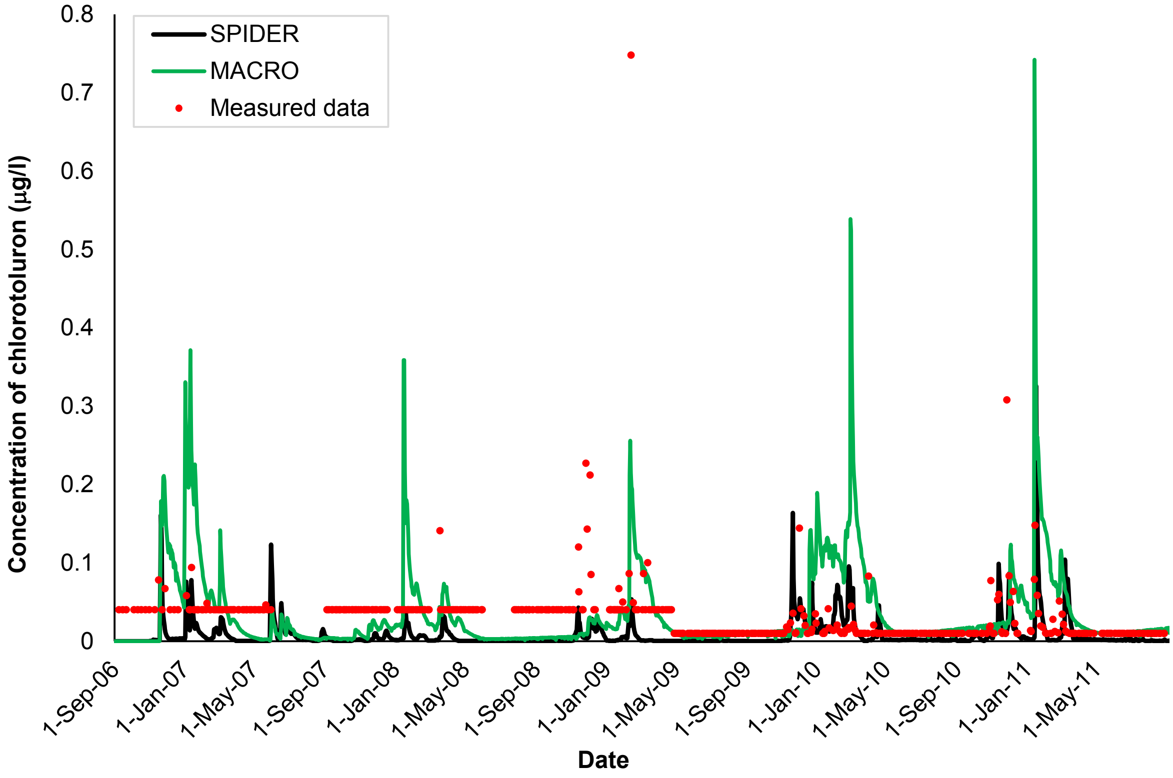


Figure 4-14 Comparison of measured concentrations of chlorotoluron with those simulated by SPIDER and MACRO.

For mecoprop (Figure 4-15), SPIDER also simulated a larger number of peaks starting from November while for MACRO emissions varied between hydrological years; in 2006 emissions started from the end of November, in 2007 from the middle of January and for the rest of the years from February. In addition, emission peaks from MACRO lasted longer than those from SPIDER. Simulations also showed differences in the timing of the peaks; both models did not simulate emissions occurring in spring and summer periods such as in April and beginning of autumn 2007, April and May 2008 and July to August 2009.

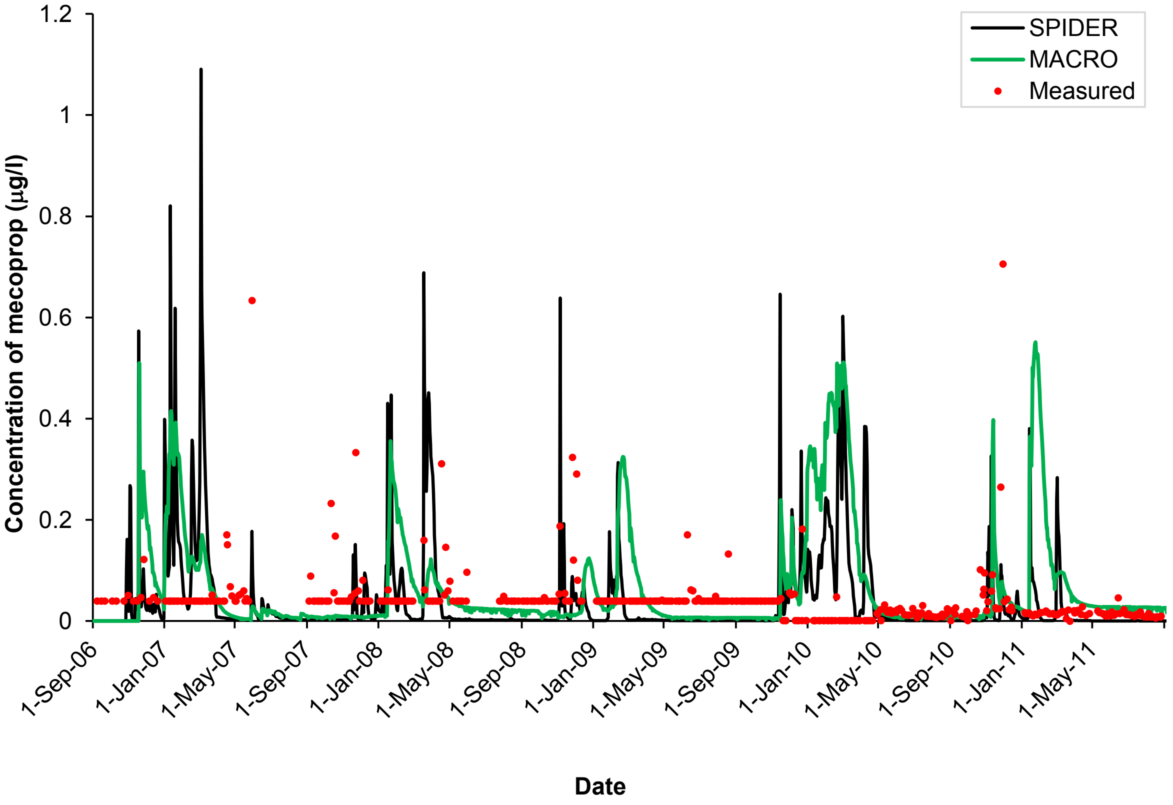


Figure 4-15 Comparison of measured concentrations of mecoprop with those simulated by SPIDER and MACRO.

In the case of carbetamide and propyzamide (Figure 4-16 and Figure 4-17, respectively), both models generally under-estimated pesticide concentrations by the same order of magnitude. The exception for carbetamide was in November 2006 when SPIDER simulated a large peak that was closer to the maximum concentration observed for this year. In addition, SPIDER again simulated earlier peaks usually from the beginning of November while MACRO from the end of December. Better simulations for carbetamide were observed using SPIDER than MACRO, especially in 2009-2010 and 2010-2011 where a good match in the pattern and timing of the peaks was obtained.

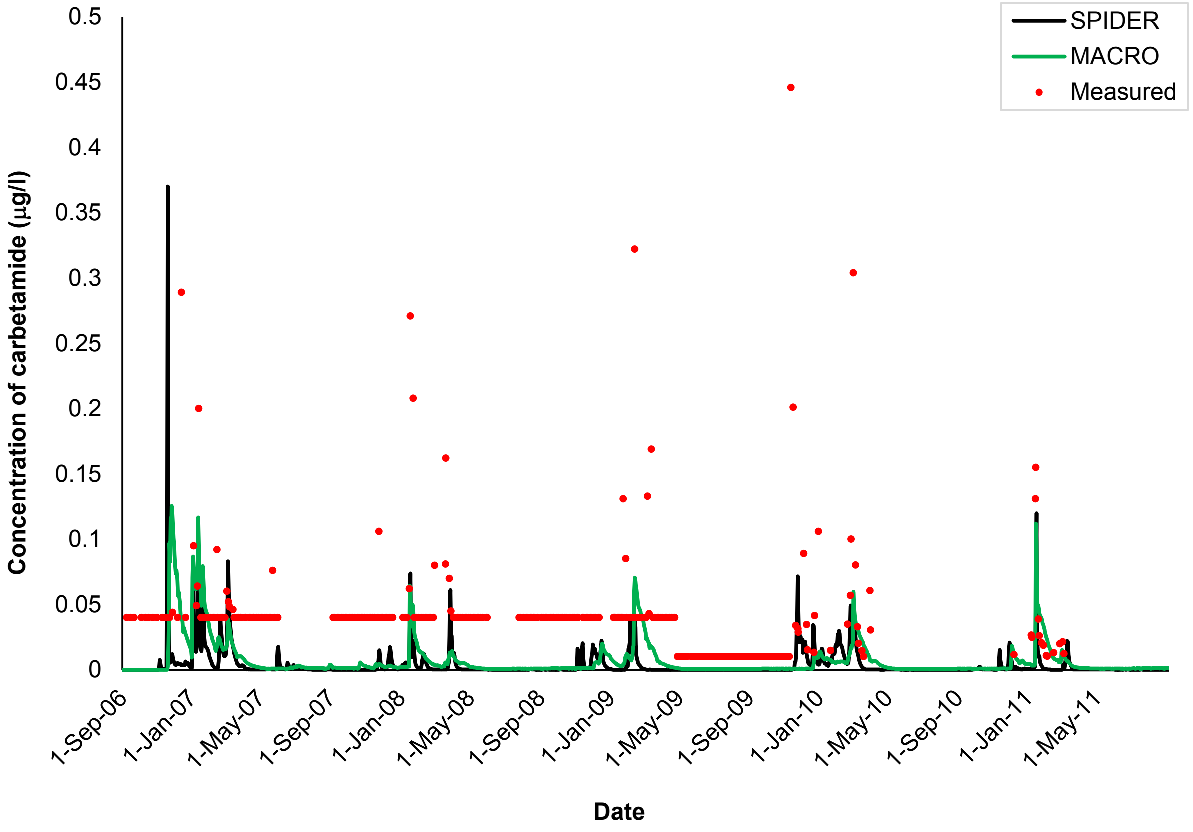


Figure 4-16 Comparison of measured concentrations of carbetamide with those simulated by SPIDER and MACRO.

Under-estimation in propyzamide concentrations was mainly observed for SPIDER between 2007-2008 and 2010-2011 by one order of magnitude (Figure 4-17); except for 2006-2007 when SPIDER simulated concentrations by the same order of magnitude than the measured data. MACRO greatly over-estimated the concentrations in 2006-2007 but was able to predict single emissions in January 2008 and 2011 and March 2010 but missed and under-estimated autumn and winter peaks, respectively. SPIDER showed a better match in the size of the peaks occurring in January 2007. MACRO did not simulate any concentration for May and June 2007 when SPIDER simulated peaks that could not be evaluated since no monitoring was carried out in that month.

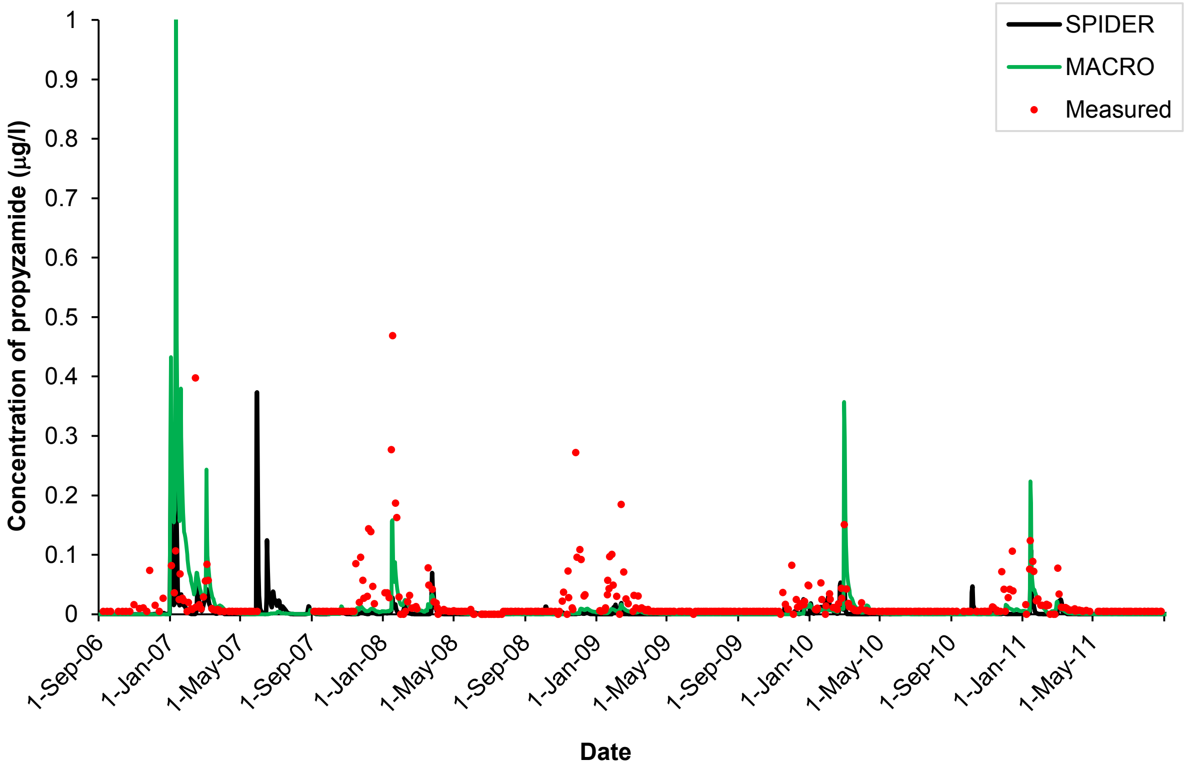


Figure 4-17 Comparison of measured concentrations of propyzamide with those simulated by SPIDER and MACRO.

For clopyralid (Figure 4-18), SPIDER achieved better simulations and was able to simulate most of the observed peaks, while MACRO only simulated two small peaks above the LOQ that were not reflected in the measured data and one below the LOQ.

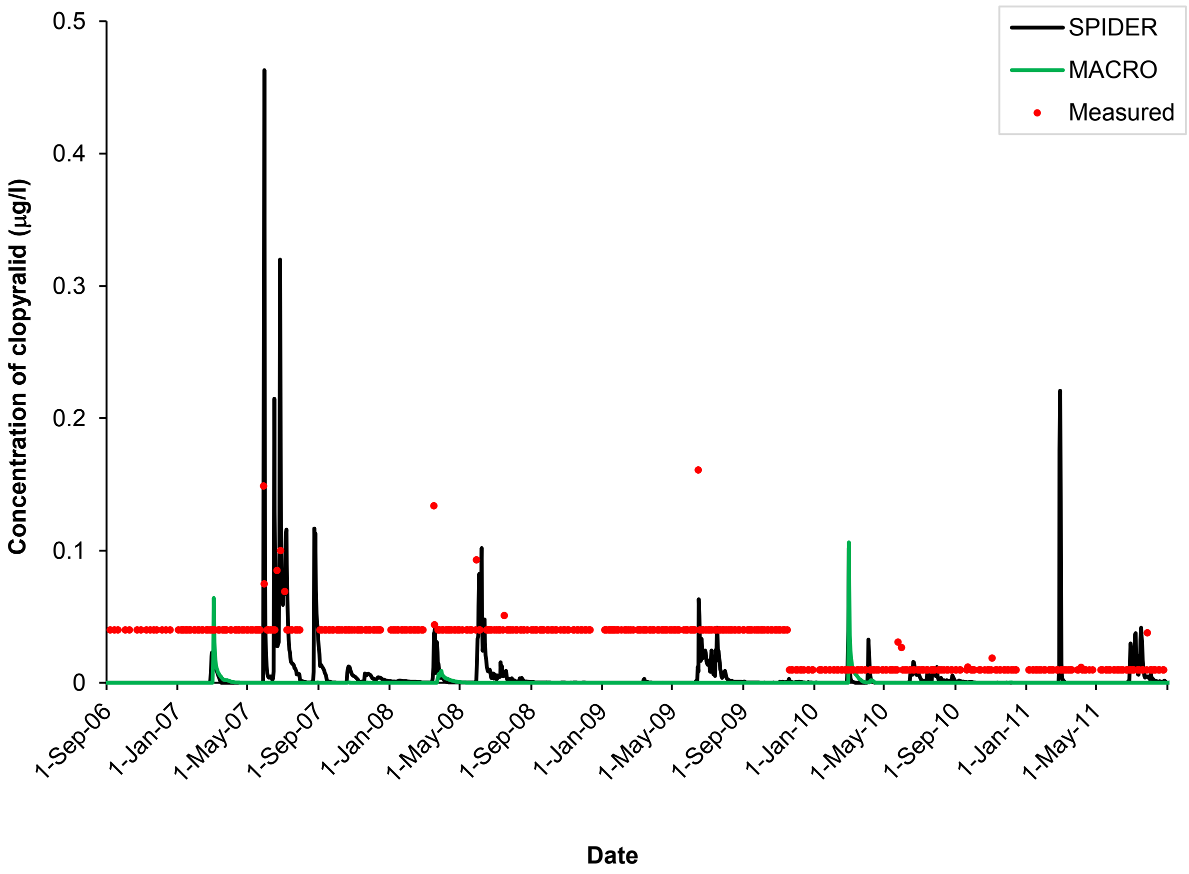


Figure 4-18 Comparison of measured concentrations of clopyralid with those simulated by SPIDER and MACRO.

Simulations for MCPA (Figure 4-19) from both models generally showed disagreement with the measured concentrations throughout the simulation that were also different between models. The exception was for the hydrological year 2006-2007 when both models showed good prediction in the timing of the detectable concentrations. MACRO showed a better agreement in the magnitude of the peaks in 2006-2007 than SPIDER; particularly for outlier on June 26th 2007 that SPIDER apparently over-estimated by one order of magnitude. For the rest of the simulation both models were not able to simulate the timing of the peaks.

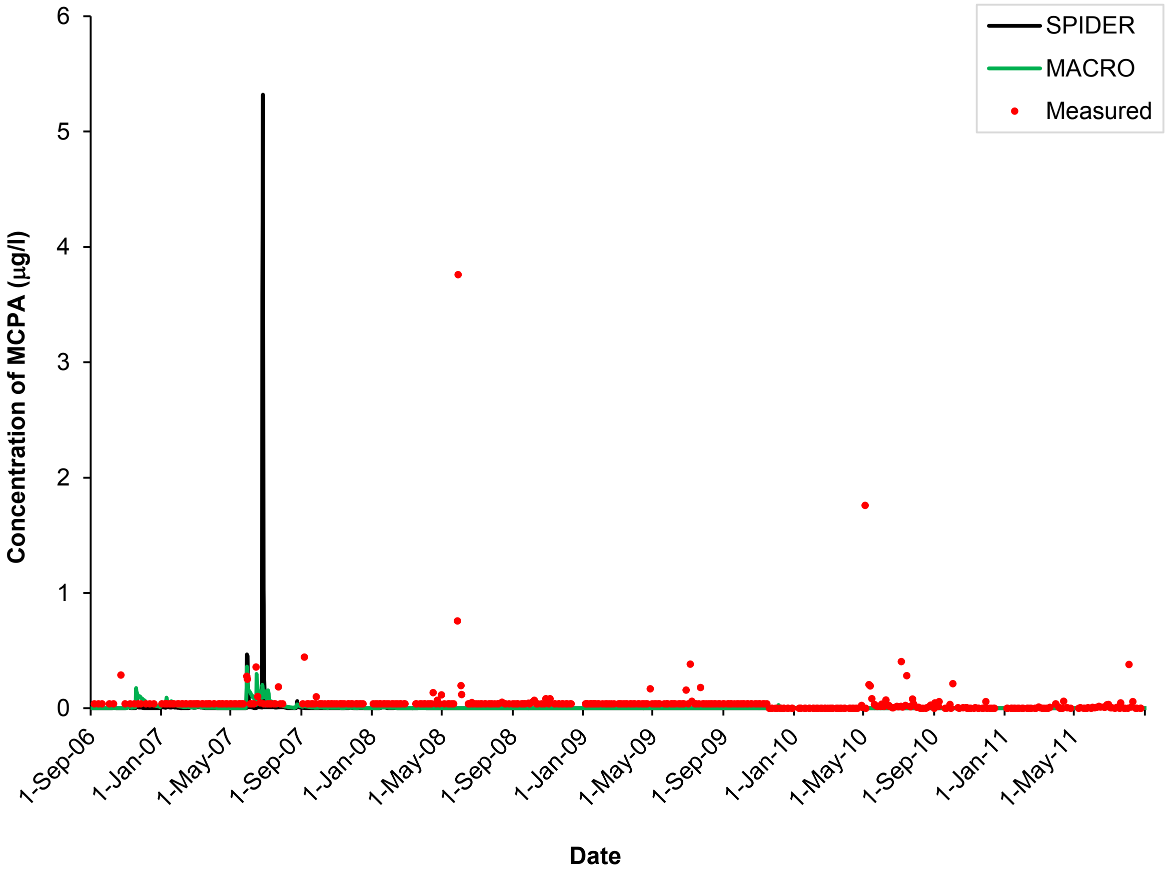


Figure 4-19 Comparison of measured concentrations of MCPA with those simulated by SPIDER and MACRO.

4.4.3.3 Maximum concentrations of pesticides

Figure 4-20 shows a comparison of simulated and measured maximum concentration of pesticides for the entire period (2006 – 2011). SPIDER simulations are presented as hourly and average daily maximum values to illustrate their differences since the model predicts hourly concentration. Simulations for the maximum concentrations varied between models and pesticides. SPIDER showed better results than MACRO, usually within a factor of two for most of the pesticides. SPIDER achieved good predictions of maximum concentrations for carbetamide, chlorotoluron, MCPA, mecoprop and propyzamide estimating within factors of 1.1 (hourly), 1.1 (daily), 1.4 (daily), 1.5 (daily) and 1.3 (daily). Both average daily and hourly data showed good results, with slightly better matches for average daily concentrations. MACRO only achieved a good prediction within a factor of two for mecoprop (1.3) and clopyralid (1.5); estimates were within factors of 2.4 and 2.1 for chlorotoluron and propyzamide, respectively.

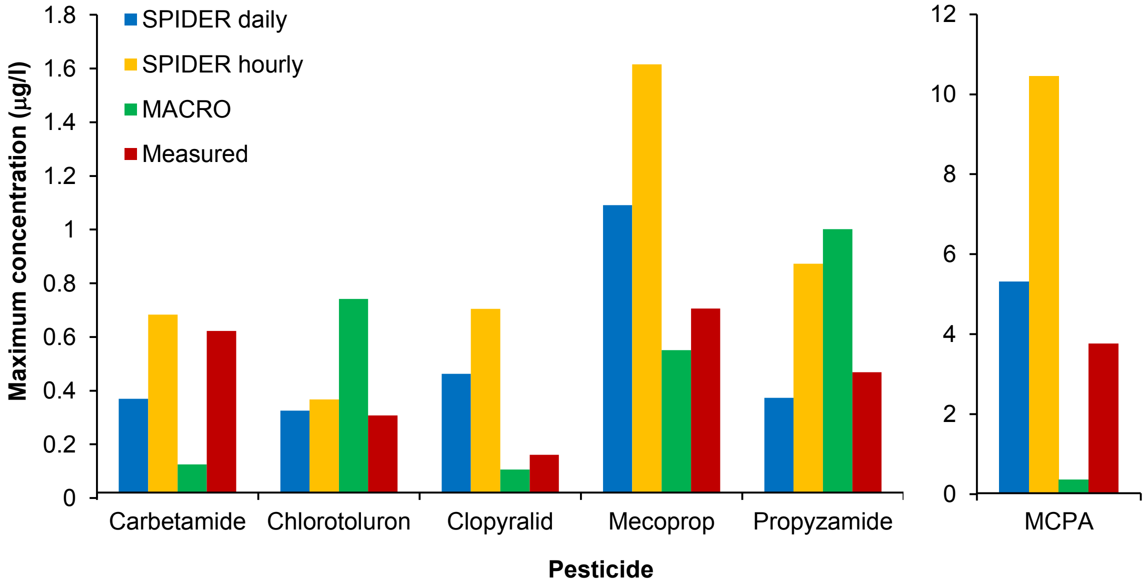


Figure 4-20 Simulated and measured maximum concentrations for the entire period 2006-2011 using SPIDER and MACRO. SPIDER simulations are presented as hourly (SPIDER hourly) and average daily maximum values (SPIDER daily).

Simulated and observed maximum concentrations are compared for all pesticides with SPIDER and MACRO in Figure 4-21 and Figure 4-22, respectively. Graphs include the 1:1 fit line, with the best simulations being closest to this line. The models did not achieve good simulations of any pesticide for all hydrological years. Most of the maximum concentrations are scattered around the 1:1 line. The exceptions were for carbetamide where systematic under-estimation of the maximum concentrations was obtained with both models; conversely, for mecoprop and chlorotoluron, systematic over-estimation of the concentrations was observed for most of the years using both SPIDER and MACRO. The simulation for MCPA mostly disagrees with the observed data for both models since there is no relationship between the observed and the predicted values; however, MACRO achieved a perfect matched of the maximum concentration in 2006-2007. In the case of SPIDER, the best simulations were for two years for chlorotoluron, two years for carbetamide and one year for clopyralid. For MACRO, good simulations of the maximum concentrations were obtained for most of the hydrological years for mecoprop and one hydrological year for chlorotoluron, carbetamide and MCPA.

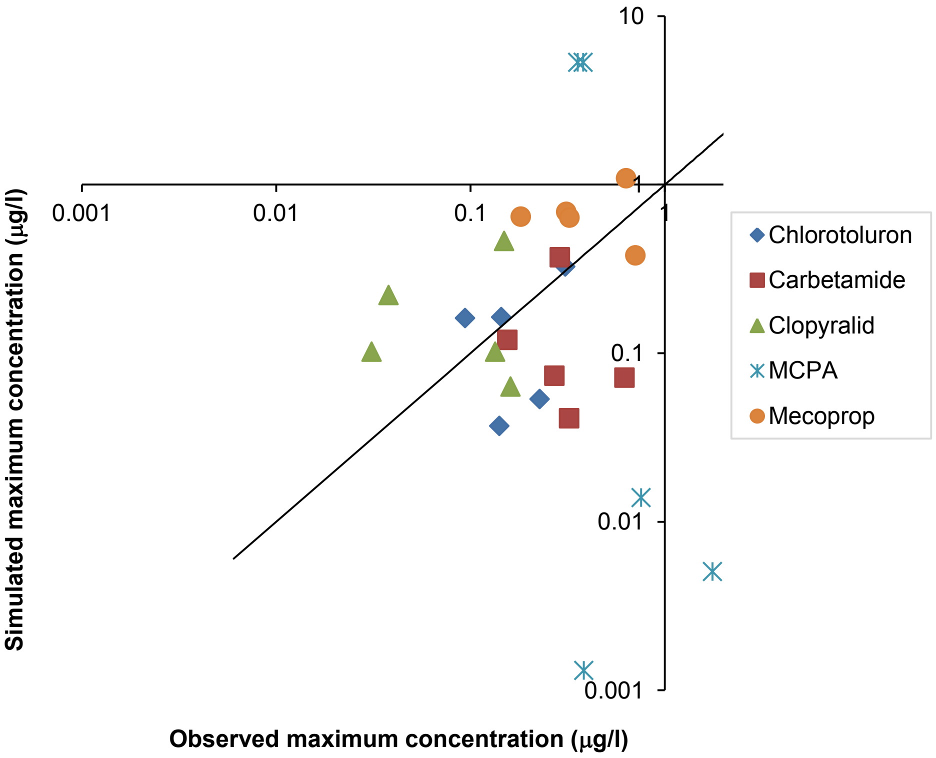


Figure 4-21 Annual maximum concentration for six pesticides simulated by SPIDER plotted on a log-log scale against measured maximum concentrations, together with the 1:1 line.

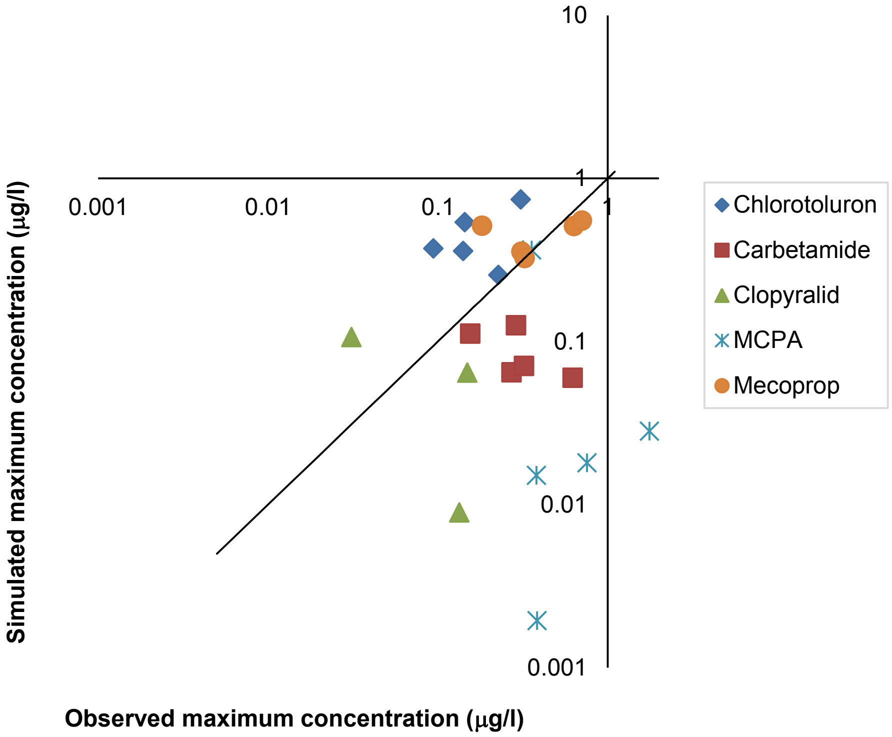


Figure 4-22 Annual maximum concentration for six pesticides simulated by MACRO plotted on a log-log scale against measured maximum concentrations, together with the 1:1 line.

4.4.3.4 Pesticide loads

Graphs of simulated against observed loads were used to evaluate the annual load simulations from SPIDER and MACRO for each hydrological year between 2006 and 2011, including the 1:1 line as well as lines for differences by factors of 2 and 10 (Figure 4-23 and Figure 4-24, respectively). A good simulation was considered to be one differing by a factor equal or less than two compared to the observed load. There were no pesticides where the load simulations completely agreed for all hydrological years with the measured load; however, most of the loads were simulated within a factor of 10. The exceptions were for MCPA, propyzamide and clopyralid where between one and three hydrological years were greatly under-estimated by both models. The best load simulations within a factor of two using SPIDER were observed for mecoprop (three hydrological years) and chlorotoluron (two years). In the case of MACRO, the best loads simulations were achieved for mecoprop (three years), propyzamide (two years) and carbetamide (two years).

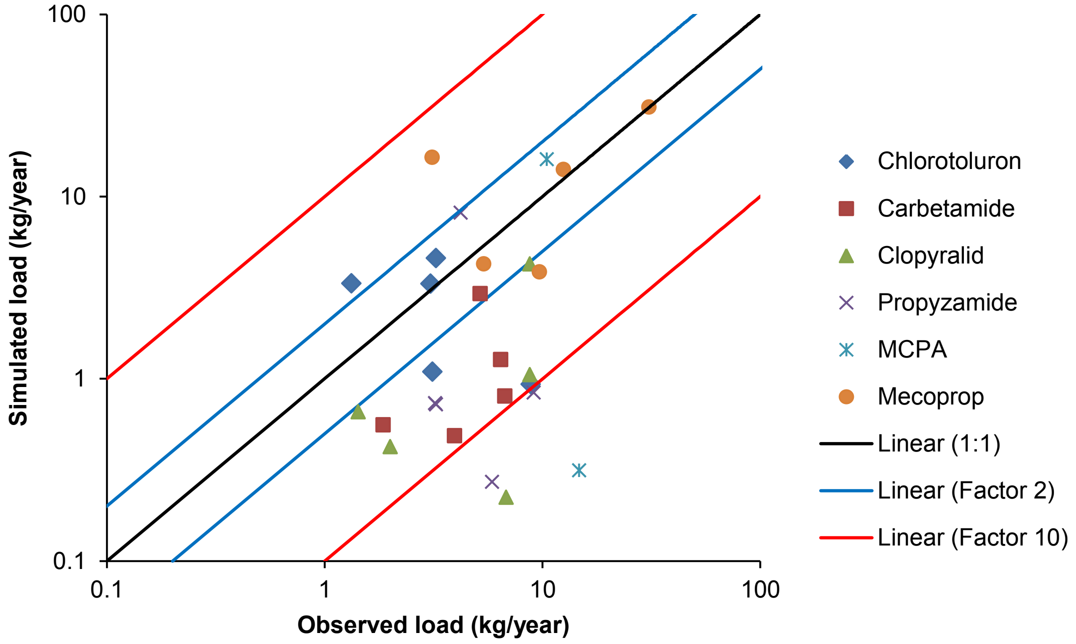


Figure 4-23 Annual pesticide load for six pesticides simulated by SPIDER plotted on a log-log scale against observed loads, together with the 1:1 (black line), factor of 2 (blue line) and factor of 10 lines.

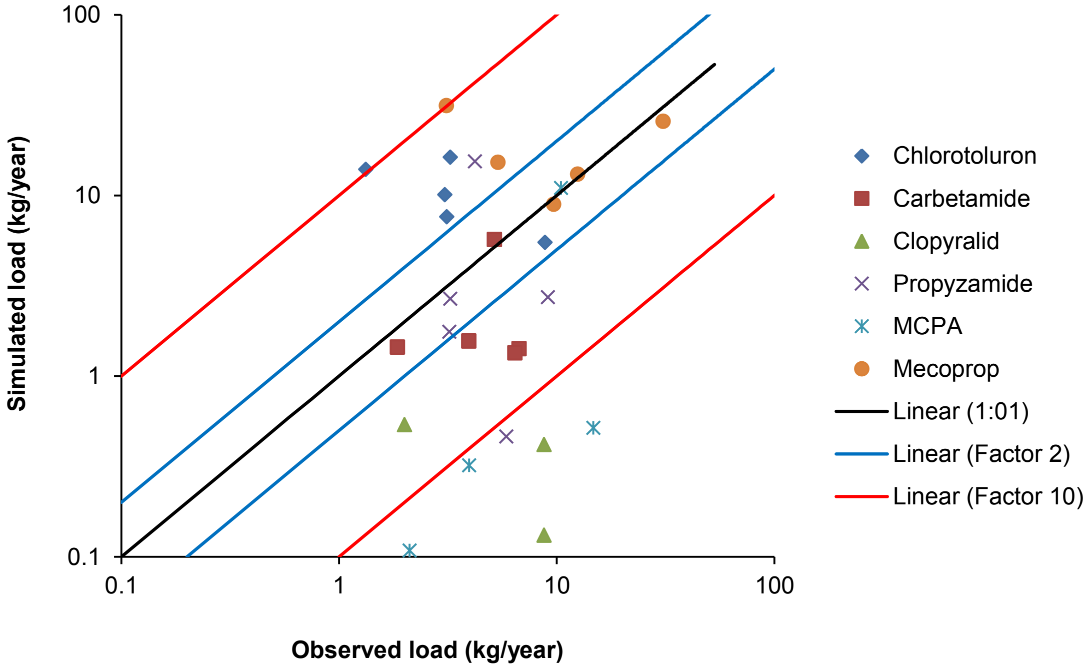


Figure 4-24 Annual pesticide load for six pesticides simulated by MACRO plotted on a log-log scale against observed loads, together with the 1:1 (black line), factor of 2 (blue line) and factor of 10 lines.

4.4.4 Uncertainty analysis for SPIDER and MACRO simulations

Results to assess the effect of uncertainties on SPIDER and MACRO simulations due to key input parameters are shown below.

4.4.4.1 Uncertainty in the rainfall data

The effect of uncertainties in rainfall measurements on the simulation of water volume from SPIDER and MACRO was evaluated by running simulations with rainfall data increased and reduced by 10% (Figure 4-25). The observed water volume for each hydrological year and for the simulation period 2006 – 2011 was usually bounded by the simulations from the two rainfall datasets for both models in terms of the total water volume for each hydrological year. The exceptions were for hydrological years 2008-2009 and 2010-2011 when both models and only SPIDER, respectively, under-estimated the flow even after increasing the rainfall data by 10%. The main issue on the original simulation from both models was under-estimation of the water volume; however, when increasing the flow by 10% the simulation over-estimated observed flow by 11.9 and 12.3% for SPIDER and MACRO, respectively. The 10% increment in the rainfall caused an increase in flow of 23.9 and 14.9% for SPIDER and MACRO, respectively, showing that SPIDER is more sensitive to rainfall than MACRO.

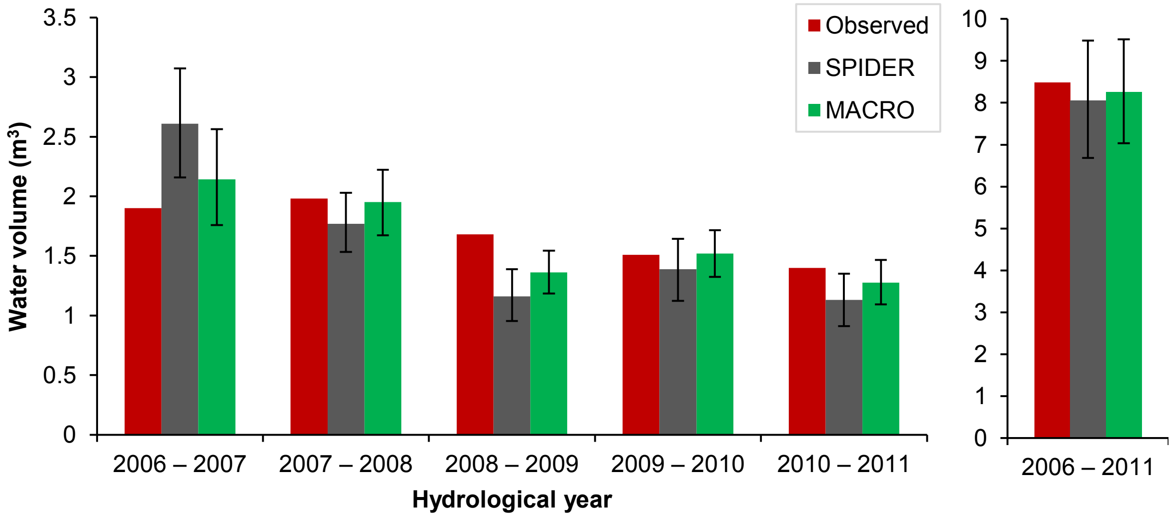


Figure 4-25 Effect of the uncertainty in the rainfall data on the simulated water from SPIDER and MACRO including error bars for the simulations using rainfall data increased and reduced by 10%.

The simulated flow for both rainfall datasets was also plotted to compare simulations with the observed data (Figure 4-26 and Figure 4-27). The measured data were often bounded by both simulations but some periods of under- and over-estimation were still observed. Uncertainty in the rainfall data has a big impact in the simulation of the water flow for the two models in both high- and low-flow periods but the greatest relative change during storm flow events when increasing the rainfall by 10%. A big impact was observed for the end of low-flow periods from MACRO; a great improvement was observed by increasing the rainfall data by 10% since the model predicted some of the peaks that were not simulated in the calibrated model. A similar behaviour was observed from SPIDER but the impact was smaller than for MACRO during low-flow periods. In addition, the difference in flow recovery between both rainfall datasets was approximately 15 days for SPIDER, but almost one month for MACRO.

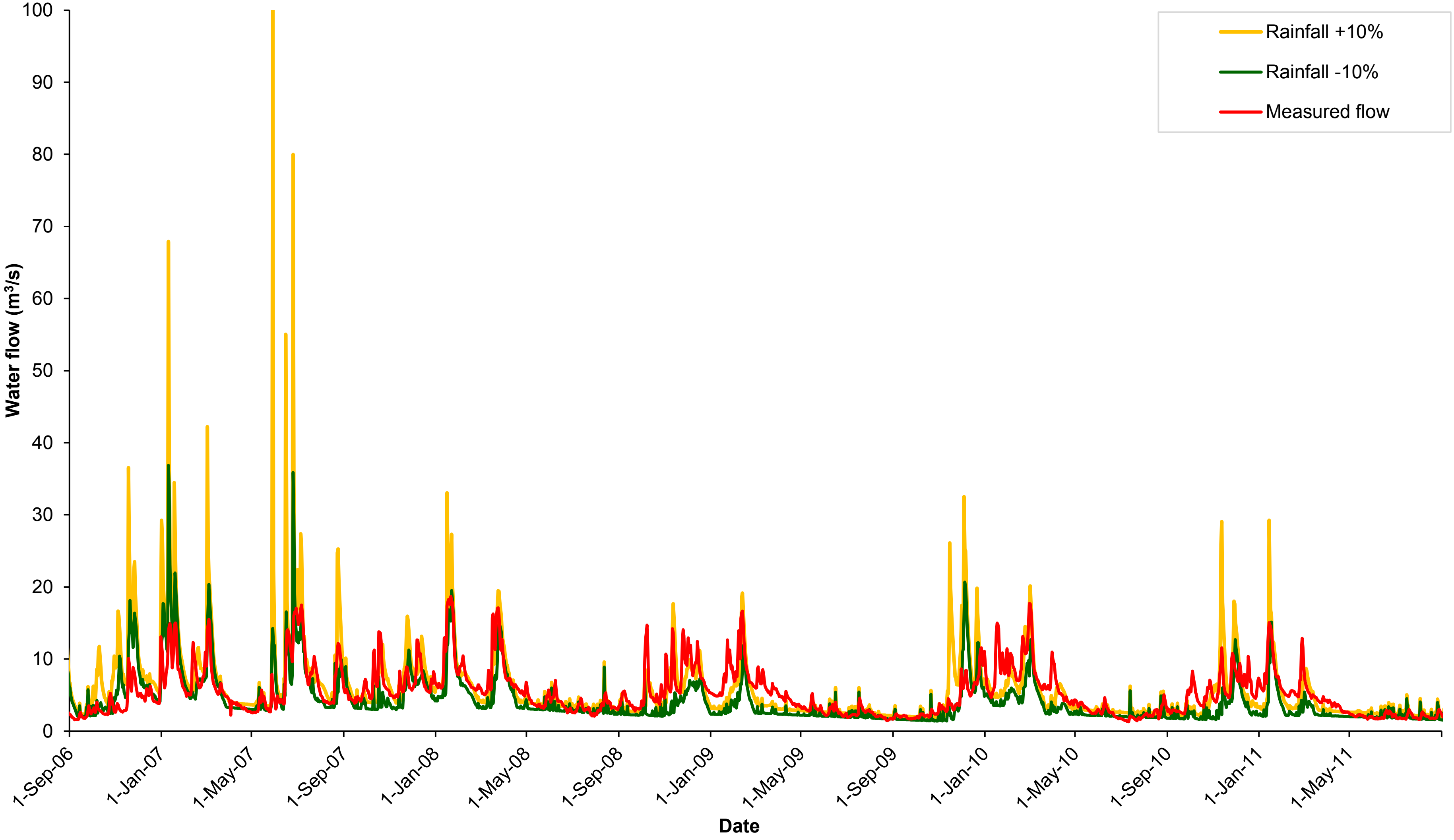


Figure 4-26 Effect on the simulated water flow when decreasing and increasing the rainfall data by 10% (-10 and + 10%, respectively) using SPIDER.

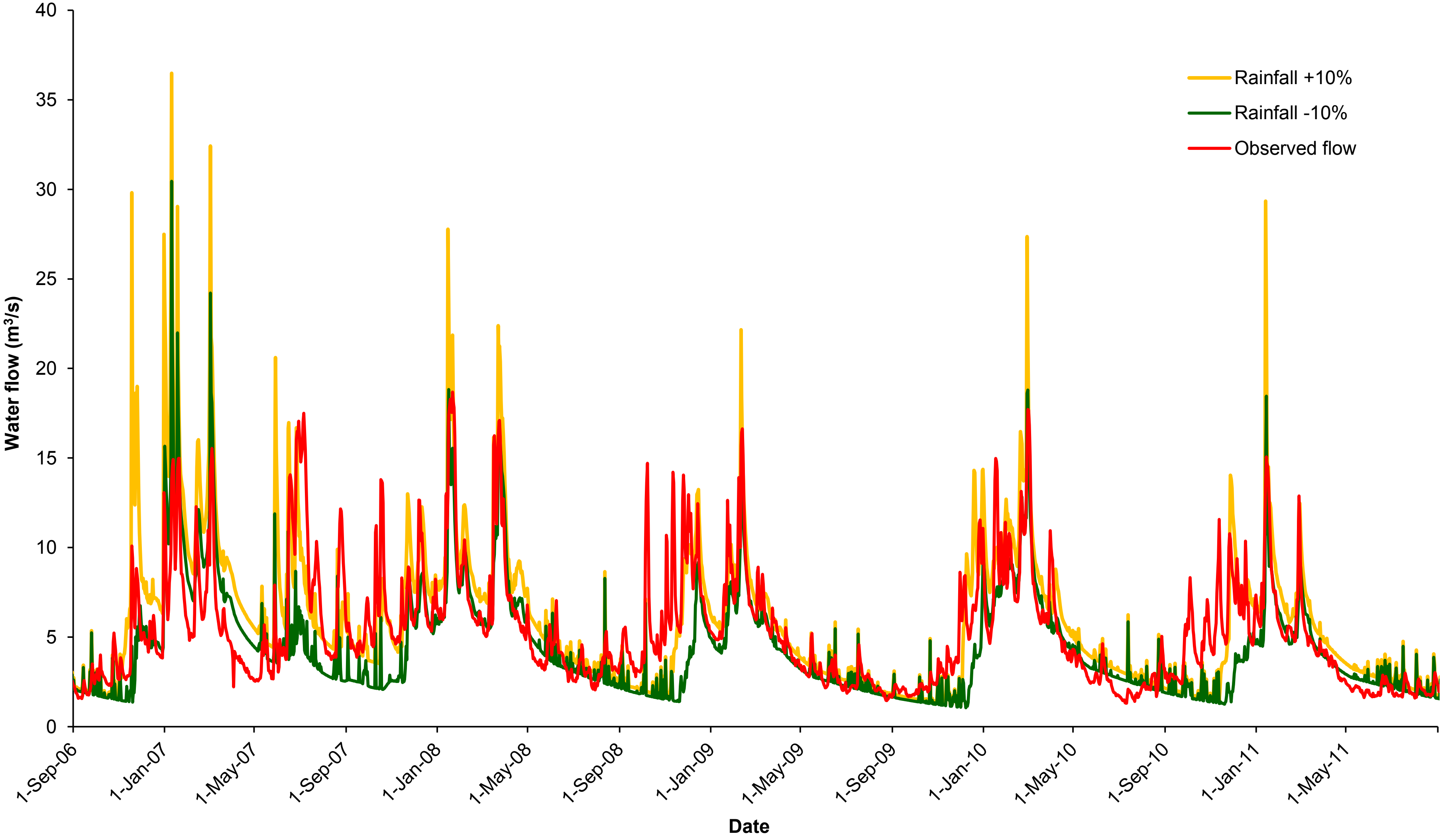


Figure 4-27 Effect on the simulated water flow when decreasing and increasing the rainfall data by 10% (-10 and + 10%, respectively) using MACRO.

4.4.4.2 Uncertainty in the application date

Simulations for carbetamide concentrations showed a consistent under-estimation of observed behaviour by both models. Carbetamide has a short half-life in soil (10.9 days) so any small difference between the application date used in the model and the real day can lead to under- or over-estimation of the concentrations. Figure 4-28 shows the effect of varying the application date on the simulated shape and size for two peaks in January and March 2011. The maximum measured concentration for this period was 0.155 µg/l, and the simulated peaks varied between a concentration < 0.01 µg/l for an application on February 27th and 0.252 µg/l for January 12th.

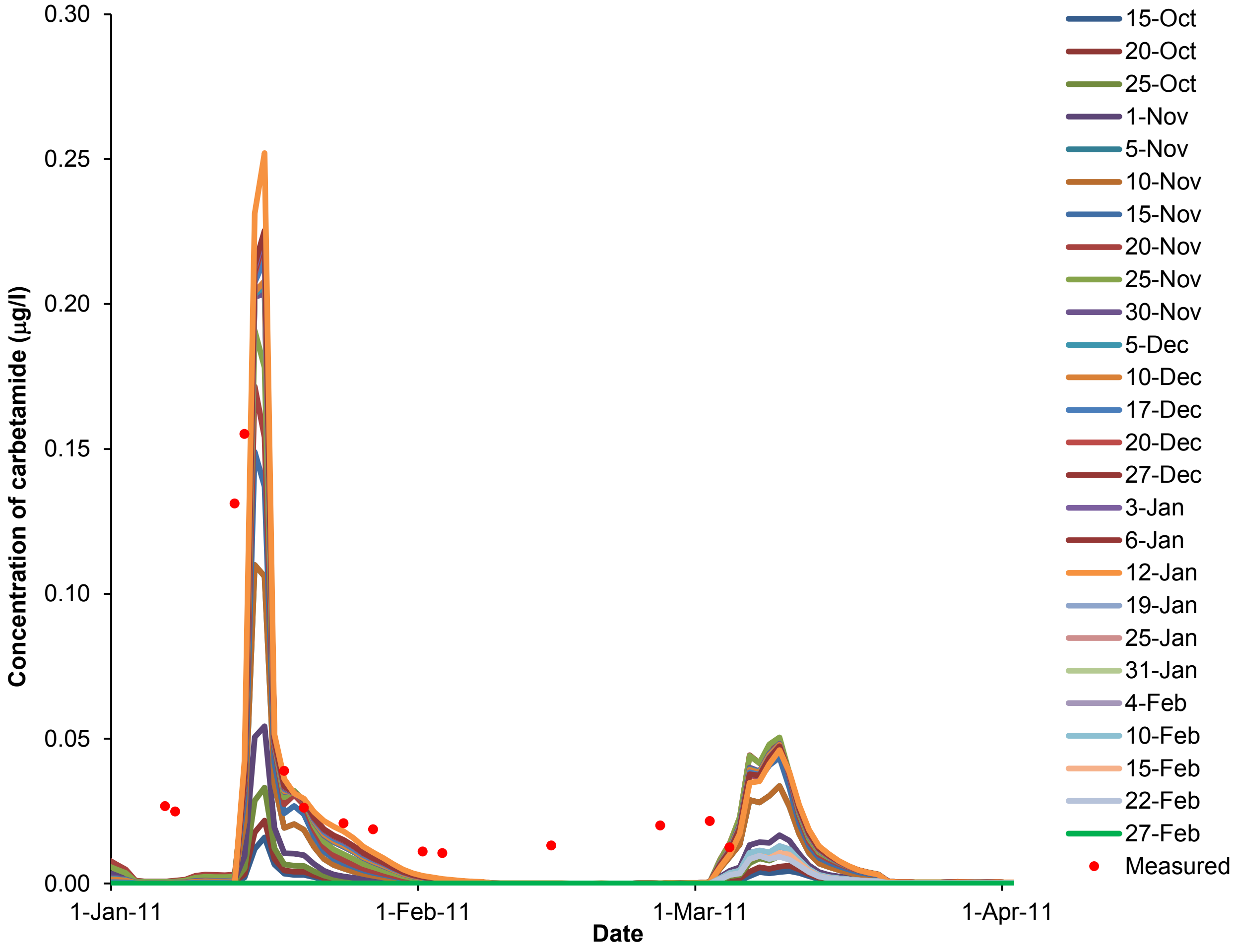


Figure 4-28 Effect of the uncertainty due to pesticide application date on the simulation of the emissions for carbetamide using SPIDER for the crop year 2010.

Carbetamide is mainly applied in November (CSF, 2012) so the variation in the simulation of maximum concentration and pesticide loads for different application dates during this month predicted by both models is shown in Table 4-14. A similar behaviour for the maximum concentration was observed for both models. The maximum concentration was obtained when applying pesticides on November 15th. SPIDER simulated higher maximum concentrations of carbetamide than MACRO; most of them were within a factor of two compared to the measured data. MACRO only simulated two maximum concentrations within a factor of two on November 15th and 30th. However, for the observed loads both models simulated values within a factor of two for most of the application dates in November.

Table 4-14 Simulated maximum concentrations and loads using MACRO and SPIDER for different application dates in November together with the observed data. Highlighted values showed the best results within a factor of two compared to the observed values.

	1 Nov	**5 Nov**	**10 Nov**	**15 Nov**	**20 Nov**	**25 Nov**	**30 Nov**	**Measured data**
				Maximum concentration (μg/l)				
SPIDER	0.370	0.676	0.876	1.267	0.545	0.759	0.992	0.622
MACRO	0.126	0.207	0.295	0.480	0.232	0.257	0.325	
				Loads (kg/5 years)				
SPIDER	6.05	9.99	14.09	19.29	17.28	21.70	22.72	23.27
MACRO	11.49	14.52	21.50	22.51	15.32	14.16	20.10	

4.4.4.3 Uncertainty in pesticide sorption and degradation

The effect of the uncertainty from using average sorption and degradation data was analysed by comparing the resulted maximum concentration and pesticide loads of simulations using extreme input data (maximum and minimum sorption and degradation values derived from the literature (AERU, 2007)). The results are shown in Table 4-15. Load simulations showed similar behaviour for both models with differences in their magnitude. Greatest load values were obtained from the combination of minimum K_{oc} and maximum half-life data while the smallest loads were observed from using maximum K_{oc} and minimum half-life. Greater loads were generally obtained from MACRO than from SPIDER. Load values from SPIDER ranged between 0.14 and 43.1 kg for the simulation period 2006 – 2011, whereas, for MACRO the loads varied between 1.6 and 74.1 kg. The simulated ranges for both models covered the observed load of 23.3 kg.

Table 4-15 Simulated maximum concentrations and pesticide loads for carbetamide using combinations of maximum and minimum sorption and degradation values, together with the average input simulation and the observed data.

	Avg. Koc Avg. DT_{50}	**Max. Koc Max DT_{50}**	**Max. Koc Min. DT_{50}**	**Min. Koc Max DT_{50}**	**Min. Koc Min. DT_{50}**	**Measured data**
			Maximum concentration (μg/l)			
SPIDER	0.370	0.527	0.052	0.697	0.093	0.622
MACRO	0.126	0.272	0.066	0.566	0.044	
			Loads (kg/5 years)			
SPIDER	6.05	11.32	0.14	43.07	0.48	23.27
MACRO	11.49	28.61	1.56	74.12	1.83	

A different behaviour was obtained for the simulation of the maximum concentrations. Greatest values of maximum concentrations were obtained for both models from the combination of minimum K_{oc} and maximum half-life. However, the smallest value of maximum concentration was obtained for SPIDER from the maximum K_{oc} and minimum half-life i.e. when the pesticide degrades quickly and is more attached to soil particles so it is less likely to leach and reach the drains; in contrast, for MACRO the smallest value of maximum concentration was obtained from minimum data for both K_{oc} and half-life, i.e. when the pesticide degrades quickly but is less sorbed to the soil. This result shows soil sorption had a bigger impact on maximum concentration results in SPIDER and a smaller impact in MACRO. Therefore, degradation was more sensitive in MACRO than soil sorption for the simulation of maximum pesticide losses. In addition, maximum concentrations from the different combinations of sorption and degradation data ranged between 0.044 and 0.566 μg/l for MACRO and between 0.052 and 0.697 μg/l for SPIDER. Hence, sorption and degradation had a bigger impact on maximum concentrations from SPIDER than from MACRO and that only the range of maximum concentrations obtained from SPIDER covered the maximum measured concentration of 0.622 μg/l.

4.4.5 Analysis of pesticide trends in the catchment

Rainfall and water flow are important factors to take into account when analysing pesticide emissions. The Wensum has shown a reduction in rainfall and water flow over the study period of 400 mm and 78 mm, respectively from 2006 to 2011 (Figure 4-29). A reduction in rainfall and flow can cause a reduction in pesticide emissions. An analysis of pesticide trends using fate models like SPIDER and MACRO would take these changes in rainfall and flow into account.

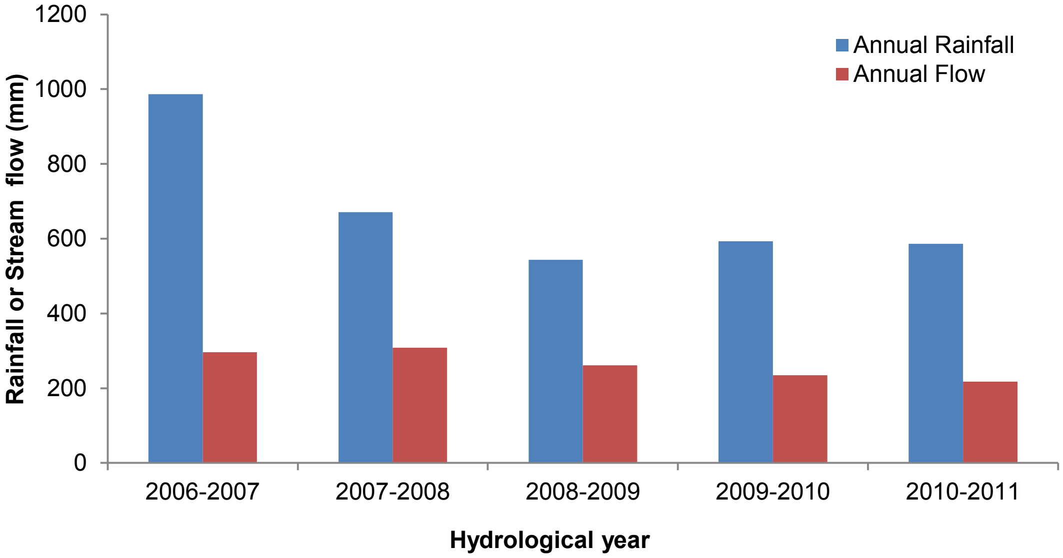


Figure 4-29 Annual rainfall and water flow for each hydrological year in the Wensum catchment.

Calculations of changes in the simulated and observed load between hydrological years and for the entire simulation are shown in Table 4-16. Negative and positive values show reductions and increases in the loads, respectively. Both the observed and the simulated loads showed a reduction in pesticide loads from 2006 to 2011. In addition, the percentage of reduction between models for most of the herbicides showed comparable changes. The exception was for mecoprop where SPIDER (86%) simulated almost double the reduction in load of MACRO (41%).

Similar percentages of reduction in pesticide load between simulations and observed data were observed for mecoprop (using SPIDER), clopyralid, carbetamide and MCPA. However, for chlorotoluron and propyzamide, the models predicted considerably larger reductions than those that were actually observed. In the case of mecoprop the observed percentage of reduction in load was the double of larger than the simulated reduction from MACRO, while SPIDER predicted a similar percentage of reduction than the observed value. Changes between hydrological years showed fluctuations in pesticide loads in both the observed and the simulated loads. However, differences were observed between the model predictions and the observed data.

Table 4-16 Comparison of the changes in the estimated and simulated loads between hydrological years and for the entire simulation period.

Pesticide/ Hyd. Year	**2006-07 to 2007-08 (kg/year)**	**2007-08 to 2008-09 (kg/year)**	**2008-09 to 2009-10 (kg/year)**	**2009-10 to 2010-11 (kg/year)**	**2006-2011 (kg/year)**	**2006-2011 (%)**
Chlorotoluron						
Observed	-0.12	5.71	-7.5	1.73	-0.18	-5.56
SPIDER	-3.5	-0.16	2.41	-0.02	-1.27	-27.67
MACRO	-8.68	-2.13	8.48	-3.88	-6.21	-38.12
Mecoprop						
Observed	-18.41	-2.77	-6.58	2.25	-25.51	-82.61
SPIDER	-16.91	-10.2	12.54	-12.14	-35.23	-86.24
MACRO	-12.58	-4.17	22.4	-16.11	-16.11	-40.72
Carbetamide						
Observed	1.53	-2.76	2.49	-4.59	-3.33	-64.29
SPIDER	-2.13	-0.31	0.78	-0.71	-2.37	-80.89
MACRO	-4.29	0.14	-0.22	0.11	-4.26	-74.61
Propyzamide						
Observed	4.9	-3.24	-2.64	-0.03	-1.01	-23.93
SPIDER	-7.3	-0.57	0.45	0.02	-7.4	-90.91
MACRO	-12.69	-2.28	2.21	-0.91	-13.67	-88.59
Clopyralid						
Observed	-0.01	-1.93	-4.81	-0.58	-7.33	-83.77
SPIDER	-3.23	-0.83	0.2	0.24	-3.62	-84.58
MACRO	-0.29	-0.13	0.54	-0.54	-0.42	-100.00
MCPA						
Observed	4.27	-7.26	-11.44	-1.85	-8.35	-79.83
SPIDER	-15.72	-0.31	0.01	-0.02	-16.03	-99.97
MACRO	-10.50	-0.48	0.28	-0.21	-10.91	-99.02

4.5 Discussion

4.5.1 Water flow

As a new model, only a few studies have applied SPIDER to simulate pesticide losses to surface water (Beulke et al., 2009; Renaud and Brown, 2008). Evaluation studies, conducted in the UK, concluded that the model was able to simulate hydrographs and pesticide losses reasonably well with little or no calibration. The hydrograph simulation from SPIDER showed a reasonably good match in the timing and size of the peak flow compared to the measured data. Since no soil moisture information was available for the beginning of the simulation, the initial water content in the models was set to the water content at field capacity. This caused a great over-estimation of the flow at the beginning of the SPIDER simulation but the flow rapidly stabilized after a few days. Additional over-estimation of the flow from SPIDER was observed in January and June 2007 in response to an unusually wet hydrological year (2006-2007), particularly during summer (Figure 4-30). The rainfall previous to those events was characterized by periods of frequent and unusually large volumes of rainfall which affected the hydrological response of SPIDER by the simulation of large volumes of drain flow for those days (Figure 4-31); in contrast, MACRO did not simulate drain flow in such magnitude. This difference in the hydrological response of the models indicates that SPIDER can be more responsive to large and frequent rainfall events than MACRO. Figure 4-31 also shows that SPIDER usually predicted drain flow events earlier in the autumn than MACRO; this means that SPIDER was able to simulate more drain flow events which is very likely to affect simulated pesticide losses at the beginning of winter flow periods, especially for pesticides that are applied around those dates.

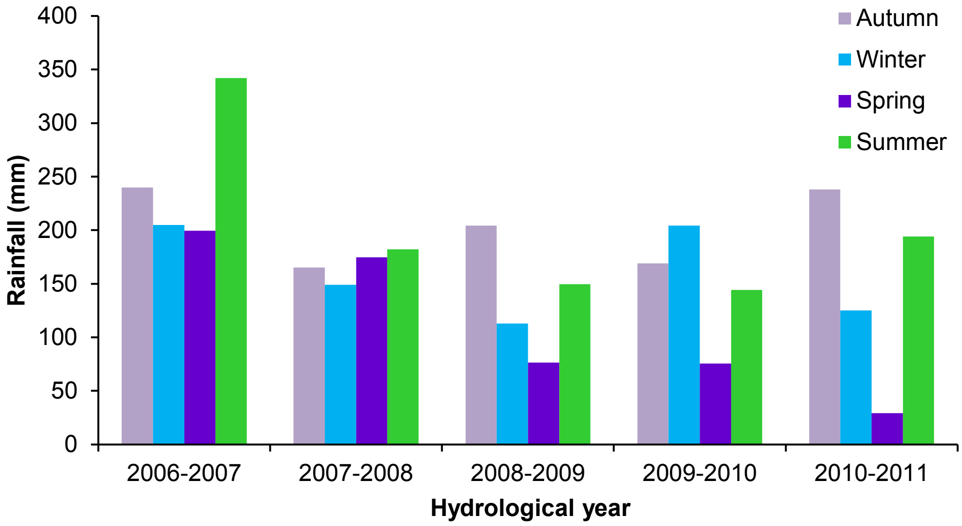


Figure 4-30 Seasonal rainfall per hydrological year.

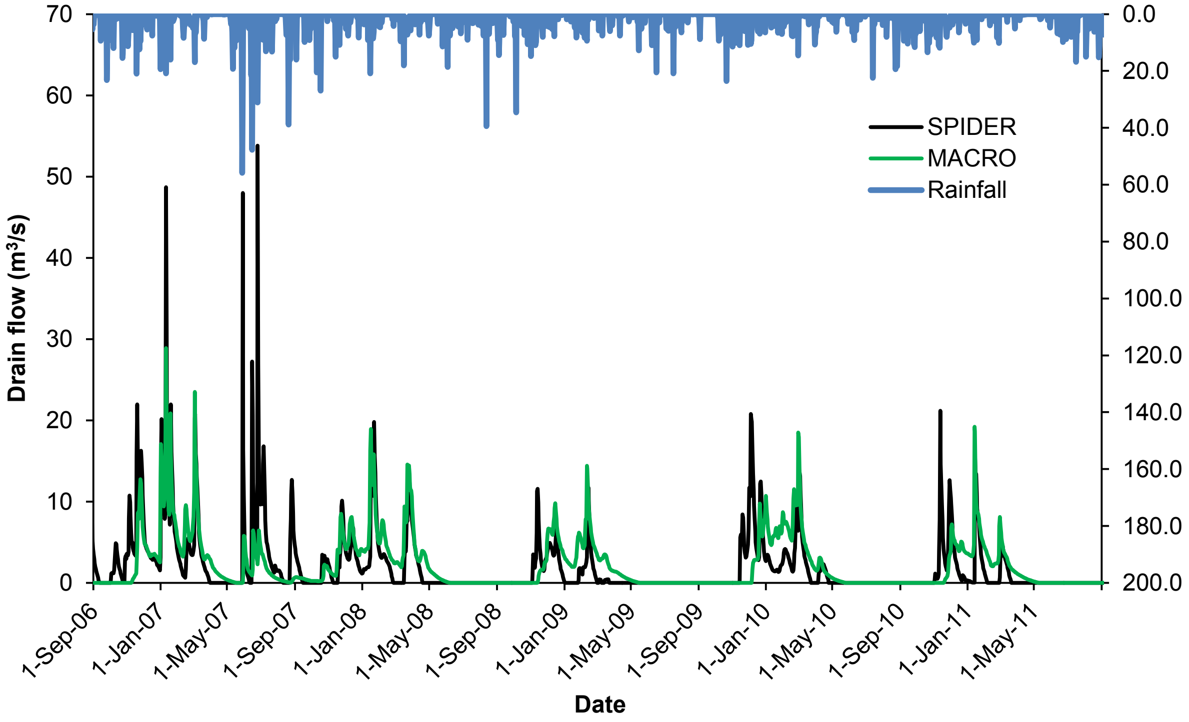


Figure 4-31 Comparison of the simulated drain flow by SPIDER and MACRO.

Water flow simulations from SPIDER and MACRO also showed a trend for the models to over-estimate flow during periods of greatest flow and this may be attributable to structural errors within the models but might also relate to flood control measures within the catchment that were not included in the model. Flood management in the Wensum includes changes in the course and dimensions of the river channel, changes in the connectivity between the river and the floodplain, removal of the bed substrate and deposited fine sediment and desilting, control of aquatic and riparian vegetation and alterations to the water levels within the channel and downstream movement of sediment (mill weirs, sluices) (Sear et al., 2006).

The water flow simulation for the Wensum using SPIDER was mostly affected by under-estimation in the simulation. Some of the peaks for periods of great flow were completely missed by the model which can be due to run-off events that the model could not simulate. However, under-estimation was mainly observed during periods of lowest flow (spring and summer). The simulated hydrograph showed large disagreement in the behaviour of the baseflow at these times which reflects the simplicity of the groundwater mixing model. Abrupt reductions in the flow were observed at beginning and end of low-flow periods which was different to the more gentle behaviour observed for the measured flow.

Model calibration was applied to both SPIDER and the GW model to increase water flow and to improve the simulation of the flow recession and recovery during low-flow periods. Evapotranspiration coefficients for all crops were reduced taking into account winter conditions in the Wensum which is prone to freezing during this period. The new values were selected according to the ranges reported by Allen (1998). Model calibration was successful in reducing flow under-estimation in the simulation by increasing the flow from 82.5 to 95.1%. However, the GW model failed to accurately simulate the recession and recovery periods of flow during periods of low flow.

Periods of over- and under-estimations of the flow also affected the goodness-of-fit when plotting the residuals. Patterns in the plot were characterized by consecutive negative residuals during periods of over-estimations and U-shape in the residuals during lowest flow periods. When comparing SPIDER and MACRO residuals for water flow simulation, similar patterns were observed; this can be expected since both models use a similar approach to simulate the water flow. The effect of over-estimation of the flow affected SPIDER more than MACRO, with higher negative values. Hydrographs for MACRO seem to show a better performance of the groundwater mixing model for this model. During periods of lowest flow, residuals from SPIDER tended to be positive whereas negative values were mostly observed for MACRO. These non-random patterns indicate that the models were not capturing some explanatory information that was reflected in the residuals. This explanatory information during periods of greatest flow could be the mentioned flood management measures in the catchment and for periods of lowest flow would be due to the poor simulation of the baseflow behaviour.

Nash-Sutcliffe model efficiency coefficients (*E*) showed that the water flow simulation from MACRO was better than the one achieved from SPIDER even after calibration. Model efficiency values of 0.35 and 0.43 were obtained for MACRO before and after calibration, respectively, while for SPIDER the model efficiency did not improve after calibration (it changed from -0.02 to -0.09), mainly due to the high over-estimation of the flow in 2006-2007. However, it is important to note that no rainfall data were available from Norwich Airport for the hydrological years 2006 and 2007 so extrapolation of daily rainfall data from another station near the catchment was used instead. This approach was an important source of uncertainty in model results for the hydrological year 2006 since precipitation is a very sensitive parameter in hydrological models (Arnaud et al., 2011; Obled et al., 1994). Thus, model efficiency was also calculated for the simulation period with less uncertainty in the rainfall data, 2008 – 2011 which was again better for MACRO (*E* = 0.60) than for SPIDER (*E* = 0.36). Renaud and Brown (2008), obtained very similar model performance for SPIDER in two field studies in the UK that compared water flow simulation from SPIDER and MACRO but in both cases SPIDER simulations were not calibrated. The authors found slightly better model performance for MACRO (*E* = 0.35) than for SPIDER (*E*= 0.32) for a site located at Cockle Park but differences between models were smaller than in the present study. Another evaluation for a different site located at Maidwell showed that model performance for SPIDER was considerably better than for MACRO (*E* = -0.61) without calibration (*E* = 0.23) which was then considerably improved after little calibration (*E* = 0.55). However, both studies were carried out at the field-scale where input parameters had small variability so that little uncertainty was expected in models results. Considering that the hydrological responses of the models only come for rainfall, drain flow, interlayer flow (in the case of SPIDER) and runoff coming from hard surfaces, the models achieved a relatively good simulation of flow, particularly of the major drain flow events.

4.5.1.1 Evapotranspiration

SPIDER generally simulated peaks in drain flow earlier than MACRO at the end of the lowest flow periods. It was found that one possible reason is an over-estimation of the evapotranspiration by MACRO (Tediosi et al., 2013; Roulier and Jarvis, 2003; Besien et al., 1997). Besien et al. (1997) suggested that over-estimation of evapotranspiration by MACRO caused the model to miss drain flow events generated by low rainfall in early spring affecting both drain flow and pesticide simulations for that period. In this study, it was found that over-estimation of evapotranspiration was also critical for the early autumn period (i.e. at the beginning of the winter flow period), which causes the model to misrepresent the flow recovery rate.

When comparing the evapotranspiration, calculated by the two models, that for MACRO was 12.1% bigger than that for SPIDER over the simulation period. This difference in evapotranspiration is very evident particularly during the summer periods (Figure 4-32) which reduces soil moisture content and prevents the soil from wetting up as rapidly as for SPIDER, consequently causing the simulation to miss drain flow and pesticide peaks at those times.

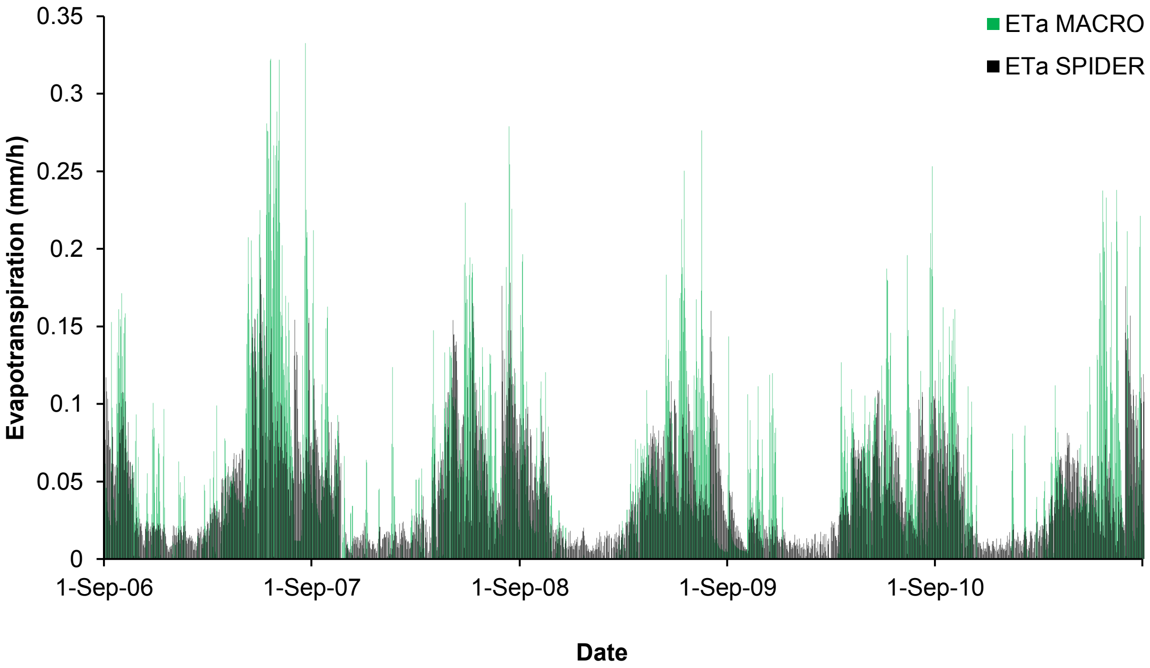


Figure 4-32 Comparison of the simulated evapotranspiration by MACRO and SPIDER.

Pre-calculated evapotranspiration from SPIDER was then used in MACRO simulations. The resulting simulations of drain and river flows are shown in Figure 4-33 and Figure 4-34, respectively. Both drain flow and river flow showed an improvement in simulation of earlier drain flow events and in the flow rate at the end of the lowest flow periods; this suggests that the FAO Penman–Monteith equation (Allen, 1998) used by SPIDER may be a better approach than the original Penman–Monteith equation (Monteith, 1965) used by MACRO for the calculation of the evapotranspiration under the UK conditions. The FAO Penman–Monteith equation is recommended by Allen (1998) as it provides more consistent evapotranspiration values in all regions and climates. The new simulated drain flow from MACRO, using pre-calculated evapotranspiration from SPIDER, showed additional small summer peaks in the simulation that SPIDER did not simulate; for example, the flow peaks from August to October 2008, and in August 2009 and October 2010.

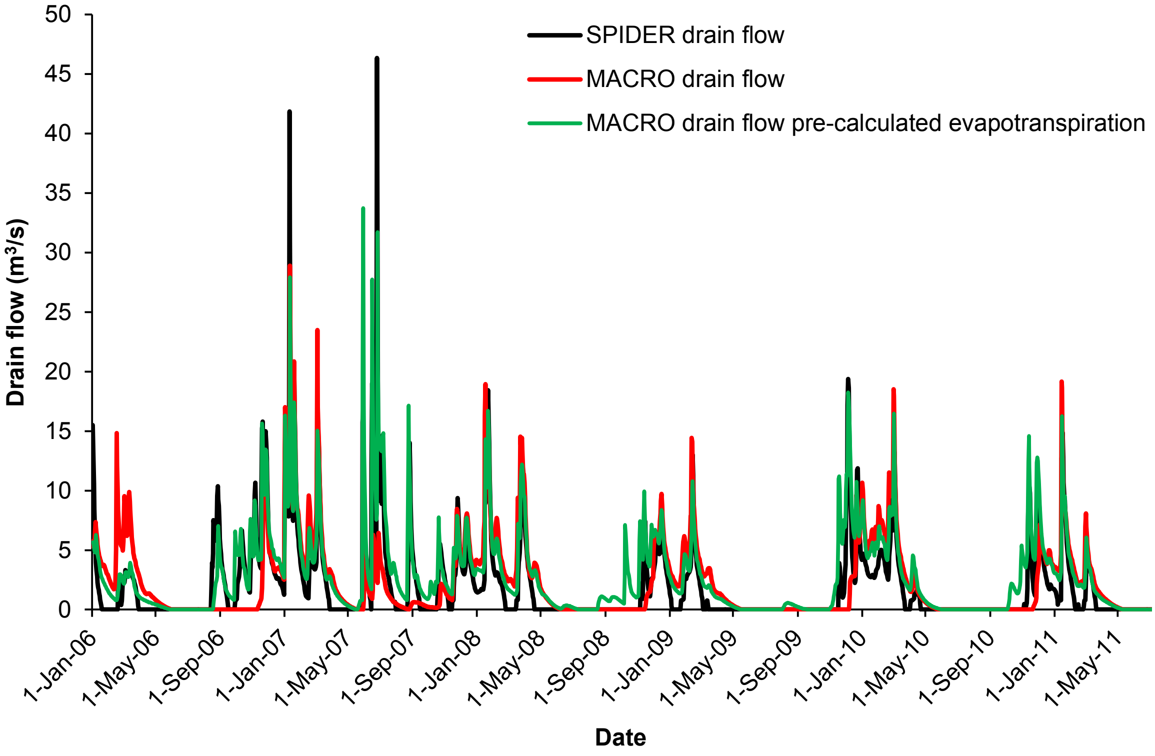


Figure 4-33 Effect on the simulation of drain flow in MACRO from using the pre-calculated evapotranspiration from SPIDER and comparison with SPIDER and MACRO original simulation.

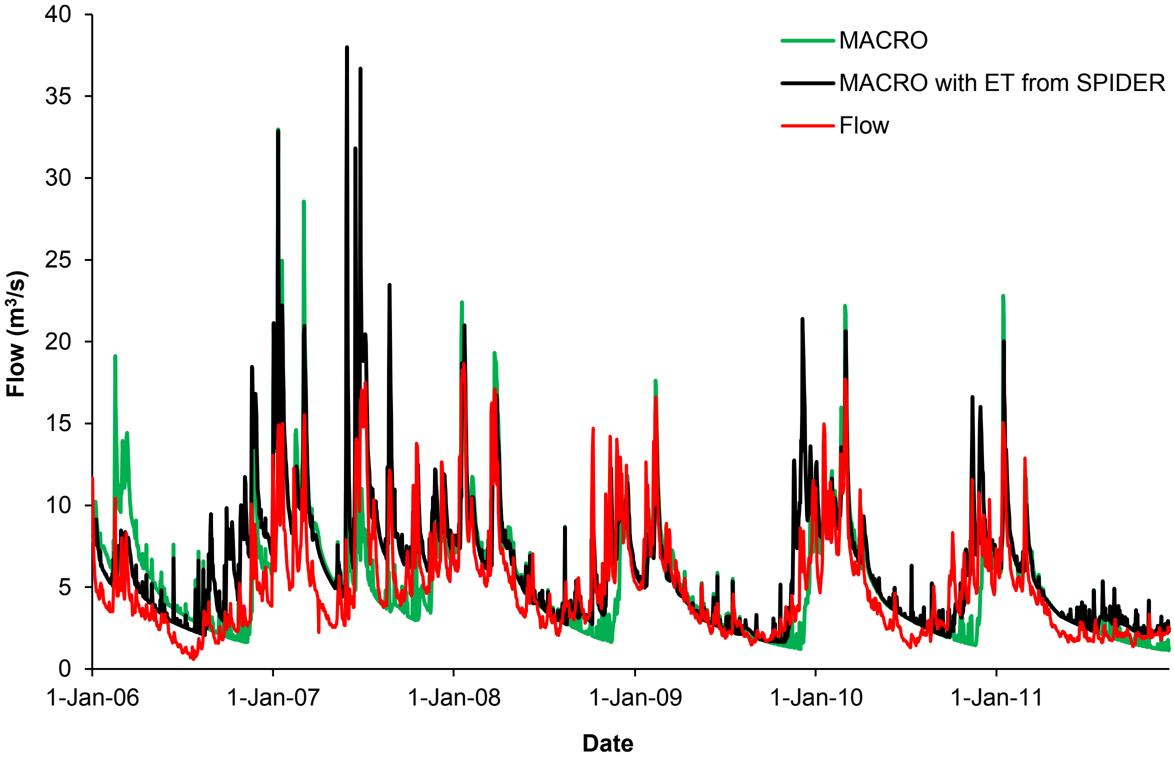


Figure 4-34 Effect on the simulation of water flow in MACRO from using the pre-calculated evapotranspiration from SPIDER and comparison with the original MACRO simulation and the measured flow in the Wensum catchment.

4.5.1.2 *Uncertainty in rainfall*

Precipitation is well known to be a sensitive parameter in hydrological models (Arnaud et al., 2011; Obled et al., 1994). Here, since no hourly and daily rainfall data were available for 2006 and 2007 from Norwich Airport or any other station within the Wensum catchment, it was necessary to extrapolate rainfall recordings from the nearest station at Mannington Hall. Daily rainfall data were extrapolated by taking into account reported monthly and annual precipitation data for Norwich Airport and then converting to hourly rainfall using a rate of 2.0 mm/h which is the average rainfall rate in Europe (Adriaanse et al., 2014). In addition, precipitation measurements from rain gauges are subject to uncertainties (Krajewski et al., 1998; Goodrich et al., 1995). The UK Meteorological Office (2010) uses the tipping-bucket rain gauge for the automatic recording of rainfall rates which is particularly affected by the rainfall intensity (Wang et al., 2008; Ciach, 2003; Nystuen et al., 1996) and timescale (Wang et al., 2008; Ciach, 2003). The impact of uncertainty from rainfall measurements on water flow was studied by running two simulations by increasing and decreasing the rainfall data by 10%. A standard error of 10% was estimated by Ciach (2003) for hourly recordings and rainfall intensities similar to those observed at Norwich Airport. Simulated range of water flow for this uncertainty includes the complete match to the water flow; from 78.8 to 111.9% for SPIDER and 83 to 112% for MACRO. However, rain gauges are more likely to under-estimate rainfall recordings due to wind and turbulent effects nearby (Yang et al., 1998). Actually, an increase by 10% in the rainfall data gave a better match to water flow at the end of low-flow periods, particularly for flow peaks that were missed by MACRO in early autumn.

4.5.2 Pesticide simulations

SPIDER was tested for the first time against high resolution monitoring data and at a relatively large catchment-scale as the Wensum. Six contrasting pesticides were simulated using the preferential flow models, SPIDER and MACRO. Both models were able to simulate a large number of the observed peaks as well as the overall pattern of behaviour of most of the pesticides despite the simple nature of the models and not including runoff in the simulations. Apart from the peaks that MACRO missed in early autumn due to under-estimation in the flow, most of the simulations showed agreement in the peaks simulated by SPIDER and MACRO; the exception was for clopyralid and MCPA where significant differences in the simulations were observed with the observed data and between models.

For clopyralid, MACRO only predicted three small peaks that were due to pesticide drain flow but the model missed other emissions that SPIDER predicted. It was observed that important losses of clopyralid could be due to interlayer flow; SPIDER simulates this whereas MACRO does not account for this entry route. Figure 4-35 a) and b) show the pesticide emission through drain flow and interlayer flow simulated by SPIDER for clopyralid for Burlingham soil; the data show that interlayer flow was the most frequent route of simulated clopyralid losses but losses were larger from drain flow when these occurred (2007). These findings are in agreement with Carter (2000) who suggested that interlayer flow generally contains less pesticide residues than drain flow. Clopyralid was different from other compounds where drain flow dominated because emissions occurred in spring when drains are not often flowing and interlayer flow is the only predicted flow in the catchment.

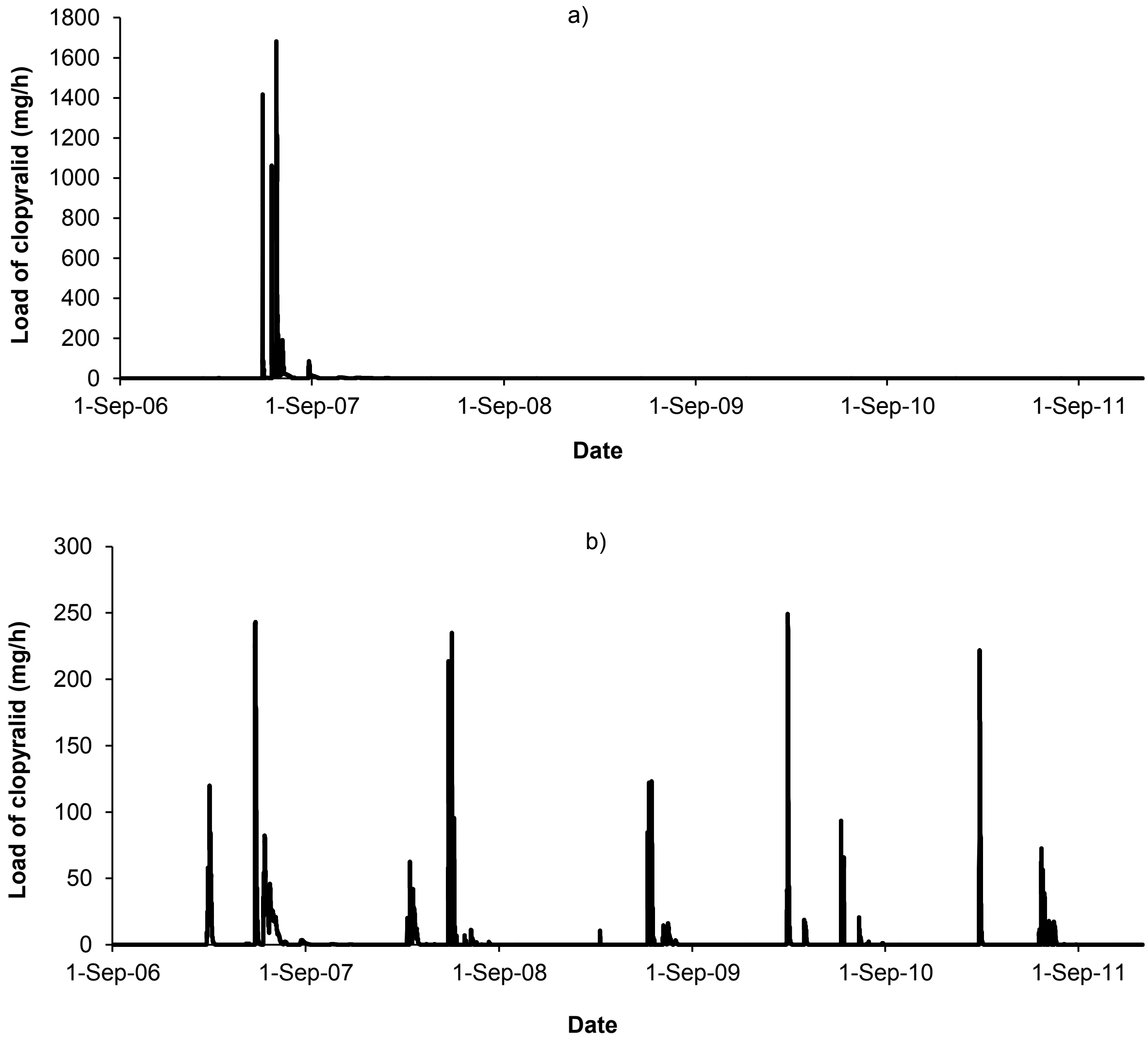


Figure 4-35 Clopyralid emissions to Burlingham soil simulated by SPIDER through (a) Drain flow (b) Interlayer flow.

The poorest pesticide simulation in the Wensum catchment was for MCPA as the models were unable to simulate pesticide peaks in the summer. Most of the observed detections occurred in spring and summer when the pesticide is normally applied but little or no drain flow was simulated by the models for those periods so pesticide loss could not be simulated. A study in an 830-ha catchment in southern Sweden compared the use of deterministic and stochastic approaches using MACRO to study MCPA loss (Lindahl et al., 2005). Probability distributions accounting for the spatial variability of soil properties and crops were used and pesticide usage including application date was gathered from personal interviews with the farmers. The deterministic approach using soil average data was able to simulate water flow well, but the model failed to simulate small but critical peaks to capture pesticide loss during the summer. Conversely, the stochastic model was able to simulate the small outflows at the field- and catchment- scales. However, MCPA simulations were better at the field-scale than at the catchment level; stochastic simulations under-estimated MCPA concentrations by up to two orders of magnitude at the catchment outlet and also missed pesticide losses in the summer. Possible causes for under-estimation of pesticide concentrations were attributed by the authors to possible point-source pollution due to farmyard losses such as cleaning or filling spray equipment which may cause short-term high concentrations in surface water. Other explanations included model errors, modeller subjectivity or inadequate selection of some of the input distributions (Lindahl et al., 2005).

In the present study, the lack of site-specific input data such as the uncertainty in application timings and the lack of flow simulation by both models during summer periods may explain some of the missing peaks for MCPA. In addition, pesticide losses due to runoff events can be more common during the summer and would be particularly important for a pesticide with a short half-life like MCPA.

4.5.2.1 Uncertainty analysis in pesticide simulations

Studies about uncertainties in pesticide fate models highlight the importance of considering uncertainties in the input parameters when analysing results to avoid erroneous interpretations (Dubus et al., 2003b; Dubus and Brown, 2002; Sohrabi et al., 2002). Uncertainty in input parameters is critical for the parameters that are most sensitive in the model. Studies on uncertainty analysis for MACRO input parameters showed that the use of mean input parameters might have little impact on flow rate simulation at the field-scale but uncertainties related to pesticide concentrations can be two to three orders of magnitude higher than that of the corresponding input data because of non-linear relationships between model inputs and outputs (Lindahl et al., 2005; Sohrabi et al., 2002).

The influence of uncertainties on model results would vary depending on the sensitivity of the parameters; higher uncertainties on the most sensitive parameters would generate a greater impact on the accuracy of the simulation. Sensitive input parameters in pesticide fate models usually include precipitation, pesticide sorption and degradation among others. Half-lives and sorption coefficients should be considered as variable and uncertain given the inherent spatial variability of these parameters in the environment (Dubus et al., 2001; Walker et al., 2001; Wood et al., 1987). Given the high sensitivity of these parameters within fate models, this will be transferred into uncertainty in model simulations (Dubus et al., 2003b). In order to reduce uncertainties in input parameters, the use of site-specific data for model parameterisation is recommended. However, these data are not always available or easy to collect. Depending on the level of accuracy needed and the sensitivity of the model, parameters can be left at their default values, taken from databases, derived from empirical equations or estimated using expert judgment, but any of these procedures will introduce uncertainty into the model (Dubus et al., 2003b).

Large under-estimation of pesticide concentrations was observed for carbetamide and propyzamide. Key sources of uncertainty were tested for carbetamide simulations in order to identify their effect on the prediction of pesticide losses. The variation of the application date in the simulations showed changes in the size of the peaks but there was still great under-estimation of the concentrations for some hydrological years. Tediosi et al. (2012) also found under-estimation of carbetamide concentrations at the same order of magnitude as the present work, even when the day of pesticide application was known. They considered that this under-estimation was due to the small half-life used in their model (8 days), which is two days shorter than the one used in the present work, and also due to sample handling, particularly lack of testing for sample stability and pesticide sorption.

Pesticide parameters used in the model are not site-specific for the Wensum catchment; instead average input data of pesticide sorption and degradation were used in the model. The effect of the uncertainties associated with the use of average pesticide sorption and degradation data was analysed. Sensitivity analysis of pesticide fate models including SPIDER and MACRO have determined that simulations are greatly influenced by pesticide sorption and degradation parameters (Dubus et al., 2003a; Dubus and Brown, 2002; Soutter and Musy, 1998; Persicani, 1996; Boesten, 1991; Boesten and Vanderlinden, 1991). SPIDER sensitivity was found to be close to that of MACRO; this is expected as the description of macropore flow in SPIDER is based on that in MACRO (Renaud and Brown, 2008). Renaud and Brown (2008) found that the most sensitive parameters for SPIDER were soil parameters describing transport in the macropores as well as parameters describing pesticide sorption; however, SPIDER appeared to be slightly more sensitive to variations in input parameters than MACRO. In the present study, a combination of extreme sorption and degradation data for carbetamide was used to study the impact of uncertainties from these input parameters on the simulated maximum concentrations and pesticide loads.

Both parameters but especially pesticide sorption had a big impact on the simulation of loads and maximum concentrations from the models but especially from SPIDER. The simulated ranges of maximum concentration and loads from SPIDER were wider than the ones obtained from MACRO. In the case of maximum concentrations, the simulated range from SPIDER did cover the observed data while MACRO slightly under-estimated the maximum concentration (by a factor of 1.1). These results are in good agreement with the findings of Renaud and Brown (2008); they also observed that soil parameters were generally equally or more sensitive than parameters describing pesticide degradation in SPIDER. The reason was that transport out of the mixing layer where macropores are loaded with pesticide would be the limiting factor for losses via preferential flow (Renaud and Brown, 2008). Results from uncertainty analyses for carbetamide in the present study showed that uncertainty from individual input parameters could not explain by themselves the observed disagreements in the simulation from both models and a combination of different sources of uncertainties for this pesticide would be needed to explain the under-estimation in simulated concentrations.

Lindhal et al. (2005) showed that model sensitivity can also be site- and compound-specific. The authors carried out a sensitivity analysis for MCPA simulations using MACRO at the field- and catchment-scale. Soil properties controlling macropore flow, precipitation following application and organic carbon content were among the most important factors affecting the simulations. Field-scale and catchment-scale sensitivity analyses were very similar for both MCPA load and maximum concentration. Leaf area index and consequently, application days were also sensitive parameters for MCPA simulations; a late application of MCPA will result in less pesticide reaching the soil surface due to crop interception when the soil is also drier. Contrary to findings from other studies, Lindhal et al. (2005) showed that sensitivity due to degradation rates for MCPA was small compared to that from other variables.

The variability in pesticide concentrations over short timescales can also lead to some bias when comparing simulated average daily values from hourly simulations to measured values from a sample taken at a particular time of the day. Monitoring samples of carbetamide on several occasions over the day showed significant changes in the concentration particularly after rainfall that triggered drain flow events (Tediosi et al., 2012). Holvoet et al. (2005) found after using automatic samplers collecting water every 15 min to create composite samples every six or eight hours that hourly pesticide concentrations in river flow were particularly high when frequent rainfall events took place. Temporal variability in the concentrations is also evident in the present study when comparing simulated average daily and hourly maximum concentrations from SPIDER to the measured concentration. The best approach to avoid discrepancies in grab samples due to temporal variability of pesticide concentrations would be to use an auto-sampler set to take hourly samples and then arrange a composite sample that represents the real mean daily concentration. Holvoet et al. (2007b) also commented about the importance of avoiding grab sampling to obtained more reliable monitoring results.

4.5.3 Catchment Sensitive farming programme

The most recent available report into the progress of the Catchment Sensitive Farming (CSF) programme (2012) used statistical analysis of monitoring data to assess trends in pesticide emissions in six catchments including the Wensum (fate modelling of pesticide was not used for this analysis). The study focused on available monitoring data for the six indicator pesticides used in the current study. The simulated pesticides in the present work were all amount these indicator pesticides. Calculations for the analysis included total annual loads (TAL), time-weighted and flow-weighted mean concentrations (TWMC and FWMC, respectively) across all six sites and for all seven pesticides. The Theil-Sen estimator was used to analyse the trends between years of these parameters (CSF, 2012). The Theil-Sen estimator is a non-parametric method for robust linear regression that looks to the slopes between all pairs of points in the data and calculates the median slope among all lines. The estimator is insensitive to outliers and it is said to provide a better estimation of the trend than a simple linear regression model when few points are available as the estimator accounts for the time series as a whole instead of looking to the absolute changes between years (CSF, 2012; Gilbert, 1987).

The available monitoring data were used for the calculations without accounting for days when samples were not collected (CSF, 2012). This approach is different to the one used in their previous report where a regression model was used to estimate pesticide concentrations for days with missing data using mean daily flow data (CSF, 2011). In the most recent report, a simpler approach in the estimations was thought to be more appropriate since the analysis was looking across systems and the results were expected to be un-biased because gaps were assumed to be randomly distributed (CSF, 2012).

The main issue that emerges from the methodology applied by the CSF (2012) in this report is that gaps between monitoring days can prevent the detection of important peaks which generates uncertainty in load estimations and can lead to erroneous interpretation of the results. In addition, these calculations of pesticide load and concentration do not account for all variables including rainfall or river flow and are also unable to understand the mechanisms of pesticide transport in the studied catchments. An alternative approach to study the effects of the CSF pesticide management programme within the catchments would be the use of pesticide fate modelling at the catchment-scale. Fate models can provide a better understanding of all the different variables that contribute to pesticide emissions by reducing uncertainties from excluding the effect of the weather or ignoring pesticide emissions on days when samples are not collected.

CSF (2012) calculated estimators by crop year (i.e. each crop year running from September to August) from 2006 to 2011 and changes in load and concentration of pesticides were examined by comparison of results between years and for the whole period. The TAL was calculated from instantaneous load rates which is said to generate an over-estimation of the loads. Calculated TAL showed a reduction in pesticide emissions from 2006 to 2010 for the six catchments. Individual load calculations showed a decrease of the TAL in the Wensum, except for chlorotoluron and mecoprop which had an increase of 1.73 and 0.02 kg/year from 2006 to 2011, respectively. The increase in chlorotoluron loads was explained by the possible replacement of isoproturon with this pesticide. The TWMC also showed an increase of 0.006 μg/l-year for chlorotoluron in the Wensum but not for mecoprop (CSF, 2012). In the present study, estimated observed loads were calculated by interpolation of the observed values for days when data were not available. Both observed and simulated loads by the models showed a decrease in all pesticides losses, including chlorotoluron and mecoprop, from 2006 to 2011 (Table 4-16). It is important to note that good pesticide simulations by MACRO and SPIDER were achieved for these two compounds. The estimated observed load for chlorotoluron showed a decrease in the loads of 0.18 kg/year (from 3.24 kg/year in 2006-2007 to 3.06 kg/year in 2010-2011); the simulated loads also showed reductions of 1.27 kg/year using SPIDER and 6.21 kg/year using MACRO. A bigger reduction in the load was observed for mecoprop; the estimated observed decreased in 25.51 kg/year and the simulated loads showed reductions of 35.23 and 16.11 kg/years for MACRO and SPIDER, respectively.

The rainfall and water flow in the Wensum catchment reduced markedly during the study period (2006 – 2011) by 400 mm and 78 mm, respectively (Figure 4-29). It is known that higher rainfall volumes can generate increases in pesticide emissions and concentrations may gradually increase until dilution is reached (Wolfe, 2001) but reduced rainfall and flow can also reduce emissions since there is insufficient carrier water to trigger diffuse pollution. The CSF report (2012) analysed the effect of rainfall on pesticide concentration using a series of linear regression models for mean monthly total pesticide concentration against mean monthly rainfall. The approach included a single model for the entire study period per catchment along with two additional models using separate subsets of data for the periods 2006-2009 and 2009-2011. The models aimed to determine whether rainfall was a significant factor in explaining pesticide concentrations. The differences between the mean monthly observed of total indicative pesticides for the period 2009-2011 and 2006-2009 showed that the Wensum experienced lower concentrations from the period 2009-2011 for a given rainfall than would have been expected for 2006-2009 (CSF, 2012).

Modelling results were used to analyse the trend of pesticides in the catchment and to identify factors influencing pesticide loss in the Wensum. None of the models used in the present study are able to simulate management measures; for this reason, the predicted pesticide loss by these models would only be caused by the input parameters describing the physical properties of the catchment such as soil and land use, pesticide usage and weather data. Therefore, differences between observed and simulated loads can be due to additional factors; such as the effect of the management strategies currently in placed at the catchment. In contrast, if modelling results are comparable to the observed data, this would mean that input parameters are the most likely factors affecting the dynamic of pesticides in the catchment; in terms of trends this would be mainly due to pesticide usage or the weather.

Changes in the observed and predicted pesticide loads between 2006 and 2011 were analysed; reduction in pesticide load for most of the herbicides showed to have a comparable behaviour. This was the case of mecoprop (using SPIDER), clopyralid, carbetamide and MCPA. Pesticide usage in the Wensum for modelling pesticide was estimated from regional survey data and crop areas. These estimates showed an increase in the usage of chlorotoluron, carbetamide, clopyralid, propyzamide while the usage of mecoprop remained stable and MCPA was reduced. Since pesticide usage for mecoprop (using SPIDER), clopyralid and carbetamide could not explain this reduction in pesticide emissions, modelling results suggest that the reduction of rainfall and flow are more likely to explain them instead of the actions taken by the CSF. Since the usage of MCPA was estimated to have reduced in the catchment, the reduction in pesticide emissions from this pesticide can be due to the joint effect of the changes in pesticide usage, weather and flow.

In the case of chlorotoluron and propyzamide, the models predicted considerable larger reductions than those that were actually estimated from the observed data. Predicted larger emissions from the model can be due to several factors including bad resolution of the measured data which can lead to a wrong estimate of the observed loads or inconsistencies in model simulation from the sources of uncertainty.

4.6 Conclusions

The evaluated field-scale models (SPIDER and MACRO) along with the modelling methodology used were able to simulate the overall pattern of the behaviour of the pesticides in the catchment. In-stream processes did not show a big effect on the simulations when applying field-scale models. A good simulation by the models will be particularly useful for refining dates in the monitoring programmes for drain flow emissions in the catchment. However, this is not possible for emissions due to runoff events as the models were unable to simulate this pathway.

Modelling results also showed that pesticide concentrations in water were driven by field-scale processes, and that fate within the river system had a relatively minor influence on pesticide concentrations at the catchment outlet. The results also show that pesticide loss through tile drainage is the major routes of water contamination in the catchment in most cases. SPIDER was able to simulate more emission events than MACRO. The reasons include that MACRO does not account for interlayer flow and tend to miss drain flow events occurring at the end of the summer as the model takes more time to wet up in this period due to over-estimation of the evapotranspiration.

Key uncertainties in the modelling were associated with water flow (groundwater connectivity, flood control measures, abstractions from the river) and pesticide use (timing, rate and location of specific applications). Whilst simulations matched some elements of the observed behaviour, they were not sufficiently accurate to allow filling of gaps in the measured data.

SPIDER did a good job at predicting moderately persistent pesticides such as chlorotoluron and mecoprop that are mainly applied during autumn when drains are flowing. The results helped to identify critical input parameters that should be refined in order to achieve better simulations and how important they are according to the physicochemical properties of the pesticide being simulated. Uncertainties in degradation values, sorption, pesticide amounts and application dates are critical for pesticides with short half-life values or when they are applied in different seasons. Models show very poor simulation of pesticides that are applied during periods of low flow which is the case for MCPA. Even though clopyralid is applied in spring, SPIDER was able to simulate some of the peaks due to interlayer flow.

Pesticide load is an important parameter in deciding whether the Catchment Sensitive Farming programme is reaching the goal of reducing pesticide emissions. Pesticide results can also help to interpret the trends of pesticide emissions in the catchment. Both models and estimated loads showed a reduction in pesticide loads. A comparison of percentage of reduction between observed and simulated loads suggested that most of the reductions could be explained by the effect of the observed reduction in rainfall and flow in the catchment. An influence of the management strategies applied through CSF cannot be excluded, but results suggest that care should be taken in assigning observed reductions solely to management changes.

5 Modelling the fate of pesticides in the valley of the River Cauca, Colombia using the AnnAGNPS model

5.1 Introduction

The contamination of water bodies due to agricultural activities has been widely recognised and continues to be of concern. The geographical valley of the River Cauca in the Valle del Cauca department, Colombia, is characterized by intensive agriculture where sugarcane is the main crop covering about 200,000 ha (approximately 50% of the arable land in the area) for the production of sugar and bioethanol (Moreno, 2012). A monitoring study in 2010 and 2011 showed high levels of pesticides along the river (Sarria, 2014). In particular, the herbicides atrazine and simazine were found in several samples at levels exceeding the established international standards for surface water and drinking water.

Atrazine and simazine are used in Colombia for pre-emergence and early post-emergence weed control in sugarcane, maize and sorghum crops. Despite the high potential risk for water contamination due to pesticides, no catchment management or monitoring programmes are currently in place by the government in order to reduce and investigate emissions; and only a few independent research studies have measured pesticide levels in the river (Sarria, 2014; Piedrahita and Paez, 2008; Belalcazar and Paez, 1999; Barra, 1993). The main reasons for not tackling pesticide contamination in the area (and in general for the whole country) are that these programmes are especially expensive and require large investment from the government. An alternative to refine and reduce costs of water monitoring is to use mathematical modelling of pesticide fate as a tool to understand the dynamics of these substances in the catchment. The main characteristics of the study area and a strategy for applying pesticide fate modelling are described below.

5.1.1 Aim and objectives

The aim of this chapter was to study the dynamics of the herbicides atrazine and simazine along with their routes of entry to the River Cauca by conducting catchment pesticide fate modelling for the first time in the area using a spatially distributed model in the geographical valley of the river. The specific objectives to meet this aim were to:

1. Examine the predictive capacity and applicability of the AnnAGNPS model under Colombian conditions.
2. Assess the effect on model simulations from uncertainty in the input parameters.
3. Determine the areas of risk in the study area for water contamination by atrazine and simazine.
4. Identify practices and conditions that influence pesticide loss in the catchment.
5. Evaluate pesticide losses from using triazine alternatives in the catchment.

5.2 Study area and background information

5.2.1 Catchment characteristics of the River Cauca in the Valle del Cauca department

The River Cauca is located between the west and the central Andean ranges in Colombia and is one of the two main rivers of the country. The river flows from its source in the Colombian Massif in the Cauca department for approximately 1,350 km, draining a watershed of 63,300 km^2 to its confluence with the River Magdalena in the Bolivar department and finally flowing out into the Caribbean Sea (Figure 5-1). The river flows through 183 municipalities in Cauca, Valle del Cauca, Quindío, Risaralda, Caldas, Antioquia, Córdoba, Sucre and Bolivar departments (Colombia comprises 32 country subdivisions called departments that have a certain degree of administrative autonomy and each department comprisesa group of municipalities; Colombia has 1,119 municipalities). About 16 million people live in this catchment (38% of the population of Colombia). The watershed of the River Cauca in the Valle del Cauca department is particularly important to the economy of the country; most of the sugarcane industry and part of the coffee plantations are located in this area (CVC and Univalle, 2007, 2001). The River Cauca in the Valle del Cauca receives domestic and industrial discharges from 33 municipalities; the main ones are Cali, Jamundí, Yumbo, Palmira, Buga, Zarzal, Florida, Tuluá and Cartago (CVC and Univalle, 2004). Other main characteristics of the climate, hydrology, soils and land use in the watershed are described below.

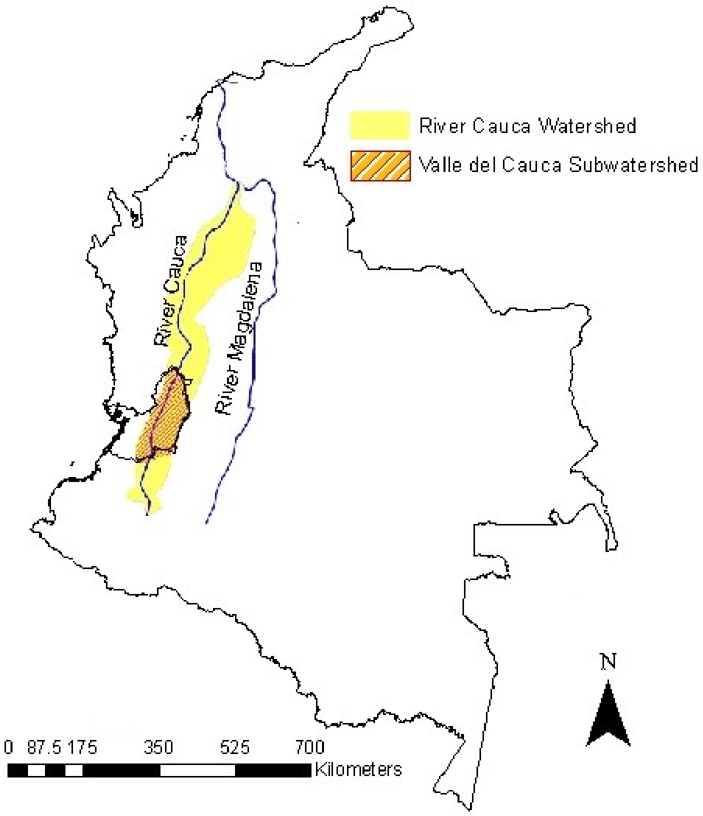


Figure 5-1 Location of the River Cauca catchment in Colombia and its watershed in the Valle del Cauca (Adapted from CVC and Univalle (2001)).

5.2.1.1 Climate

The region is characterized by a tropical climate with high and uniform temperatures throughout the year. In contrast to temperate regions, it is not possible to distinguish between seasons using temperature criteria. There is also change in the temperature with elevation that varies by about 1ºC every 170 m. A major characteristic of the climate is the presence/absence of periods or seasons of rain; two low and two high rainfall seasons take place during the year. Low rainfall seasons normally occur from January to February and from June to September; and greater precipitation occurs from March to May and from October to December. The mean temperature is 24ºC, varying between 10 and 38ºC (CVC and Univalle, 2007). The relative humidity varies between 65 and 90%, and the annual precipitation between 800 and 3800 mm (IDEAM, 2012a).

The spatial distribution of precipitation is mainly influenced by the topography, the trade winds and the prevalence of calm equatorial or inter-tropical convergence zones. Most of the precipitation that occurs in the region can be classified as convective or orographic in origin, often presenting specific microclimate phenomena. Normally, 80 to 90% of the precipitation during large storm events occurs during the first three hours of the storm, which is distinctive of the torrential character of the rainfall and the flashy behaviour of the tributary rivers of the River Cauca in the area. In addition, higher rainfall rates usually occur in the proximity of the central Andean ranges which is consistent with the higher number of important tributary rivers to the east margin of the River Cauca (Figure 5-2) (CVC and Univalle, 2001). Another important climatic phenomenon that greatly affects the hydrology of the River Cauca is the El Niño-Sourthern Oscillation (ENSO) cycle including its warm (el Niño) and cold (la Niña) phases which affect the normal timing and intensity of precipitation.

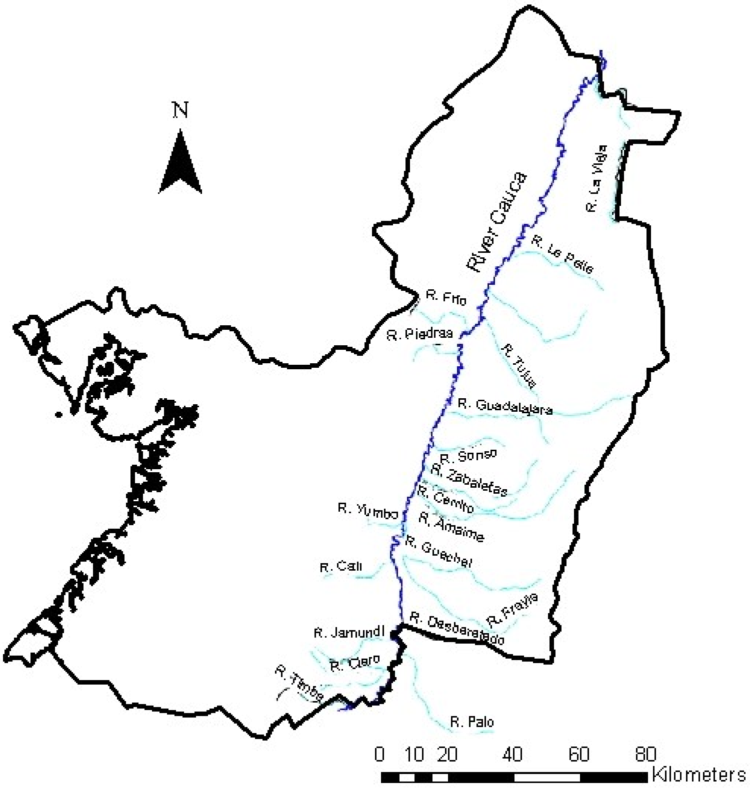


Figure 5-2 Location of the River Cauca and its tributaries in the Valle del Cauca (Adapted from CVC and Univalle (2001)).

5.2.1.2 Hydrology

The watershed of the River Cauca in the Valle del Cauca covers a drainage area of 19,349 km^2 and the river width varies from 80 m at the top (La Balsa) to 150 m at the bottom (Anacaro) of the river (CVC and Univalle, 2004, 2001). Figure 5-3 shows the hydrograph for both stations from 2008 to 2011 (CVC, 2011b, c). The water flow of the River Cauca and of its tributaries is strongly related to the rainy seasons. In general, the maximum flows occur during November and May, whereas the minimum flows are recorded in August and September. Most of the tributary rivers are classified as flashy rivers according to their physiographic and morphometric characteristics of the sub-basins that they underlie; these circumstances involve a critical response to short intense rains, with relatively low flows being observed for most of the year and high flows occurring in peaks of short duration (CVC and Univalle, 2001).

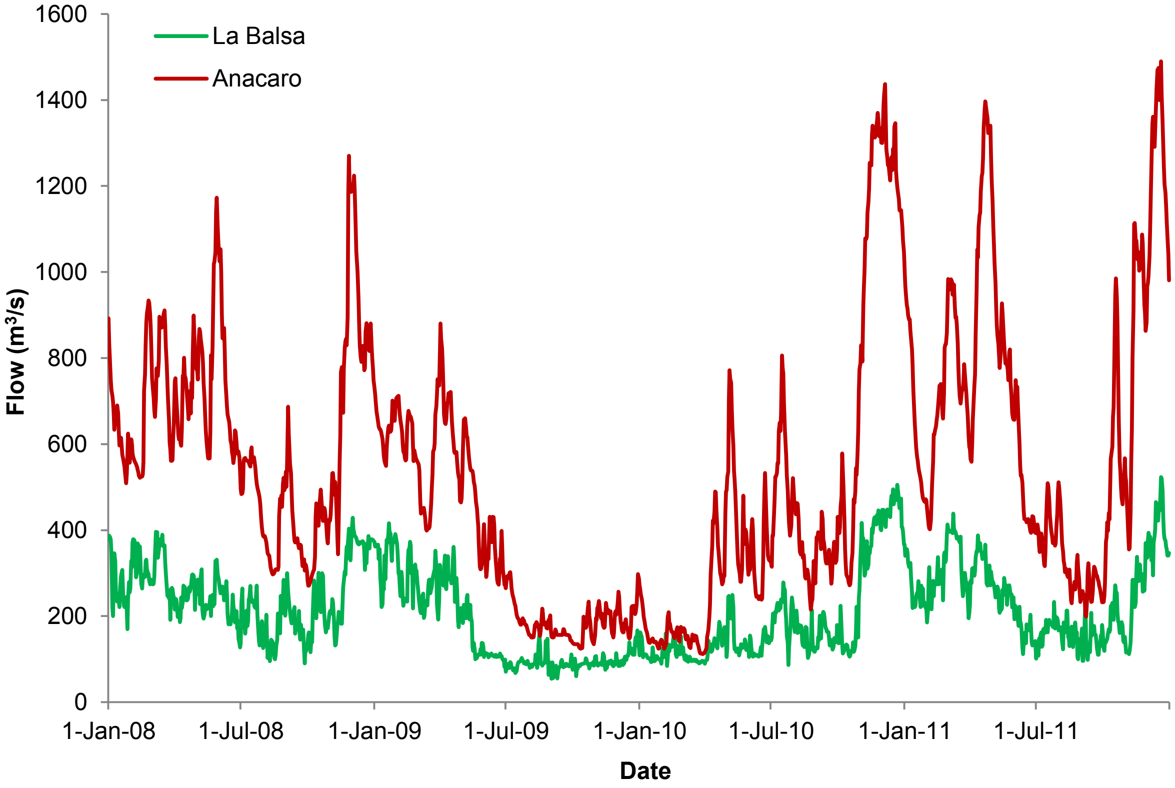


Figure 5-3 Hydrograph for La Balsa and Anacaro stations.

5.2.1.3 Soils and land use

The rapid growth of the sugar industry in the last three decades has exerted a strong pressure on natural resources, mainly on land use in the geographical valley of the River Cauca (Cortes Ortiz, 2010). Since 1986, there has been an increase of 67% in the crop area of sugar cane in the valley, nowadays accounting for half of the available arable land (ASOCAÑA, 2009). In order of importance, the main land uses in the geographical valley are grass (natural grass 38.2% and cutting grass 5.3%), sugar cane (26.2%), urban areas (14.4%), brush (4.5%), maize (3.3%) and sorghum (3.0%) (CVC, 2011a).

There are about 84 soil series in the area that belong to the following orders Mollisol (36%), Inceptisol (26%), Vertisol (21%), Entisol (10%), Anfisol (5%) and Ultisol (1%) (ESRI, 1992). Most of them are clay and loam soils with pH values between 5.5 and 7.0 (CVC, 2011d) and organic matter content between 2 and 4% (Ramirez, 1983).

5.2.2 Atrazine and simazine

The use of herbicides for controlling weeds is an important practice for agricultural production in the Valle del Cauca. The use of herbicides has rapidly replaced manual and mechanical techniques of weed control due to their speed of use, crop security, prolonged residual action and replacement of extra human labour. It is reported that in 1970, agrochemicals were used on only 30% of the total crop area in the Valle del Cauca (Gomez et al., 1970); nowadays, almost all the crop land is treated with pesticides (Cárdenas and De la Cruz, 1981). Weed control is particularly important in the initial stages of the crops to avoid competition for solar radiation, water and nutrients between crops and weeds; weeds can cause slow crop growth, poor crop development and reduced yields.

The triazines constitute a group of herbicides with residual and systemic action. The main triazines used in the Valle del Cauca are atrazine and simazine. These herbicides are used in several crops to kill broadleaved and grassy weeds on agricultural and non-agricultural land (Abate and Masini, 2005); in the Valle del Cauca region, they are primarily used as a pre-emergence herbicide on maize, sorghum and sugarcane (ATSDR, 2003a; US EPA, 2003a). Triazines are absorbed by the roots of the weed and translocate inside the plant to interrupt photosynthesis. These herbicides can also be used early post-emergence on recently emerged weeds (no more than 1-2 leaves), but in this case contact action by foliar absorption is favoured which usually requires the use of surfactants or oils.

Atrazine and simazine are commercially available in a variety of products either as single active ingredients or as a mixture of both substances. They are usually applied at concentrations of 2 to 4 kg a.i. ha^{-1}. These herbicides have similar physicochemical properties; both are only slightly soluble in water (atrazine more than simazine) and have moderate sorption to organic matter which increases their persistence in the environment and decreases their bioavailability (Table 5-1). Degradation in soils is mainly due to microorganisms; half-lives in soil and water are between one and three months (Mudhoo and Garg, 2011).

Atrazine and simazine were withdrawn from use in the EU in 2004 after failing the review process because of the risk they pose to groundwater and their high persistence (European Commission, 2004b, a). Other European countries decided to ban atrazine earlier; for example Sweden, Denmark and Finland since 1994 as well as Germany and Italy, two big maize producers, in 1991. In the USA, where these herbicides are still in use, atrazine is one of the most widely applied herbicides and also the most commonly detected pesticide in surface water (US EPA, 2012). Table 5-2 shows a list of the maximum permissible levels of atrazine and simazine in drinking water in different countries. In Colombia, permitted levels are based on the toxicology, carcinogenic, mutagenic and teratogenic characteristics of the substance and their LD_{50} (Ministerio de Salud, 1998), but there is no official list of levels per pesticide as in other countries.

Table 5-1 Physicochemical properties of atrazine and simazine (AERU, 2007).

Property	Atrazine	Simazine
Molecular mass (g mol^{-1})	215.68	201.66
Solubility (mg l^{-1})	35	5
pKa	1.70	1.62
Log Kow	2.7	2.3
Henry's law constant at 20ºC (dimensionless)	1.5×10^{-7}	1.3×10^{-8}
K_{oc} (ml g^{-1})	100	130
DT_{50} in soil (typical lab.)[1] (days)	75	60
DT_{50} in soil (field) (days)	29	27
Aqueous hydrolysis at 20ºC and pH 7 (days)	86	96
DT_{50} in water (days)	>200*	46

*ATSDR (2003b)

[1] DT_{50} (typical lab.) refers to typical laboratory values in the literature

Table 5-2 Maximum permissible levels of atrazine and simazine in drinking water in different countries.

Country/organization	Atrazine (μg/l)	Simazine (μg/l)	Reference
USA	3	4	US EPA (2008)
EU	0.1	0.1	Council of the European Communities (2008)
Canada	5	10	Health Canada (2012)
New Zealand	2	2	NZ Ministry of Health (2000)
World Health Organization	2	2	WHO (2008)
Mexico	2	2	ANEAS (2007)
Uruguay	3		OSE (2006)
Brazil	2	2	Conselho Nacional de Meio Ambiente Brasil (2005)

5.2.3 Triazine concentrations in the River Cauca

A study by Sarria (2014) measured atrazine and simazine levels at different monitoring stations along the River Cauca. Samples were collected in June and October 2010 and May 2011. Table 5–3 shows the reported concentrations and sampling dates for the monitoring stations. Atrazine and simazine were always detected in each campaign at least in two stations. Detected concentration for atrazine varied between 26.00 and 240.49 μg/l; and for simazine between 24.77 and 172.00 μg/l. However, when referring back to the method used inconsistencies in the calculation of the concentrations were observed. Samples of 500 ml of water from the River Cauca were used in the analysis. The pesticides in samples were extracted by a solid-phase method. It seems likely that reported concentrations were based on the concentration in the extracted sample without accounting for the original sample volume of 500 ml of water from the river. Reported concentrations were corrected to represent the original pesticide concentrations in the samples; results are shown in Table 5–3. Corrected detectable concentration for atrazine ranged between 0.052 and 0.481 μg/l; and for simazine between 0.050 and 0.344 μg/l.

Table 5-3 Sampling dates and concentrations for samples taken at different monitoring stations along the River Cauca in the Valle del Cauca reported by Sarria (2014). Corrected concentrations referred to the original river samples are shown.

Sampling Month-Year/ location	Day	Reported		Corrected	
		Atrazine (µg/l)	Simazine (µg/l)	Atrazine[1] (µg/l)	Simazine[2] (µg/l)
June 2010					
La Balsa	9	59.4	ND	0.119	ND
Puente Hormiguero	9	ND	ND	ND	ND
Juanchito	9	ND	ND	ND	ND
Puerto Isaacs	10	ND	ND	ND	ND
Paso de la Torre	10	ND	ND	ND	ND
Mediacanoa	10	240.5	ND	0.481	ND
Puente Guayabal	11	25.9	24.8	0.052	0.050
Anacaro	11	ND	ND	ND	ND
October 2010					
La Balsa	11	ND	NQ	ND	NQ
Puente Hormiguero	11	79.00	ND	0.158	ND
Juanchito	26	ND	56.0	ND	0.112
Puerto Isaacs	11	ND	ND	ND	ND
Paso de la Torre	11	ND	52.0	ND	0.104
Mediacanoa	25	26.0	NQ	0.052	NQ
Puente Guayabal	25	29.0	ND	0.058	ND
Anacaro	25	ND	ND	ND	ND
May 2011					
La Balsa	10	ND	ND	ND	ND
Puente Hormiguero	10	ND	ND	ND	ND
Juanchito	10	ND	ND	ND	ND
Puerto Isaacs	11	112.0	ND	0.224	ND
Paso de la Torre	11	ND	ND	ND	ND
Mediacanoa	12	ND	NQ	ND	NQ
Puente Guayabal	12	44.0	172.0	0.088	0.344
Anacaro	12	ND	ND	ND	ND

[1] LOD = 0.0046 µg/l and LOQ = 0.0154 µg/l; [2] LOD = 0.0101 µg/l and LOQ = 0.0337 µg/l

5.2.4 AnnAGNPS model

The Annualized Agricultural Non-Point Source pollution model (AnnAGNPS) (USDA ARS, 2006) is based upon the single event model, AGNPS (Young et al., 1989), which simulates non-point pollution from agricultural watersheds to surface water. A comprehensive description of all routines used in the model can be found in the AnnAGNPS manual (Bingner et al., 2011). The model was built as a series of interconnected modules by integrating different models that simulate the hydrology, sediment, nutrient (nitrogen and phosphorus) and pesticide transport along the watersheds. The model operates on a daily time step using a cell approach by dividing the watershed into grid cells according to the specified degree of resolution. This cell approach enables analyses at any point in the watershed. Pollutants including pesticides are transported from cell to cell in a stepwise process. The cells and the stream network are generated from a digital elevation model of the watershed by using the TOPAGNPS, which has a set of modules from the topographic parameterization program (TOPAZ) that provides all the required topographic information (Garbrecht and Martz, 1995). The resulting topographic data can be visualized in tabular and GIS formats (Bingner et al., 2011).

The simulated hydrology in AnnAGNPS includes interception, evapotranspiration and surface runoff. The runoff is simulated using the soil conservation service (SCS) curve number (CN) method (USDA, 1986). The soil moisture balance is simulated for two composite soil layers, located above (up to 20 cm from the surface) and below plough depth (Bingner et al., 2011). Erosion is calculated using the revised universal soil loss equation (RUSLE) (Renard, 1997).

Pesticide transport is simulated using a modified version of GLEAMS (Leonard et al., 1987) where pesticide mass balance is calculated on a daily step for each cell and dividing the chemical in two phases, dissolved in the solution phase (C_w in mg/l) and adsorbed in the soil phase (C_s), using a simple linear adsorption isotherm. Pesticide transfer in the runoff is calculated using Equation 5-1 where C_{av} is the runoff-available pesticide concentration in the surface soil layer in mg/kg and B is the soil mass per unit of overland flow, kg/l (Leonard et al., 1987).

Equation 5-1 $C_w + C_s = C_{av}\,B$

AnnAGNPS also allows the simulation of any number of pesticides without accounting for any interactions between them. Information about management practices in the watershed can be provided for each cell in the model which also allows the simulation of the spatial and temporal variation of the behaviour of contaminants.

Modelling such complex and large catchments as the geographical valley of the River Cauca, requires a model able to simulate high variability of spatially-distributed information. The AnnAGNPS model provides this possibility for soil and land use data as well as the use of meteorological data from different stations along the catchment.

5.3 Methodology

The AnnAGNPS model version 5.41 was used for the first time under Colombian conditions to simulate the fate of atrazine and simazine in the geographical valley of the River Cauca in the Valle del Cauca Department. Details on data acquisition, modelling methodology, model evaluation and analysis are described below.

5.3.1 Data acquisition

Information for use in deriving model input parameters for the study area was gathered from different sources.

- Daily weather data from six meteorological stations along the watershed including Palmasola, Candelaria, Guacari, ICA, Univalle and Cabuyal stations as well as pan evaporation class A and maximum and minimum temperature data for Univalle station for 2010 and 2011 were provided by the Institute of Hydrology, Meteorology and Environmental Studies of Colombia, IDEAM (IDEAM, 2011a).
- Soil properties information and spatial data including soil and land use vector maps (1:50,000 scale) for the geographical valley (flat area of the catchment) were supplied by the local environment agency (Corporación Autónoma Regional del Valle del Cauca, CVC) (CVC, 2011a, d, 2003).
- A digital elevation model for the south west region of Colombia was obtained from the CGIAR-CSI SRTM 90m Database v4.1 (Jarvis et al., 2008).
- Pesticide application rates were gathered from the information sheets of the commercial formulation (Inveragro, 2013; Nufarm, 2012; Calister, 2011; Proficol, 1991, 1979).

5.3.2 Digital elevation model preparation

The digital elevation model (DEM) was pre-processed using Arc Hydro 2.0 for ArcGIS 10 (ESRI, 2011) before its use in AnnAGNPS (Figure 5-4). The general sequences of terrain pre-processing were followed, including stream enforcement by burn-in of the main river network using a river coverage DCW (Digital Chart of the World) map for Colombia (ESRI, 1992). Stream enforcement modifies the DEM surface allowing a more accurate representation of the stream routing which is particularly important for an accurate calculation of the streams in flat terrain such as in the valley area (Pullar and Springer, 2000). Afterwards, the watersheds for the Valle del Cauca were calculated and those hydrological response units draining to the River Cauca were selected as the study area (Figure 5-5).

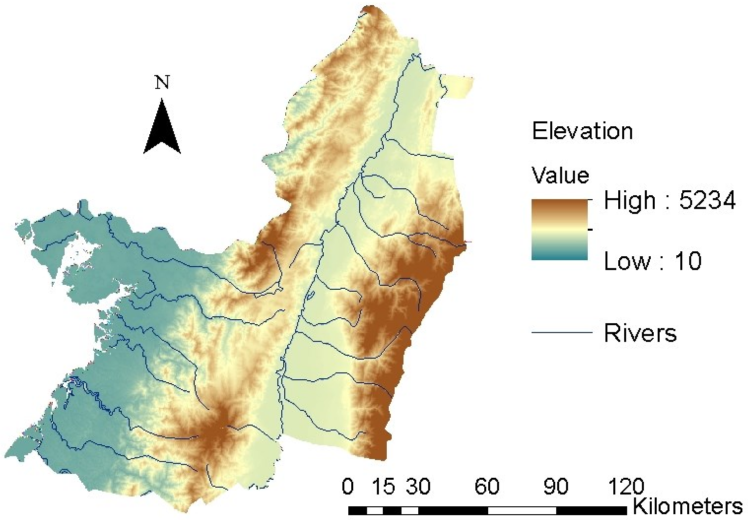


Figure 5-4 Map of the pre-processed digital elevation model and burn-in of rivers.

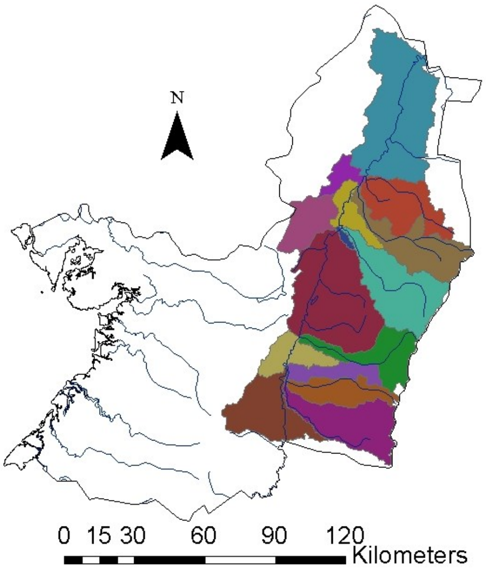


Figure 5-5 Calculation of the watersheds that comprise the River Cauca in the Valle del Cauca department using Arc Hydro. The administrative area and rivers of the Valle del Cauca department are also shown.

5.3.3 Study area and watershed delineation

The study area corresponds to a main river length of 303 km and a drainage area of 8,638 km^2 in the geographical valley between the CVC monitoring stations of Puente Hormiguero

(W 76°28’36.5”, N 03°18’0.5”) and Anacaro (W 75°57’58.1”, N 04°47’0.6”); these points were defined as the catchment inlet and outlet in the model, respectively (Figure 5-6).

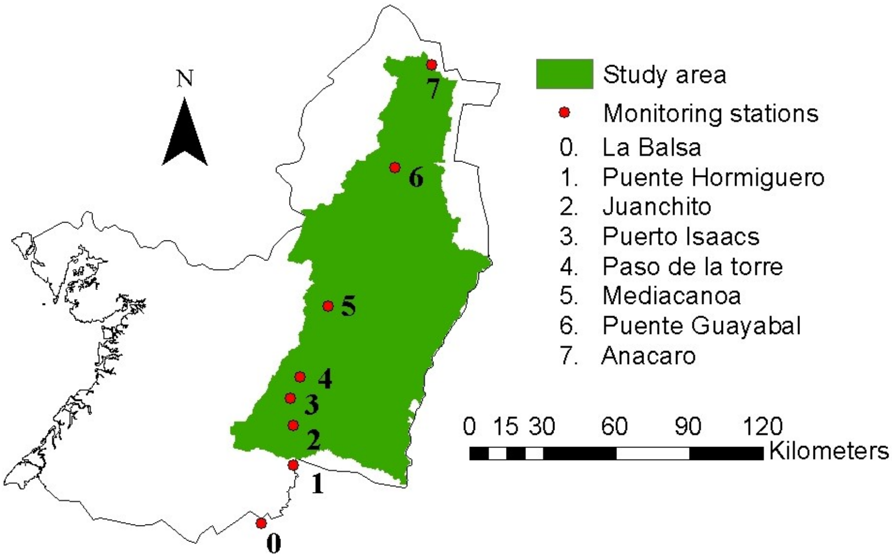


Figure 5-6 Map of the studied watershed of the River Cauca in the Valle del Cauca (study area) and the CVC monitoring stations. The administrative area of the Valle del Cauca department is also included.

The pre-processed DEM was used in the TOPAGNPS module of the AnnAGNPS model to generate grid data with topographic information to delineate the watersheds of the study area and to calculate the stream network (Figure 5-7). The values for critical source area (CSA) and minimum source channel length (MSCL) were set to 600 ha and 2000 m, respectively, which divided the watershed into 1410 cells. Then, the AGNPS GIS tool was used to fill the cell and reach databases generated by TOPAGNPS. The process comprised the interception of the soils, land use and climate maps. The resulting cell and reach databases were then used together with all the other input parameters (Section 5.3.4) to execute the simulation. Outputs were selected to provide water and pesticide information of each monitoring station along the catchment; relevant information consisted of runoff flow and pesticide loads to each of these points and to the catchment outlet.

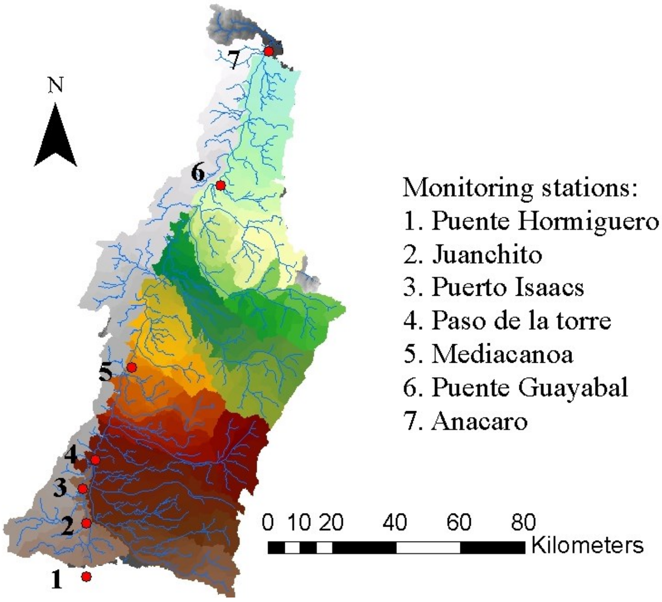


Figure 5-7 Generated watersheds (cells: 1410) and stream network (reaches: 567) of the study area including the location of the monitoring stations. The catchment outlet is located in Anacaro.

5.3.4 Model parameterisation

The AnnAGNPS model requires over 400 input parameters distributed in 34 modules (Bingner et al., 2011). The following sections describe only the relevant input data and project preparation for the simulation of pesticide emissions to surface water in the studied area.

5.3.4.1 Weather data

AnnAGNPS allows the use of weather data from multiple meteorological stations in the catchment. The weather information used in the model comprised daily precipitation data for six meteorological stations along the studied area, namely Palmasola, Candelaria, Guacari, ICA, Univalle and Cabuyal stations (Figure 5-8).

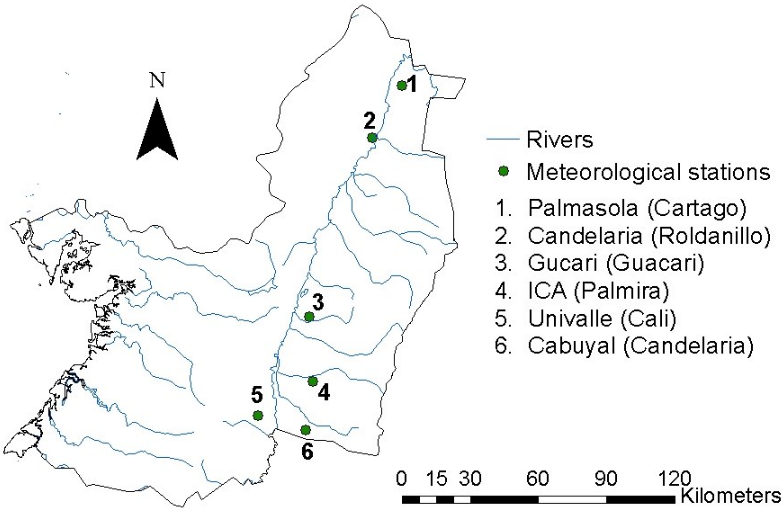


Figure 5-8 Location of the meteorological stations.

Pre-calculated actual evapotranspiration was supplied to the model using pan evaporation data for the meteorological station of Univalle. Pan evaporation data (Ev_{pan} in mm) can be used to estimate actual evapotranspiration (Ev_{actual}) by using a multiplicative factor called the crop coefficient (K_c) of a reference crop (Equation 5-2) (Jensen et al., 1990).

Equation 5-2 $Ev_{actual} = K_c\ Ev_{pan}$

The value of the crop coefficient depends on the crop type, crop growth stage, climate, and soil evaporation. The reference crop used for the calculation of evapotranspiration was sugarcane since it is one of the main crops in the catchment with available local data from previous studies. In the geographical valley of the River Cauca, studies have found that sugarcane has crop coefficients of 0.3 and 0.7 during its initial (2 to 4 months) and development (4 to 10 months) stages, respectively (Torres, 1995). Since sugarcane is sown in the valley at any time during the year (there are no specific dates for sugarcane sowing) and crops are present at different stages of development along the catchment, an annual average crop coefficient value of 0.57 was used to calculate the daily actual evapotranspiration supplied to the model.

In addition, measured pan evaporation data from the meteorological station of Univalle was used as potential evapotranspiration in the model. Other weather data supplied to the model included measured maximum and minimum temperature data for Univalle station for 2010 and 2011 (IDEAM, 2011a) and monthly historical average values of solar radiation, wind speed, cloud cover and relative humidity (CVC and Univalle, 2001).

A climate map was also prepared to be used in the TOPAGNPS module of the AnnAGNPS model. The climate map was generated by the calculation of the Thiessen polygons from the location of the meteorological stations along the catchment (Bingner et al., 2011). The climate map is shown in Figure 5-9.

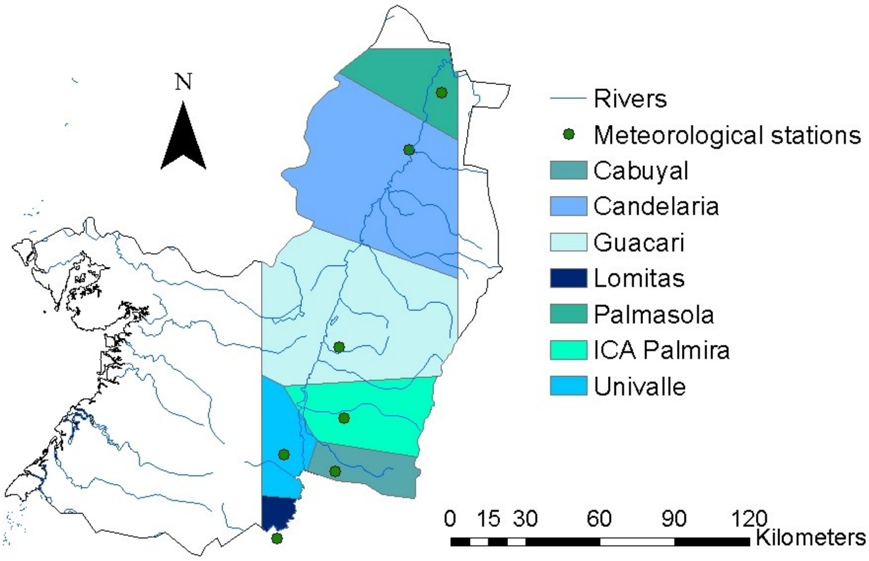


Figure 5-9 Location of the calculated Thiessen polygons for the meteorological stations. The administrative area and rivers of the Valle del Cauca department are also included.

5.3.4.2 Soil parameters

Spatial information about soils in the valley showed presence of 18 soil orders, 42 soil suborders and more than 70 soil series. In order to reduce the amount of soils input parameters and to simplify the simulation, the soils series were classified into groups with similar hydrological characteristics. The first step was to assign a potential level of risk for pesticide emissions to water bodies (from 1 to 5, with 1 the higher risk) to the soil orders based on the description of the hydrology behaviour in the soil taxonomy information (USDA, 1999).

Table 5-4 shows the assigned levels of risk for each soil order. The highest level of risk was assigned to six soils including Argiustolls, Durustalfs, Endoaquepts, Epiaquepts, Ustifluvents and Ustorthents because of their proximity to surface water bodies, high groundwater tables or poorly draining soils that are generally artificially drained; these conditions favor surface runoff and the rapid loss of pesticides to surface water. The lowest risks were assigned to three soils: Dystrustepts, Haplustolls and Ustipsamments because of their free-draining character where overland flow is not expected.

A final classification of the soil series into 10 soil groups was compiled by grouping the soils with common characteristics; this took into account the risk classification and the available description of the soil series, in particular information about the soil depth, draining behaviour, and texture properties (CVC, 2003). The resulting soil groups along with the different soils series, the draining behaviour, and the percentage of area covered by each soil group are shown in Table 5-5. This table shows roughly equal presence of all levels of risk of pesticide contamination in the catchment; soils with a high risk (levels 1 and 2) account for 29.8%, medium risk soils are 31.7% (levels 3 and 4) and lowest risk soils are 38.6% of the valley area.

Table 5-5 also shows the hydrologic soil group based on the USDA (1986) classification according to the draining behaviour of the soils (A: well drained soils; B: moderately well drained soils; C: poorly drained soils; D: very poorly drained soils) and the soil erodibility factor (K) for the Revised Universal Soil Loss Equation (RUSLE) for each soil that was estimated by interpolation of the tabulated data of soil textures to the organic matter content of the top soil (Renard, 1997). The spatial distribution of the soil groups is presented in Figure 5-10; this figure shows a fairly uniform distribution of all the soil groups along the catchment.

Table 5-4 Estimated levels of risk for the different soil orders (suborders) to water bodies contamination by pesticides (1 highest) and their relevant description of the soil hydrology based on the USDA soil taxonomy classification.

Soil order (suborder)	Risk	Soil connection to water bodies	Description*
Argiustolls (Typic)	1	Groundwater	Ustolls are freely draining. Argiustolls add an argillic horizon which indicates some vertical movement of clay particles down the horizon.
Calciusterts (Sodic, Udic)	2	Probable to surface water	Clay rich soils that are subject to cracking.
Durustalfs (Typic)	1	Surface water	Ustalfs have very little transfer of water to depth. Durustalfs are characterised by a duripan likely to impede vertical water movement
Dystrustepts (Humic)	5	Groundwater	Mainly free-draining soils. Dystrustepts are acidic.
Endoaquepts (Fluvaquentic, Vertic)	1	Surface water	Wet soils with poor drainage. Either artificially drained or groundwater will be very near the surface. Probably next to the river.
Endoaquerts (Chromic, Typic, Sodic)	3	Groundwater with strong connection to surface water	Flood plain soils. Water movement will mainly be vertical to depth and then moving in the relatively shallow groundwater
Epiaquepts (Humic)	1	Surface water	Slightly deeper groundwater than Endoaquepts
Fluvaquents (Aeric)	3	Groundwater with strong connection to surface water	Classic wet flood plain soils. Vertical to depth then moving to river in shallow groundwater.
Haplustalfs (Aquertic, Typic, Vertic)	4	Probable to groundwater	Relatively thin, dryish soils probably on the footslopes. Rather limited leaching to depth.
Haplusterts (Chromic Udic, Entic Udic, Sodic, Typic, Udic)	2	Probable to surface water	Clay rich soils that are subject to cracking

*(USDA, 1999)

Table 5-4 (cont.) Estimated levels of risk for the different soil orders (suborders) to water bodies contamination by pesticides (1 highest) and their relevant description of the soil hydrology based on the USDA soil taxonomy classification.

Soil subgroup	Risk	Soil connection to water bodies	Description*
Haplustepts (Aquertic, Aquic, Calcic, Fluventic, Oxiaquic, Udicfluventic, Vertic)	5	Groundwater	Mainly free-draining
Haplustolls (Cumulic, Entic, Fluvaquentic, Fluventic, Pachic, Typic, Udertic, Udifluventic, Vertic)	5	Groundwater	Mainly free-draining
Natraquerts (Typic)	3	Groundwater with strong connection to surface water	Flood plain soils. Water movement will mainly be vertical to depth and then moving in the relatively shallow groundwater
Natrustalfs (Petrocalcic)	3	Probable to groundwater	Relatively thin, dryish soils probably on the footslopes. Rather limited leaching to depth.
Ustifluvents (Typic)	1	Surface water	Flood plain soils prone to frequent flooding. Would have to be drained if cultivated.
Ustipsamments (Typic)	5	Groundwater	Sandy and very free draining
Ustorthents (Lithic, Typic)	1	Surface water	Very new soils on eroded surfaces. Probably not cropped, but would get runoff if there are crops

*(USDA, 1999)

Table 5-5 Soil classification, area and hydrologic properties used in the AnnAGNPS model.

Soil group	Risk	Hydrologic soil group[1]	K factor[2]	Draining behaviour	Soil series	Area (%)
1	1	B	0.0413	Free-draining	ES4	3.6
2	1	C	0.0225	Moderate draining	C41, VA9, C63	4.6
3	2	D	0.0263	Artificially drained	V26, VA4, V13, VS49, V55, V25, C13	15.2
4	2	C	0.0726	Moderate draining	V23, V62, V110, V166, V127	6.4
5	3	D	0.0726	Artificially drained Poor-draining	V10, V29, VS41A, VS36A, S24, V136, VA12, CAI, R07, PO-36, V45	14.5
6	4	C	0.0726	Moderate draining	VA10, V67, V153, V149, V4, V111, V5, V85, V2, C108, 148A	13.7
7	4	C	0.0263	Moderate draining	V91, V119, V106, V170, V115	3.5
8	5	B	0.0344	Free-draining	V32, ES9, V101, V18, V51, V155, V31	17.9
9	5	B	0.0263	Free-draining	V65, V122, V22, VA2, V56, VA16, V68, V3, V114, V17, V124, S23, V15	19.4
10	5	A	0.0225	Excessive-draining	V89, R29	1.3

[1] Hydrologic soil group based on the USDA (1986); [2] K factor: soil erodibility factor for the Revised Universal Soil Loss Equation (RUSLE).

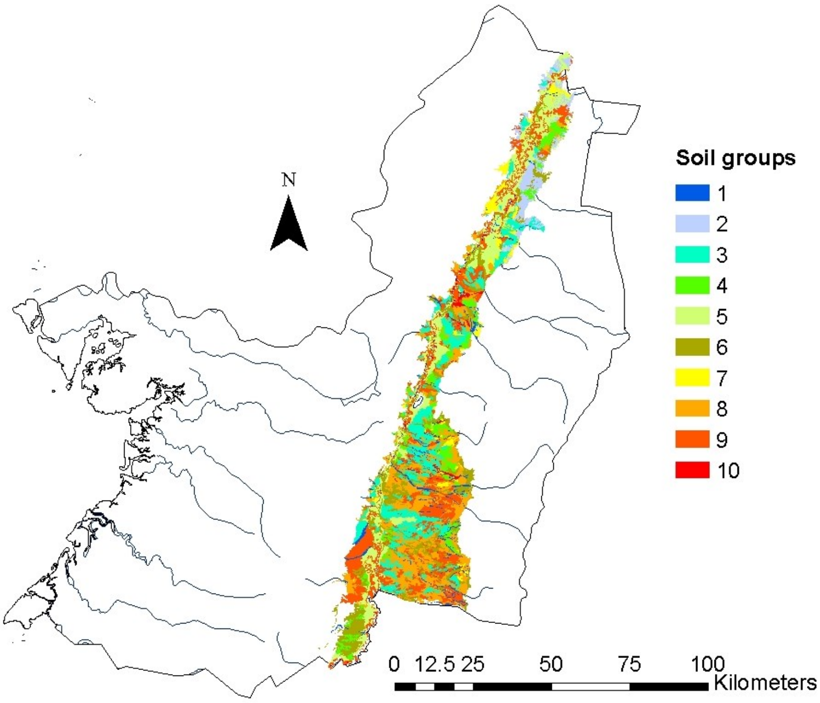


Figure 5-10 Spatial distribution of the soil groups along the geographical valley of the River Cauca in the Valle del Cauca department. The administrative area of the Valle del Cauca department and the rivers are also included.

AnnAGNPS requires detailed information about soil properties, but the available information for the soil series in the Valle del Cauca only consists of a general description of the soil draining characteristics, soil structure, texture class, soil depth and pH (CVC, 2003). For this reason, it was necessary to estimate those parameters that were not available:

- The percentages of clay, silt and sand were estimated as the midpoint value of the USDA soil textural class triangle using the texture class information for the soil group.
- Reported values of organic matter content for each municipality in the Valle del Cauca (Ramirez, 1983) were used to estimate this parameter for each soil group by identifying the main soil present in each area. Values of organic matter content for deeper horizons were estimated by applying multiplication factors to the value of top horizon; 0.25 (2nd horizon), 0.1 (3rd horizon), 0.05 (4th horizon) and 0.01 (5th and deeper horizons).
- The bulk density for the top soil layer was estimated using a regression model from a study in the coffee region of Colombia (located to the north of the Valle del Cauca) which related the bulk density to the organic carbon content with a coefficient of determination of 0.69 (Salamanca and Sadeghian, 2005). For deeper horizons, a fixed value of 1.3 g/cm^3 was used for the upper subsoil and then for the following horizons the bulk density was increased by 0.1 g/cm^3 up to a maximum value of 1.6 g/cm^3.
- The field capacity, wilting point and saturated hydraulic conductivity were estimated using pedotransfer functions from the SOILPAR2 model (Acutis and Donatelli, 2003). The British Soil Survey topsoil and subsoil LEACH functions (Hutson and Wagenet, 1992) were used to estimate the field capacity at -300 kPa and the wilting point at -1500 kPa, and the Jabro (1992) method was used for the saturated hydraulic conductivity.

The resulting soil input data are presented in Table 5-6.

Tile drainage information in the model was supplied for the soils that were reported to be artificially drained in the valley (CVC, 2003). The daily drainage rate was set to 20 mm and the drain depth to 1.50 m according to the drainage information for sugarcane which states that the water table should be reduced to between 1.20 and 1.80 m depending on the soil type and the nature of the aquifer (Cruz, 1995).

Table 5-6 Soil properties used in the AnnAGNPS model.

Depth (cm)	Layer depth (mm)	Texture class	Clay (%)	Silt (%)	Sand (%)	Bulk density (g/cm^3)	Saturated conductivity (mm/h)	Field capacity at 300 kPa	Wilting point at 1500 kPa	pH*	Organic matter %	Soil structure code*
Group 1												
0-33	330	silt loam	14	63	23	1.301	66.26	0.35	0.17	6.2	4	3
33-50	500	sandy loam	10	25	65	1.400	5.35	0.24	0.12	6.9	1	3
50-61	610	loam	20	40	40	1.500	0.81	0.30	0.16	7.3	0.4	3
61-160	1600	silt loam	14	63	23	1.600	0.60	0.31	0.15	7.6	0.2	4
Group 2												
0-16	160	sandy loam	10	25	65	1.340	131.80	0.27	0.13	5.9	3.6	4
16-54	540	sandy clay loam	26	17	57	1.400	2.32	0.30	0.18	7.1	0.9	4
54-70	700	sandy loam	10	25	65	1.500	2.27	0.23	0.12	7.9	0.36	4
70-103	1030	sandy clay loam	26	17	57	1.600	0.89	0.29	0.18	8.2	0.18	3
103-150	1500	sandy clay loam	26	17	57	1.600	0.64	0.29	0.17	7.4	0	3
Group 3												
0-28	280	clay loam	34	34	32	1.320	33.53	0.39	0.23	7.0	3.8	4
28-52	520	clay	50	25	25	1.400	12.02	0.43	0.28	7.7	0.95	2
52-94	940	clay loam	34	34	32	1.500	4.90	0.36	0.22	8.2	0.38	2
94-125	1250	clay loam	34	34	32	1.600	1.68	0.36	0.22	8.4	0.19	2
125-150	1500	loam	20	40	40	1.600	0.90	0.30	0.16	8.5	0	2
135-150	1500	sandy clay loam	26	17	57	1.600	1.36	0.29	0.17	7.3	0	3

* (CVC, 2003)

Table 5-6 (cont.) Soil properties used in the AnnAGNPS model.

Depth (cm)	Layer depth (mm)	Texture class	Clay ratio	Silt ratio	Sand ratio	Bulk density (g/cm^3)	Saturated conductivity (mm/h)	Field capacity at 300 kPa	Wilting point at 1500kPa	pH*	Organic matter ratio	Soil structure code*
Group 4												
0-35	350	clay	50	25	25	1.320	28.25	0.45	0.29	6.1	3.8	3
35-61	610	clay	50	25	25	1.400	12.02	0.43	0.28	6.6	0.95	3
61-83	830	clay	50	25	25	1.500	4.13	0.42	0.28	6.9	0.38	3
83-135	1350	clay	50	25	25	1.600	1.42	0.41	0.28	ND	0.19	4
135-150	1500	sandy clay loam	26	17	57	1.600	1.36	0.29	0.17	7.3	0	3
Group 5												
0-20	200	clay	50	25	25	1.330	25.39	0.44	0.29	4.9	3.7	3
20-35	350	clay	50	25	25	1.400	12.02	0.43	0.28	5.6	0.925	3
35-62	620	clay	50	25	25	1.500	4.13	0.42	0.28	6.0	0.37	3
62-95	950	clay	50	25	25	1.600	1.42	0.41	0.28	5.7	0.185	3
95-145	1450	clay	50	25	25	1.600	0.49	0.41	0.27	6.3	0	2
Group 6												
0-15	150	clay	50	25	25	1.350	20.50	0.44	0.29	6.0	3.5	3
15-35	350	clay	50	25	25	1.400	12.02	0.43	0.28	6.2	0.875	3
35-62	620	clay	50	25	25	1.500	4.13	0.42	0.28	7.0	0.35	4
62-80	800	clay	50	25	25	1.600	1.42	0.41	0.27	6.6	0.175	4
80-110	1100	clay	50	25	25	1.600	0.49	0.41	0.27	6.7	0	2

* (CVC, 2003)

Table 5-6 (cont.) Soil properties used in the AnnAGNPS model.

Depth (cm)	**Layer depth (mm)**	**Texture class**	**Clay ratio**	**Silt ratio**	**Sand ratio**	**Bulk density (g/cm^3)**	**Saturated conductivity (mm/h)**	**Field capacity at 300 kPa**	**Wilting point at 1500kPa**	**pH***	**Organic matter ratio**	**Soil structure code***
Group 7												
0-20	200	clay loam	34	34	32	1.320	33.53	0.39	0.23	6.4	3.8	3
20-53	530	clay	50	25	25	1.400	12.02	0.43	0.28	6.9	0.95	4
53-80	800	clay	50	25	25	1.500	4.13	0.42	0.28	7.4	0.38	3
80-125	1250	clay	50	25	25	1.600	1.42	0.41	0.28	7.2	0.19	3
125-150	1500	clay	50	25	25	1.600	0.49	0.41	0.27	ND	0	ND
Group 8												
0-30	300	loam	20	40	40	1.340	42.33	0.34	0.18	7.5	3.6	3
30-50	500	loam	20	40	40	1.400	22.30	0.32	0.17	8.1	0.9	4
50-75	750	silt loam	14	63	23	1.500	7.82	0.32	0.15	8.4	0.36	4
75-110	1100	silt loam	14	63	23	1.600	2.69	0.31	0.15	8.2	0.18	4
110-140	1400	loamy sand	3	17	80	1.600	14.30	0.19	0.08	8.2	0	2
Group 9												
0-50	500	clay loam	34	34	32	1.330	30.13	0.39	0.23	7.0	3.7	3
50-80	800	clay loam	34	34	32	1.400	4.90	0.37	0.22	7.5	0.925	4
80-105	1050	loam	20	40	40	1.500	2.63	0.31	0.16	7.8	0.37	2
105-150	1500	clay loam	34	34	32	1.600	0.58	0.35	0.22	7.9	0.185	3
Group 10												
0-26	260	sandy loam	10	25	65	1.381	85.99	0.27	0.13	7.1	3.2	3
26-65	650	sandy loam	10	25	65	1.400	69.45	0.25	0.12	ND	0.8	3
65-100	1000	sandy loam	10	25	65	1.500	23.86	0.24	0.12	ND	0.32	3

* (CVC, 2003)

5.3.4.3 Land parameters

A land use map from 2011 (Figure 5-11) showed that the main land uses in the geographical valley (flat area) were grass, sugarcane, maize, sorghum and urban areas accounting for 88.7% of land in the valley (Table 5-7). These land uses were selected to be included in the simulation and the rest were treated as either grass in the case of other crops or urban areas in the case of any developed land. The areas not covered by the land use map in the model were also treated as grass since most of the relevant crops are located in the geographical valley.

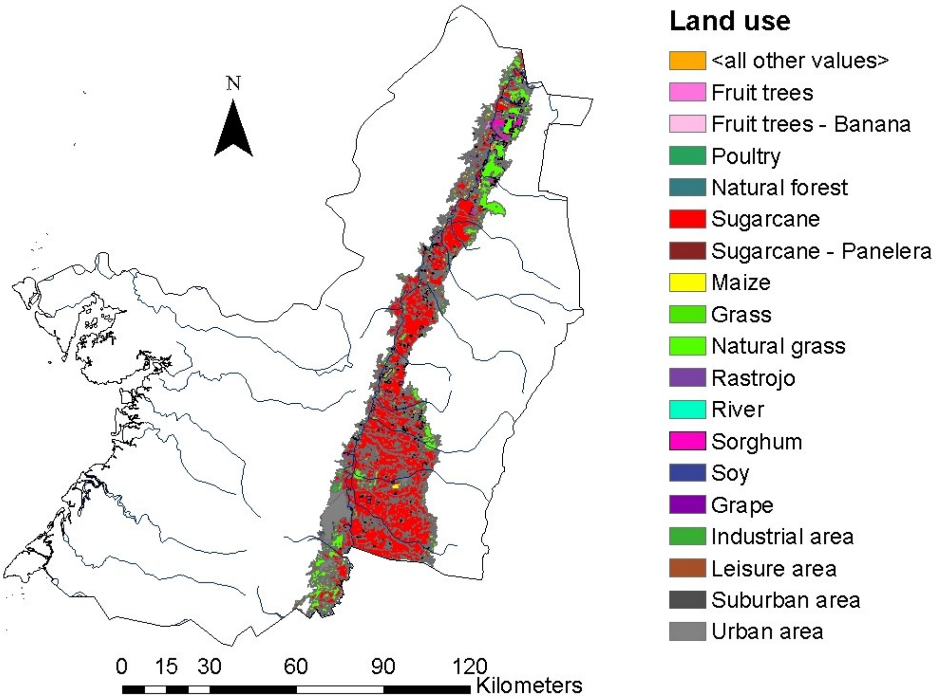


Figure 5-11 Land use map from the geographical valley of the River Cauca (adapted from CVC (2011a)). The administrative area and rivers of the Valle del Cauca department and the rivers are also included.

Table 5-7 Main land uses in the geographical valley of the River Cauca and in the simulated area.

Land use	Valley area		Simulated area	
	(ha)	(%)	(ha)	(%)
Natural grass	329,494	38.2	649,987*	75.2*
Sugarcane	211,807	24.5	168,715	19.5
Urban area	124,530	14.4	21,361	2.5
Grassland	46,017	5.3	-	-
Maize	28,878	3.3	9,597	1.1
Sorghum	26,182	3.0	14,139	1.6

*Area simulated as grassland in the model

Crop parameters

The crops simulated included sugarcane, maize and sorghum. There is normally one crop of sugar cane per year whereas two full cropping cycles are possible for maize and sorghum. Sugarcane can be sown at any time during the year, so it is common to find sugarcane crops at different growth stages along the valley. Maize and sorghum are usually sown at the beginning of the two rainy seasons; the first sowing occurs in April – May, and the second in August – September (Campuzano and Navas, 2005). Crop growth parameters were derived from FAO information on lengths of crop development stages for various planting periods and for tropical climatic regions (Table 5-8) (Allen et al., 1998). Root mass, canopy cover and canopy droplet fall height data for every 15 days after planting until harvest were taken from the USDA RUSLE handbook (Table A5– 1) (Renard et al., 1997).

Table 5-8 Data of accumulated growth fraction of time used in the model (Allen et al., 1998).

Crop	Duration (days)	Initial	Development	Mature
Sugarcane	320	0.08	0.22	0.72
Maize	125	0.16	0.44	0.76
Sorghum	130	0.16	0.44	0.76

Non-crop parameters

Non-crop land uses in the model included grass (pasture) and constructed areas (urban areas). The parameters used in the model are shown in Table 5-9.

Table 5-9 Non-crop parameters used in the model.

Parameter	Pasture*	Urban areas
Annual root mass (kg/ha)	403	0
Annual cover ratio (fraction)	0.9	0
Annual rain fall height (m)	0.488	0
Rock cover (%)	0	100

*(Renard et al., 1997)

5.3.4.4 Irrigation

Crop irrigation is routinely practiced in the Cauca valley, especially during seasons with low rainfall. Irrigation varies with crop stage and field capacity of the soil (Torres, 1995). When sugarcane sowing takes place during the dry season, irrigation is initially (during germination) carried out by sprinkling irrigation and in some cases by gravity. Irrigation of sugarcane usually takes place between months 2 to 10. During the maturation stage of the crop it is recommended to stop irrigation.

Water for irrigation is usually extracted from groundwater with secondary sources being streams, lakes and rivers. A common practice is to build water reservoirs to store the water; water is then conducted to the fields by using superficial canals. In this region, irrigation is generally conducted through altering furrows, stopping the water before the advancing front reaches the furrow end (Torres, 1995). This irrigation method minimizes the amount of water applied, irrigation costs and water losses by deep percolation; the method also reduces the leaching of agrichemicals below the root zone (Eisenhauer and Benham, 1998).

In the model, crop irrigation was adjusted to automatic applications using an alternating blocked-end furrow irrigation method. Automatic irrigation was triggered depending on the specified soil moisture depletion limits and soil parameters such as field capacity and wilting point in the top 1 m of soil (Bingner et al., 2011). The lower and upper limits for soil moisture depletion for automatic irrigation scheduling to start and stop divided by the soil moisture at field capacity were set to 0.11 and 0.21, respectively. These values were selected according to the tabulated values for soil textures (Andales et al., 2009), clay (lower limit) and loam (upper limit) because these are the maximum and minimum values for the different texture classes that are present in the catchment.

5.3.4.5 Runoff curve numbers

Runoff curve numbers were supplied to the model for four cover types: cropped, bare soil, pasture and develop areas. Values proposed by the USDA (1986) for the cover types according to their practice or treatment and hydrological condition were initially assigned to each land use. Curve numbers for straight row crop with good hydrological conditions were used for the crops, fallow information for bare soil, pasture with fair hydrological conditions for grassland and commercial/business curve numbers for the developed areas (Table 5-10).

Table 5-10 Runoff curve number data used in the model (USDA, 1986).

Hydrologic group	**Crop**	**Pasture**	**Fallow**	**Developed**
A	67	49	77	89
B	78	69	86	92
C	85	79	91	94
D	89	84	94	95

5.3.4.6 Pesticide parameters

Physicochemical information for atrazine and simazine was mostly taken from AERU (2007). The suggested field-based half-lives in soil were used for both triazines. Atrazine and simazine were simulated as pre-emergence applications to maize and sorghum on 1st May and 1st September. Application rates in the model were adjusted to the central value of the annual recommended range of application rates on the product labels (1.20 kg a.i/ha/year in maize and sorghum and 3.84 kg a.i ha^{-1} $year^{-1}$ in sugarcane) (Inveragro, 2013; Nufarm, 2012; Calister, 2011; Proficol, 1991, 1979). For maize and sorghum an application rate of 0.30 kg a.i/ha of each herbicide was assumed for each application date, assuming that each compound was used at full rate on 50% of the total crop area.

Sugarcane sowing occurs at any time throughout the year, making it difficult to simulate when pesticide applications will take place. Assuming that new sugarcane crops can be planted in different areas along the catchment every month, this frequency of application was used in the model. Therefore, application rate of each pesticide used in the model was 0.32 kg a.i/ha/month.

Table 5-11 Physicochemical properties for atrazine and simazine used in the model (AERU, 2007).

Physicochemical property	**Atrazine**	**Simazine**
Solubility (mg l^{-1})	35	5
K_{oc} (ml g^{-1})	100	130
DT_{50} in soil (days)	29 (field)	27 (field)
DT_{50} in water (days)	86	96

5.3.5 Calculation of the stream flow and baseflow in the study area

Since the study area did not cover the river source (Figure 5-1), the model would simulate less stream flow than the one observed at the catchment outlet. In order to be able to compare the simulated flow to the measured data, it was necessary to first calculate the stream flow generated only from the study area by subtracting the flow from upstream of the study area from the measured flow at the catchment outlet. The observed baseflow from the study area was also estimated by hydrograph separation from the calculated stream flow. Since the model does not simulate the baseflow, the observe baseflow had to be added to the simulated runoff in order to calculate the total stream flow. A more detailed explanation of these calculations is described below.

5.3.5.1 Stream flow

Flow data used to calculated the observed flow in the study area included measured stream flow from a station upstream (La Balsa station W 76°35'36.8", N 03°05'10.9"; see the location in Figure 5-6), near the simulated inlet (Puerto Hormiguero), and at the catchment outlet (Anacaro station) (CVC, 2011b, c). It was estimated that stream water from La Balsa would take approximately three days to reach the catchment outlet in Anacaro; based on an average velocity value of 1.30 m/s in this stream section and a river length of 400.5 km (CVC and Univalle, 2001). Therefore, the equation to calculate the total stream flow at the outlet of the study area ($Flow_{catchment,\ day\ n}$) in m^3/s was:

Equation 5-3 $$Flow_{catchment,day_n} = Flow_{outlet,day_n} - Flow_{inlet,day_{n-3}}$$

where $Flow_{outlet,\ day\ n}$ was the measured flow at catchment outlet (Anacaro station) on the day n and $Flow_{inlet,\ day\ n\text{-}3}$, the inlet measured flow in m^3/s (La Balsa station) three days before n.

5.3.5.2 Baseflow

After calculating the flow for the studied area, the baseflow was estimated by hydrograph separation. The web-based hydrograph analysis tool (WHAT) (Lim et al., 2005) was used for this purpose by applying the Eckhardt digital filtering method (Eckhardt, 2005). This is a relatively new but widely used method of hydrograph analysis which uses two parameters: the filtering parameter (α) and the maximum value of long-term ratio of baseflow to total stream flow (BFI_{max}) that can be modelled by the digital filter algorithm (Equation 5-4) (Eckhardt, 2005; Arnold et al., 1995).

Equation 5-4 $$Q_{b,t} = \frac{(1-BFI_{\max})\cdot\alpha\cdot Q_{b,t-1}+(1-\alpha)\cdot BFI_{max}\cdot Q_{s,t}}{1-\alpha\cdot BFI_{max}}$$

where, the baseflow at time *t* and *t-1* are $Q_{b,t}$, $Q_{b,t-1}$ in m^3/s, respectively; $Q_{s,t}$ (m^3/s) is the stream flow at time *t* (day) (Eckhardt, 2005).

The parameter α can be easily determined with a recession analysis of the stream flow (Eckhardt, 2005). The recession analysis focuses at the recession curves which correspond to the periods when the flow decreases after the stream flow reaches a peak or after a rainfall event. A correlation method (Langbein, 1938) was chosen for the analysis where multiple recession curves were selected and a graph of the flow (Q_o) against the flow at some fixed time (Q) was plotted for all recession periods. Finally, the recession constant α was related to the slope of a straight line fitted from the origin above the upper envelope of the scatter plot (Sujono et al., 2004; Troch et al., 1993; Nathan and Mcmahon, 1990; Zecharias and Brutsaert, 1988; Beran and Gustard, 1977; Knisel, 1963; Linsley, 1958) and rearranging Equation 5-5 (Sujono et al., 2004).

Equation 5-5 $$\boldsymbol{\alpha} = \left(\frac{\boldsymbol{Q}}{\boldsymbol{Q_0}}\right)^{\boldsymbol{1/t}}$$

All the recession curves between 2010 and 2011 for Anacaro station were used in the analysis and then plotted against the flow on the day before. The filter parameter α is the slope of the curve (Eckhardt, 2005).

The parameter BFI_{max} is dependent on the local hydrogeological conditions but it is a non-measurable parameter. Eckhardt (2012) calculated mean values for both parameters by analysing data from 65 catchments in North America. The recommended α and BFI_{max} parameters for a perennial stream with a porous aquifer were 0.97 and 0.80, respectively. For the selection of the BFI_{max} parameter for the studied area, different values were tested using the pre-calculated filtering value α (from the recession analysis) to undertake baseflow separations and then the BFI_{max} with the best separation result was selected. The tested BFI_{max} values for this analysis were 0.70, 0.80, and 0.90. The selected BFI_{max} for the hydrograph separation was 0.80.

5.3.6 Calculation of the simulated stream flow and pesticide concentrations

5.3.6.1 Stream flow at the catchment outlet

There is no groundwater routine in AnnAGNPS 5.41 so the model does not calculate baseflow but only runoff discharge. The simulated stream flow at the catchment outlet was calculated by adding the pre-calculated baseflow for the study area (Section 5.3.5.2) to the simulated runoff from AnnAGNPS. This simulated stream flow was used later for model evaluation.

5.3.6.2 Stream flow in other points of the catchment

Stream flow at the different monitoring stations along the River Cauca was calculated in order to estimate the pesticide concentrations for each monitoring point. This was possible because AnnAGNPS calculates the runoff at different points along the river network. For this analysis it was necessary to estimate another adjusted flow that took into account the flow from upstream of the study area (not only the flow coming from the valley to the simulated river section) so that the total stream volume could be estimated. The different stream flows ($Flow_{x,y}$) were calculated by adding the runoff flow ($Runoff_{x,y}$) to their respective baseflow ($Baseflow_{x,y}$) at each location (x,y) and the flow coming from upstream (recorded at La Balsa station) ($Flow_{inlet}$) (Equation 5-6). The baseflow for each point was calculated by an analysis of the cells and the draining area contributing to the flow at each monitoring station.

Equation 5-6 $$Flow_{x,y} = Runoff_{x,y} + Baseflow_{x,y} + Flow_{inlet}$$

5.3.6.3 Calculation of simulated pesticide concentrations

The AnnAGNPS model simulates the load of pesticide at any point of the river network. Simulations were carried out for individual pesticides (atrazine and simazine) and for both together in order to calculate the total emission of triazines. The total concentration of triazines was calculated in order to reduce the uncertainty associated with the assumption of a 50% usage of the two herbicides on the target crops. Selection between the two triazines would depend on different factors that cannot be estimated, such as market price, availability, product rotation. Pesticide concentrations were calculated from the simulated pesticide loads and the pre-calculated stream volume (Section 5.3.6.2) for each monitoring point.

5.3.7 Model evaluation

Modelling results for stream flow and pesticide concentrations were evaluated against measured values in the River Cauca in order to assess the predictive capacity and the applicability of AnnAGNPS under Colombian conditions and with constraints of the data available for the geographical valley of the River Cauca. Model calibration and validation were applied to the stream flow in two different periods of time.

5.3.7.1 Stream flow

The evaluation of the simulated stream flow followed the same methodology used in previous chapters (Sections 3.3.10, 4.3.3), which involved visual comparison of the stream flow simulation at the outlet to observed flow data, calculation of the goodness-of-fit, residuals analysis, Nash–Sutcliffe model efficiency coefficients and analysis of the observed against the simulated stream flow plot.

5.3.7.2 Model calibration and validation

Calibration of the runoff curve numbers was carried out for crop and pasture land in order to increase the simulated runoff volume. Curve numbers were first changed to poor hydrological conditions (USDA, 1986) and then adjusted by increasing their values 2% each time while checking the Nash–Sutcliffe model efficiency coefficients and the coefficient of determination (r^2) of the line of observed vs. simulated flow data for 2010 – 2011. Four sets of curve numbers were tested with an increase of 8, 10, 12 and 14% from the uncalibrated curve numbers. Validation of calibrated parameters was carried out using weather and flow data from 2008 – 2009. An increase of 10% of the curve numbers on top of changing from good to poor practice provided the best results of model calibration and validation (Table 5-12).

Table 5-12 Original and calibrated runoff curve numbers.

Hydrologic group	Uncalibrated CN		Calibrated CN	
	Crop*	Pasture*	Crop	Pasture
A	67	49	79	76
B	78	69	89	87
C	85	79	97	95
D	89	84	100	98

*USDA (1986)

5.3.7.3 Pesticide concentrations

Simulated pesticide concentrations of atrazine, simazine and total triazines for different monitoring locations along the River Cauca, including Juanchito, Puerto Isaacs, Paso de la Torre, Mediacanoa, Puente Guayabal and Anacaro stations were evaluated by comparing the modelling results to observed measured concentrations from previous studies (Section 5.2.3) (Sarria, 2014). A linear regression analysis and calculation of the Nash–Sutcliffe model efficiency coefficients were also carried out for each herbicide and total triazines. Simulated values and measurements below the LOD were treated as zero for the evaluation.

5.3.8 Uncertainty analysis

Uncertainty analyses were carried out to determine impact of assumptions for uncertain input parameters in the model.

A more refined cell simulation was used to evaluate uncertainty due to watershed resolution. The resolution was the doubled by using CSA and MSCL values of 300 ha and 1000 m, respectively, which divided the watershed into 2620 cells. Model evaluation was applied to the simulated flow data at the catchment outlet.

The uncertainty in the use of average values for degradation and sorption as input to the model was analysed following the methodology used in Chapter 4 (Section 4.3.6.3); four simulations of total triazines were run using the extreme values (maximum and/or minimum) of reported reference data for atrazine and simazine field studies. Reported degradation half-life and organic carbon partition coefficient for the herbicides ranged between 6 and 108 days and 89 and 513 ml/g, respectively (AERU, 2007).

Main uncertainties regarding pesticide usage were thought to arise from the application date and the average frequency of application in sugarcane. For the first, the model was run changing the application date to the 15th of the same months as in the original simulation. For the application in sugarcane, an average application every two months of the central value of the annual recommended range of application rate was used (i.e. 0.64 kg a.i/ha applied every two months) and compared to the original simulation (0.32 kg a.i/ha every month).

5.3.9 Analysis of the areas of risk, practices and conditions for water contamination using AnnAGNPS

The modelling results were finally used to identify areas of risk for pesticide pollution. This risk combines the effect on emissions from topography, soil type, land use and weather in the different watersheds. In addition, practices and conditions that increase pesticide contamination in the study area were analysed and some recommendations that can help reduce pesticide emissions as well as pesticide alternatives were proposed.

5.3.9.1 Areas of risk

The watersheds calculated using ArcHydro (Figure 5-5) were selected to identify the hydrological response units (HRU) that contribute most to triazine emissions. For this purpose two indicators of triazine emissions were calculated; the first was an indicator about the pesticide usage per area for each HRU and the second was about the relative emission of pesticides to the River Cauca. These indicators were calculated as follows.

Annual application of triazines per watershed area

A spatial analysis about the area of the maize, sorghum and sugarcane in each HRU was first undertaken by the interception of the calculated watersheds from ArcHydro and land use map. Then, this information along with the application rates of atrazine and simazine for each crop (Section 0) was used to calculate the total pesticide applied to each watershed in kg (*PA*) and then divided to the HRU area to estimate the total annual application of triazines in kg per hectare of each watershed (*AA*) (Equation 5-7).

Equation 5-7 $$AA = \frac{\left(\sum CA_j \times AAR_{atrazine,j}\right) + \left(\sum CA_j \times AAR_{simazine,j}\right)}{AHRU} = \frac{PA}{AHRU}$$

Where *CA* is the area of the crop *j* in ha, *AAR* is the annual application rate of atrazine or simazine in kg/ha and *AHRU* is the HRU area in ha.

Relative emission of triazines to the River Cauca

AnnANGPS calculates the cell routing in the grid map; this information along with the calculated stream network from AnnAGNPS was then used to identify the receiving cell at the boundary of each watershed (watershed inlet and outlet). The difference between the simulated pesticide load in each inlet and outlet was defined as the pesticide exported to the River Cauca in kg (*PE*); then this amount was divided by the annual pesticide application in kg (PA) and multiplied by 100% to calculate the percentage of relative pesticide exported to the river (RPE) (Equation 5-8).

Equation 5-8 $$RPE = \frac{PE}{PA} \times 100\%$$

5.3.9.2 *Practices and conditions*

A way of reducing pesticide emissions was thought to be by improving drainage conditions in the catchment which would decrease the runoff curve numbers and reduce the pesticide losses by runoff. This was tested to determine the reduction in pesticide emissions. Calibrated curve numbers were reduced for the studied crop covers to their values corresponding to good hydrological conditions (USDA, 1986) but keeping the additional 10% from the calibration process.

5.3.9.3 *Alternative to triazine pesticides*

Available alternatives to triazine were investigated and simulated in order to calculate pesticide losses and compare them to the simulated triazine emissions. The tested alternative was mesotrione, a triketone used as a pre-emergence herbicide and applying the maximum annual recommended application rates to avoid weed resistance: 0.27, 0.22 and 0.37 kg a.i/ha to maize, sorghum and sugarcane, respectively (Syngenta, 2012). Dyson et al. (2002) showed the big correlation of mesotrione adsorption and degradation to soil pH and organic carbon content. Paired half-life and K_{oc} values reported for a clay loam soil with pH 7.1 and 3.3% of organic carbon were used in the simulation (Table 5-13). Table 5-13 shows the pesticide reference data used in the model. Mesotrione has similar sorption behaviour to atrazine and simazine but its degradation half-life is considerably smaller.

Table 5-13 Physicochemical properties of mesotrione used in the model compared to atrazine and simazine data (AERU, 2007).

Physicochemical property	Atrazine	Simazine	Mesotrione
Solubility (mg l^{-1})	35	5	160
K_{oc} (ml g^{-1})	100	130	33*
DT_{50} soil (days)	29 (field)	27 (field)	4.5* (field)
DT_{50} water (days)	86	96	5.3

*Dyson et al. (2002)

5.4 Results

5.4.1 Calculation of the stream and baseflow in the study area

5.4.1.1 Stream flow

The observed stream flow accounting for only flow in the study area is presented in Figure 5-12 along with the upstream (La Balsa) and downstream (Anacaro) flow. The flow at the catchment outlet over the whole period comprised 63% generated within the study catchment and 37% from upstream areas not simulated by the model. This flow was then used to calculate the baseflow in the catchment and to undertake model evaluation of the simulated stream flow.

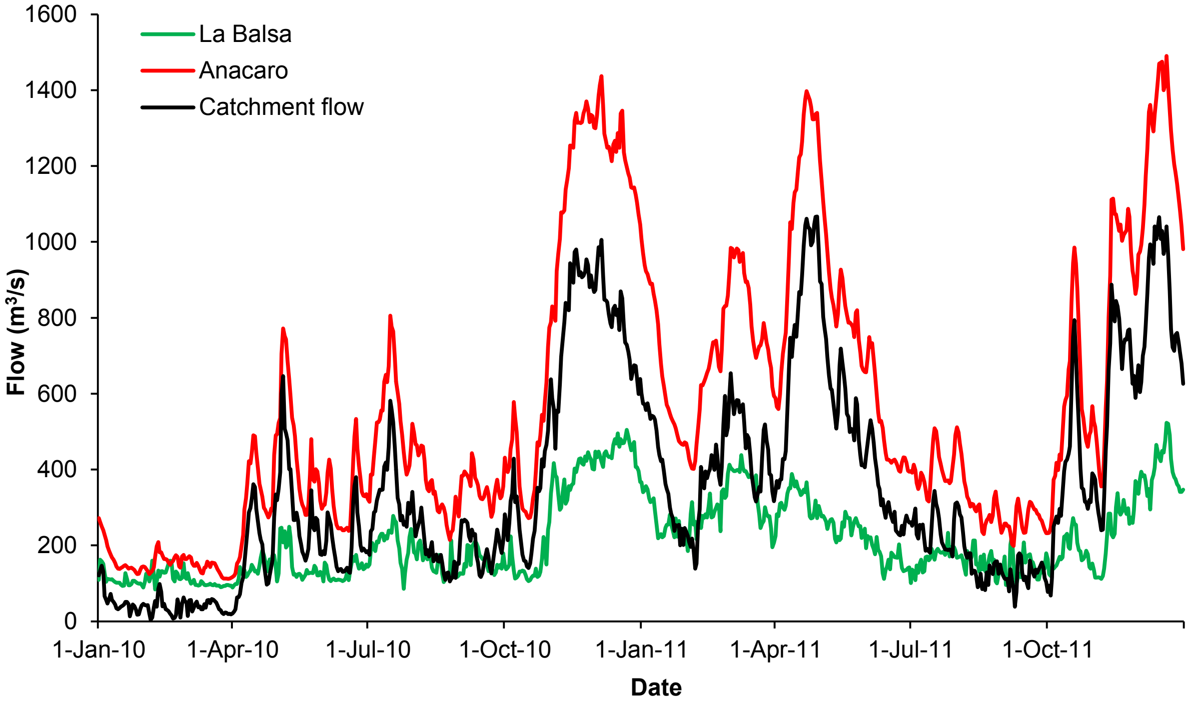


Figure 5-12 Observed stream flow in the study area for 2010 and 2011.

5.4.1.2 Baseflow

The filter parameter α was calculated to have a value of 0.9983 which is equivalent to the recession constant calculated from the slope of the recession analysis for Anacaro station (Figure 5-13). This filter parameter was then used to calculate the baseflow applying hydrograph separation to the outlet flow along with three tested BFI_{max} values, including the recommended value of 0.80, in order to select the best parameter to estimate baseflow. Figure 5-14 shows the three baseflow calcultions alongside the measured flow. It is observed that a BFI_{max} of 0.80 best separates the baseflow. The values of 0.70 and 0.90

clearly tended to under- and over-estimate the baseflow, respectively, particularly for periods of high flow such as from October to December 2010 and February to May 2011.

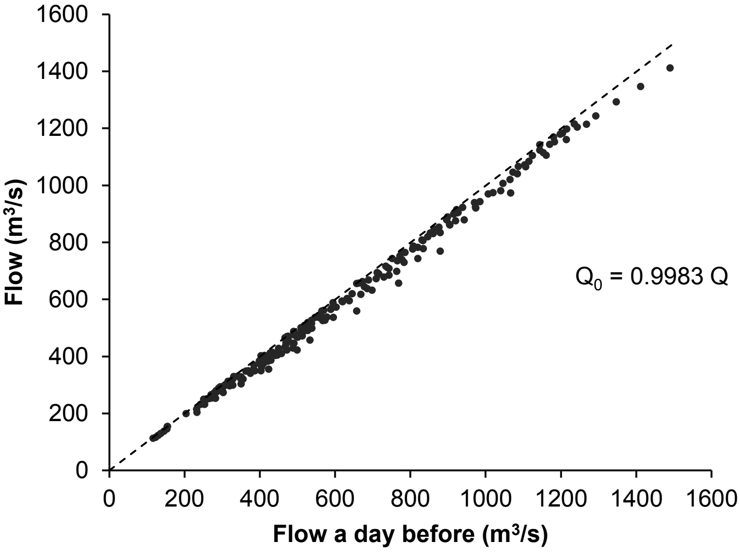


Figure 5-13 Plot of flow (Q_0) against the flow on the day before (Q) at Anacaro station together with the line fitted from the origin through the upper envelope and the regression equation. The slope corresponded to the recession constant.

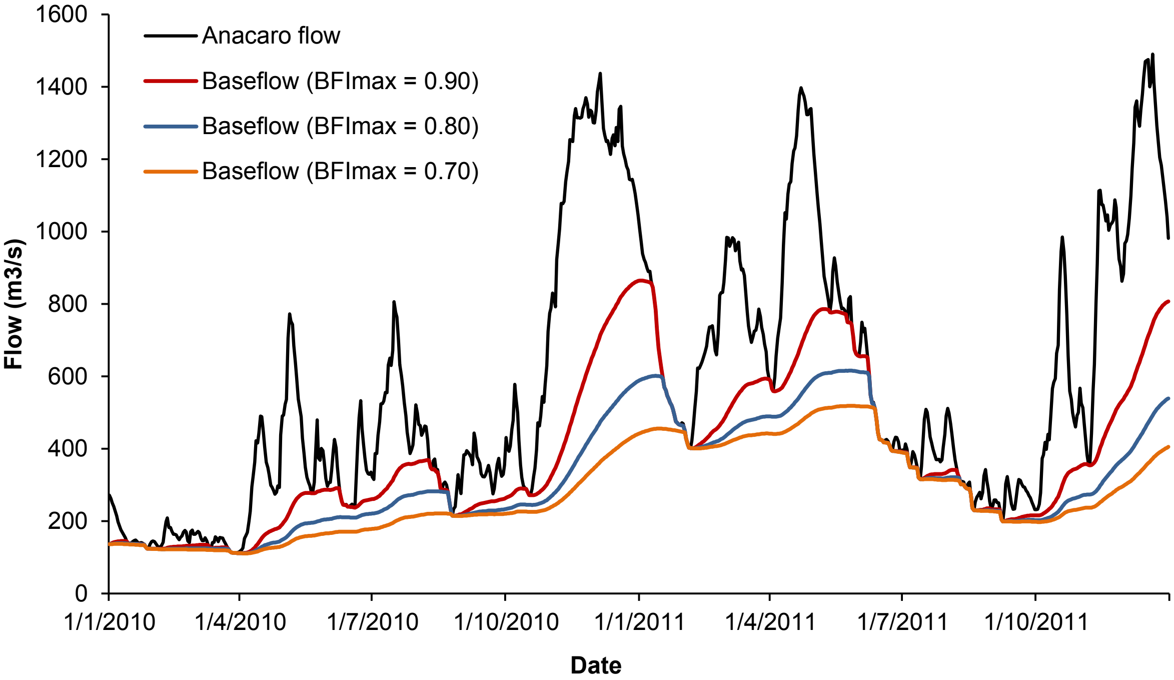


Figure 5-14 Flow at Anacaro and baseflow curves calculated by hydrograph separation using BFI_{max} values of 0.90, 0.80 and 0.70 and a filter parameter α of 0.9983.

5.4.2 Uncalibrated stream flow at the catchment outlet

The simulated stream flow at the outlet of the study area was initially calculated without any calibration by adding the estimated baseflow to the simulated runoff by AnnAGNPS. A comparison between simulated and observed flow (Figure 5-15) shows that the model tended to under-estimate the flow, particularly during periods of very high flow (more than 400 m^3/s); for example, during the highest flow occurring from October 2010 to January 2011, from February to June 2011 and October to December 2010, the discrepancy was up to a factor of two. Despite this disagreement in the magnitude of the peaks, a good agreement was observed in the general shape and timing of the peaks as well as in the baseflow behaviour observed during periods of lowest flow (e.g. January to April 2010, middle of June to October 2011 and the end of January to the beginning of February 2011). These results showed that the under-estimation was mainly due to the simulation of peak runoff and hence that model calibration should be applied. Despite under-estimation in the flow, a fairly good Nash–Sutcliffe model coefficient (0.50) was obtained.

A linear regression analysis of the observed against the simulated uncalibrated stream flow (Figure 5-16) showed that as the simulated flow increased more dispersion in the results was observed around the fitted line and most of the values were located below the 1:1 line causing the fitted line to have a lower slope (0.51) which is a consequence of the large under-estimation of runoff during periods of great flow; however, there is a good linear correlation between the simulated and the observed flow ($r^2 = 0.73$).

Discrepancy in the stream flow simulation was also reflected on the residuals which showed a non-random pattern (sinusoidal) throughout most of the simulation with mainly positive values due to flow under-estimation (Figure 5-17).

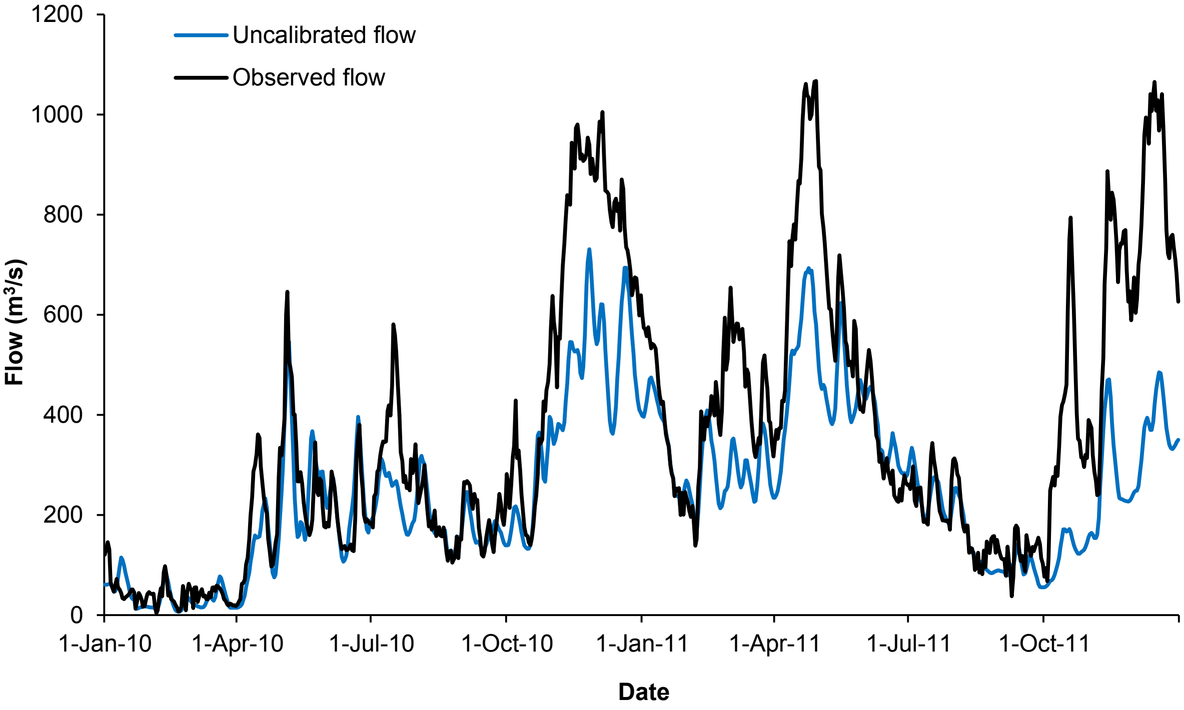


Figure 5-15 Comparison of the observed and simulated stream flow in the study area.

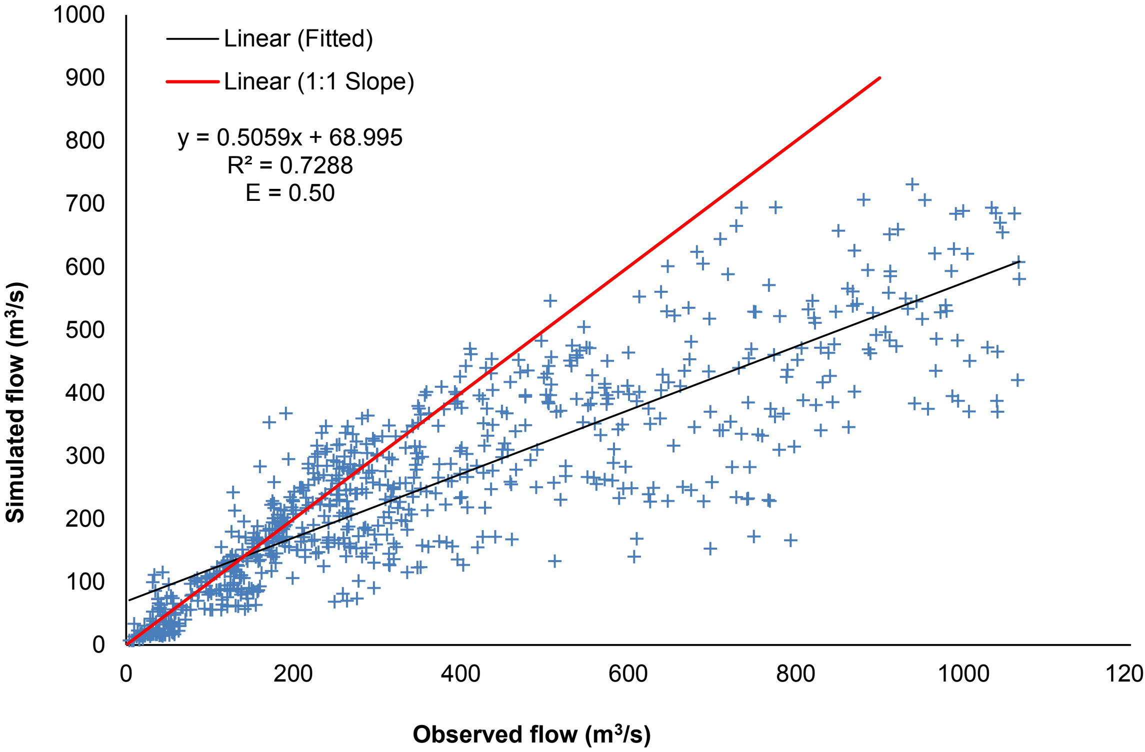


Figure 5-16 Plot of simulated versus observed flow together with the one-to-one line slope (red line) and the linear fit (black line) for the uncalibrated simulation. The plot also shows the equation fitted to the linear model, the coefficient of determination and the Nash–Sutcliffe model efficiency coefficient.

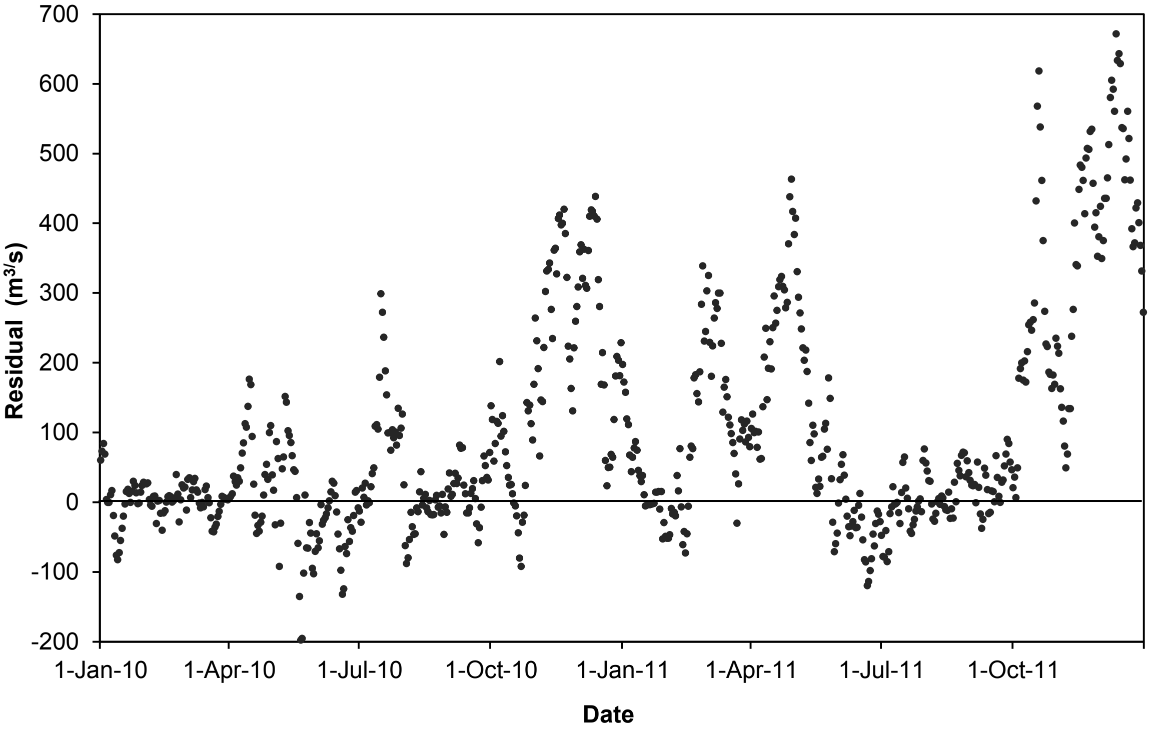


Figure 5-17 Plot of residuals for the uncalibrated simulation of the water flow using AnnAGNPS.

5.4.3 Model calibration

The runoff curve numbers were calibrated in order to increase the runoff flow and reduce the level of under-estimation in the simulation. Table 5-14 shows the resulting Nash–Sutcliffe model efficiency coefficients (*E*) and the coefficient of determination (r^2) of the observed against the simulated flow for each adjustment of the curve numbers. The *E* values gradually improved until the curve numbers were increased by 16%, when a reduction in E was observed. The best *E* value was observed for an increase of the CN by 14% (E = 0.71). In addition, a faster decrease in the value of *E* was observed for initial increments in the CN but then the incremental improvements became smaller; for example, when increasing from 8 to 10% an improvement of 11.5% was observed but when adjusting from 12 to 14%, *E* only increased by 0.3%. Similarly for the coefficients of determination, values initially increased with each increment in CN, however, when the CN were increased by 10%, r^2 started to decrease. The best r^2 was achieved when increasing the CN by 8%. For these reasons, an increment of 10% in the CN was decided to be the best calibration of the stream flow. However, in order to confirm this selection, model validation was applied to the CN for increments between 8 and 14% (Section 5.4.4).

Table 5-14 Nash–Sutcliffe model efficiency and the coefficient of determination (r^2) of the observed vs. simulated flow for each increment in CN from the model calibration. The highlighted cell shows the best CN for model calibration.

CN increment (%)	E	r^2
0 (uncalibrated)	0.498	0.7288
2	0.570	0.7263
4	0.582	0.7286
6	0.598	0.7303
8	0.624	0.7324
10	0.696	0.7268
12	0.706	0.7202
14	0.708	0.7110
16	0.677	0.6930

The effect of the model calibration is shown in Figure 5-18; there is a general increase in the simulated flow that improved the agreement to the observed flow in periods of moderate and low flow. The model calibration also reduced the flow for periods where discrepancy between measured and simulated flow was very high, but there is still some under-estimation particularly between October and December 2011 by up to a factor of 1.7. In addition, model calibration generated some over-estimation during periods of low and moderate flow for example over-estimation from May to June 2010 was by up to a factor of 1.3.

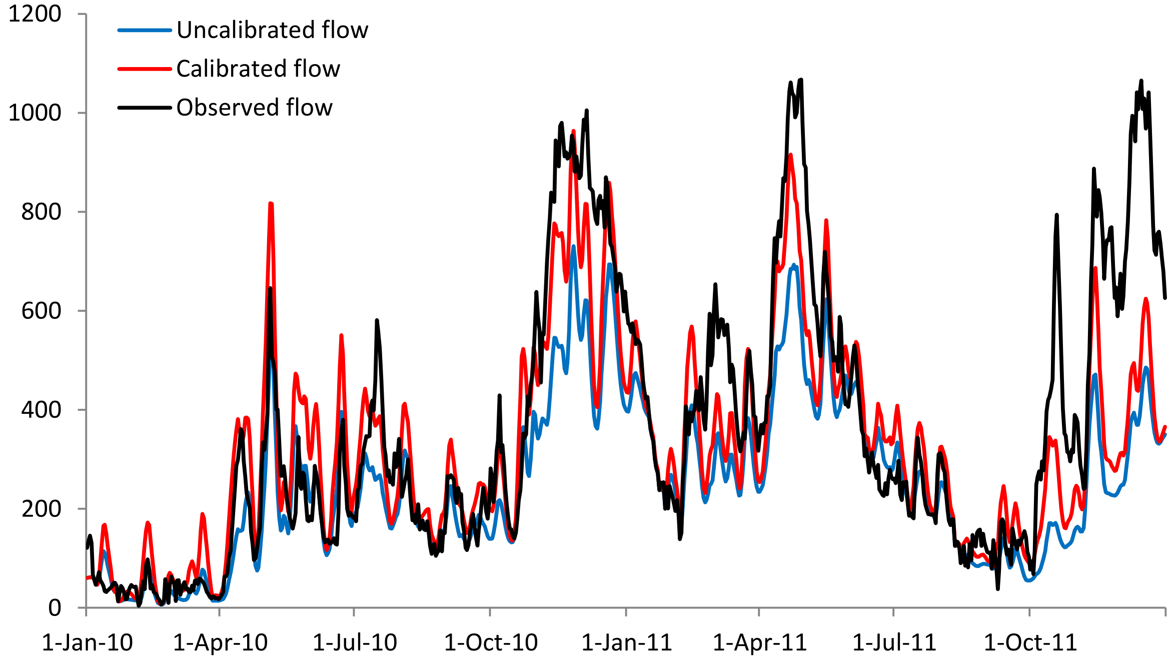


Figure 5-18 Effect of model calibration in the simulated flow (calibrated against uncalibrated flow) compared to the observed flow.

Compared to the uncalibrated simulation, the linear regression of the observed against the simulated (calibrated) stream flow showed a better agreement between values; which was reflected by an increase of 25% in the slope value (Figure 5-19). However, some dispersion was still observed around the fitted line for periods of high flow where runoff remained under-estimated. The r^2 for the calibrated simulation (0.73) was similar to the uncalibrated one (0.73).

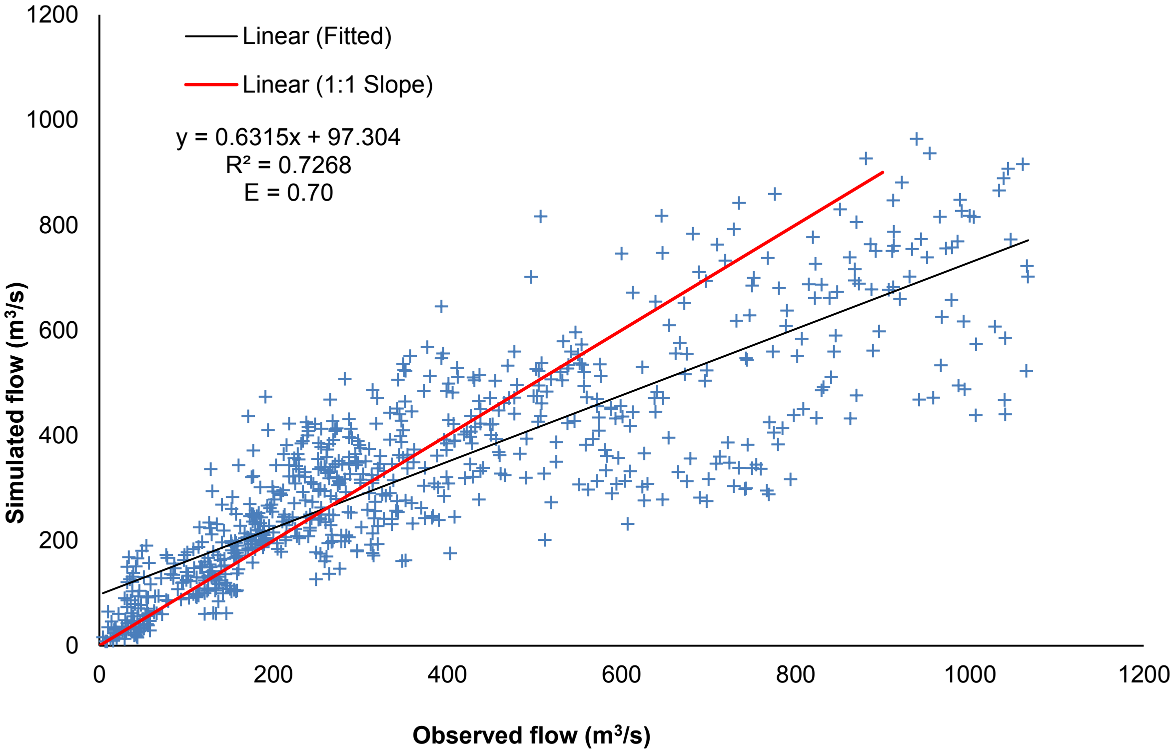


Figure 5-19 Plot of simulated versus observed flow together with the one-to-one line slope (red line) and the linear fit (black line) for the calibrated simulation. The plot also shows the equation fitted to the linear model, the coefficient of determination and the Nash–Sutcliffe model efficiency coefficient.

Model calibration greatly improved the residuals for 2010 (Figure 5-20). A reduction in the magnitude and the number of positive residuals was also observed for periods of high under-estimation; however, some sinusoidal patterns were still observed in 2011 due to under-estimation for very high flow periods (from February to May 2011 and October to December 2011).

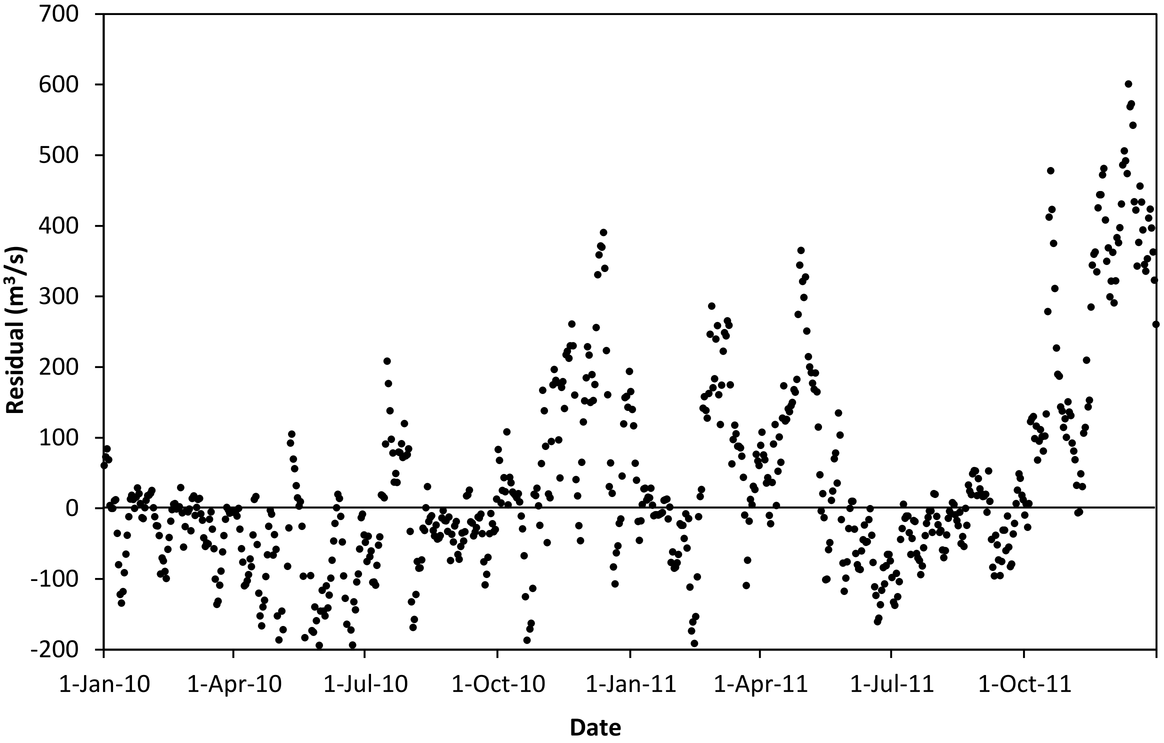


Figure 5-20 Plot of residuals for the calibrated simulation of the water flow using AnnAGNPS.

5.4.4 Model validation

Model validation was carried out against independent data by the simulation of stream flow from 2008 to 2009 using both the optimal CN (10% increase) and also checking that selection trough simulations with CN increased by 8, 12 and 14%. Table 5-15 shows the resulting E and r^2 for the validation for the selected CN; calculated statistics were generally smaller than when applying model calibration, in contrast to the behaviour when applying model calibration, E and r^2 started to decrease in the same CN value (CN + 12%). This confirms that the best simulation was achieved with an increase of the CN by 10% for model calibration (E = 0.63 and r^2 = 0.64).

Table 5-15 Resulting Nash–Sutcliffe model efficiency and the coefficient of determination (r^2) of the observed vs. simulated flow for each increment in CN from the model calibration; highlighted cells show the best result.

CN increment (%)	E	r^2
8	0.564	0.6227
10	0.629	0.6365
12	0.614	0.6265
14	0.572	0.6149

The simulated hydrograph, for the period 2008 – 2009, for model validation using the calibrated curve numbers (CN + 10%) is compared to the observed flow in Figure 5-21. A generally good agreement in the pattern, timing and magnitude of the peaks was observed throughout the simulation. Less under-estimation was generally obtained compared to the calibrated simulation between 2010 and 2011 (Figure 5-18). Period of under- and over-estimation of the flow were observed along the simulation period. Under-estimation occurred between February and April 2008 as well as between November and January 2008 up to a factor of 1.4 and over-estimation was observed for high flow periods in 2008 by up to a factor of 1.6 (from April to May, middle of June to July and August). The linear regression of the observed against the simulated flow for the period 2008 – 2009 (Figure 5-22) showed an increase in the slope value (0.69) compared to the calibrated simulation (0.63) for 2010 – 2011 (Figure 5-19) which was a consequence of the smaller level of under-estimation and better agreement to the observed flow. However, large variance in data generated a moderate linear correlation (r^2 = 0.64). Periods of under- and over-estimation of the runoff also caused some non-random patterns in the residuals (Figure 5-23). Table 5-16 summarizes the E and r^2 values for the uncalibrated, calibrated and validated simulations.

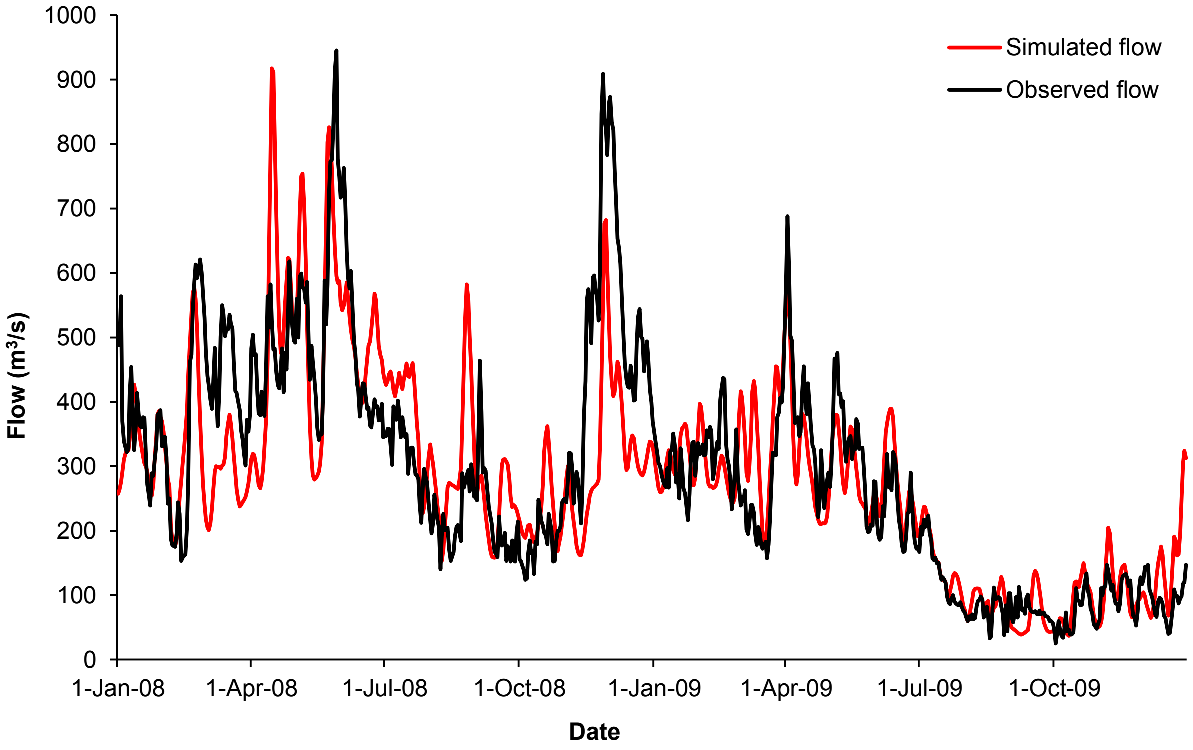


Figure 5-21 Comparison of the observed and simulated stream flow in the study area for model validation for 2008 – 2009.

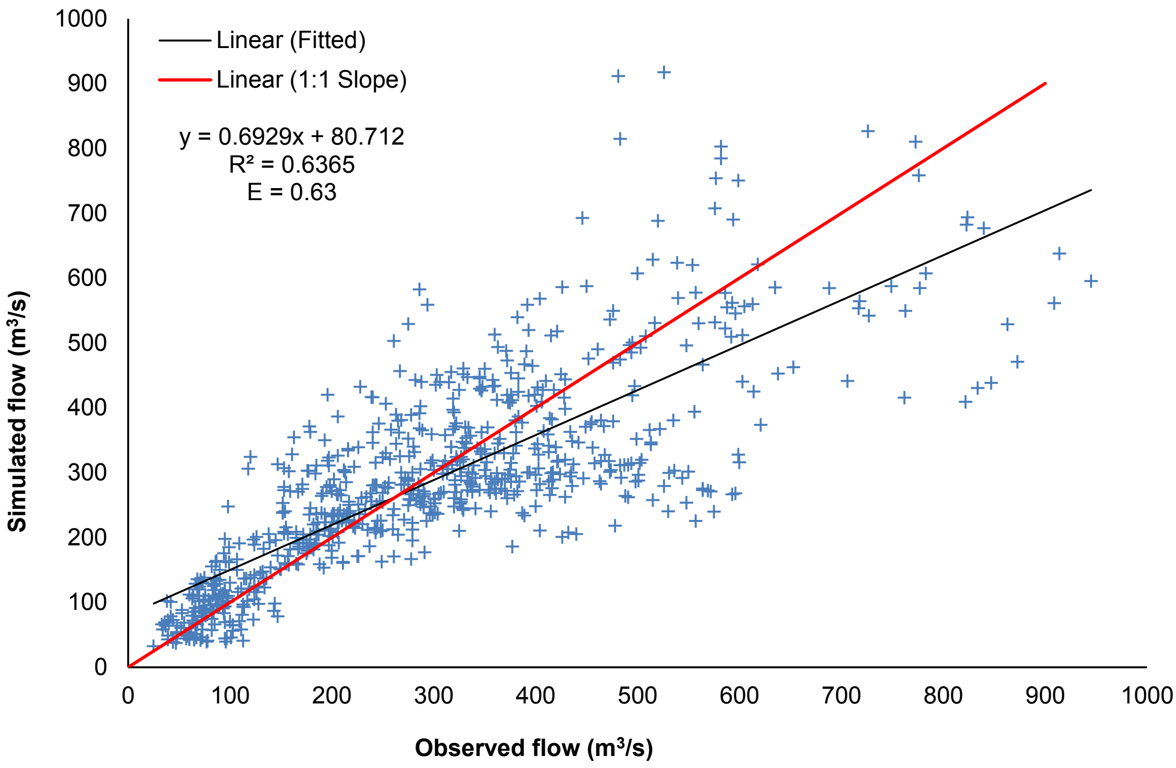


Figure 5-22 Plot of simulated versus observed flow together with the one-to-one line slope (red line) and the linear fit (black line) for the model validation. The plot also shows the equation fitted to the linear model, the coefficient of determination and the Nash–Sutcliffe model efficiency coefficient.

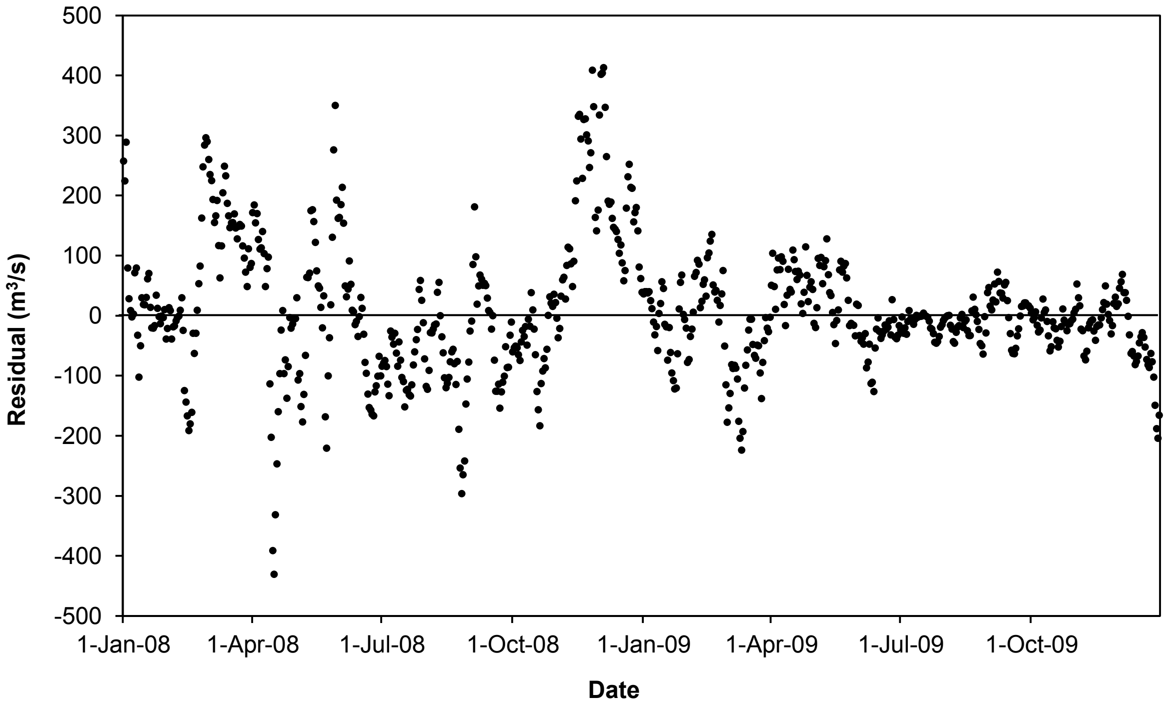


Figure 5-23 Plot of residuals for the validation of the stream flow from AnnAGNPS.

Table 5-16 Calculated Nash–Sutcliffe model efficiency coefficients and coefficient of determinations for the uncalibrated, calibrated and validated simulation of the stream flow.

	Uncalibrated	**Calibrated**	**Validation**
E	0.50	0.70	0.63
r^2	0.73	0.73	0.64

5.4.5 Pesticide concentrations

The model provides information about the cells draining to a particular point in the catchment as well as runoff information for that location. This information was first used to calculate the drainage basin for each monitoring station and its contribution to the baseflow (Table 5-17). The total stream flow for each monitoring station was then calculated by adding the baseflow contribution to the simulated runoff for each of these points (Appendix, Figure A5- 1). This stream flow information was needed in order to calculate pesticide concentrations along the river and to determine areas of high risk for pesticide contamination.

Table 5-17 Calculated contribution to the draining area of the study catchment of the different monitoring stations along the River Cauca.

Monitoring station	**Draining area (%)**
Anacaro	100.0
Puente Guayabal	91.0
Mediacanoa	56.5
Paso de la Torre	40.5
Puerto Isaacs	24.6
Juanchito	24.2

The effect of the calibration of the hydrology on the simulation of triazine concentrations is observed in Table 5-18. As expected, the increase in the CN generated more pesticide transport via runoff. Model calibration increased herbicide concentrations by up to three orders of magnitude. Calibrated concentrations matched detected concentrations better than the uncalibrated simulations even though calibration only considered hydrology.

Table 5-18 Simulated triazine concentrations for the uncalibrated and calibrated simulation along with the measured data on days were samples were taken.

Sampling location	Day	Measured (µg/l)	Uncalibrated (µg/l)	Calibrated (µg/l)
June 2010				
Juanchito	9	ND	ND	ND
P. Isaacs	10	ND	ND	ND
P. Torre	10	ND	ND	ND
Mediacanoa	10	0.481	ND	NQ
P. Guayabal	11	0.102	ND	0.068
Anacaro	11	ND	NQ	0.067
October 2010				
Juanchito	26	0.112	ND	ND
P. Isaacs	11	ND	ND	ND
P. Torre	11	0.104	ND	NQ
Mediacanoa	25	0.052	NQ	0.094
P. Guayabal	25	0.058	NQ	0.152
Anacaro	25	ND	0.044	0.259
May 2011				
Juanchito	10	ND	ND	ND
P. Isaacs	11	0.224	ND	ND
P. Torre	11	ND	ND	NQ
Mediacanoa	12	ND	NQ	0.072
P. Guayabal	12	0.432	NQ	0.076
Anacaro	12	ND	NQ	0.058

Results for atrazine, simazine and total triazine concentrations for the calibrated simulation are shown in Table 5-19 for dates when samples were collected in June 2010, October 2010 and May 2011, and for each monitoring station. Overall, the model simulated pesticide concentrations in the same order of magnitude as the measured data. Measured concentrations of atrazine and simazine varied between ND and 0.481 µg/l while the simulated values ranged between ND and 0.259 µg/l. In general, the simulated pesticide concentrations gradually increased from the top of the catchment to the outlet whereas observed data showed a different behaviour; for example, high concentrations were sometimes found upstream of the catchment while no detections were observed in some downstream stations. In addition, pesticides were never detected at Anacaro station (the catchment outlet) while the model always simulated concentrations at this point. Pesticide concentrations at Juanchito and Puerto Isaac were only detected (at high concentrations) in October 2010 and May 2011, respectively; however, the model simulated concentrations below the limit of detection.

Highlighted cells in Table 5-19 correspond to the best simulations of pesticide concentrations, following the same criteria used in Chapters 3 and 4 that good simulations were considered to be those within a factor of 2 of the observed value. Some good matches were observed for atrazine and simazine simulations. The concentrations below the limit of detection were well simulated by the model for both pesticides between Juanchito and Paso de la Torre in June 2010, for Puerto Isaacs in October 2010 and for Juanchito in May 2011, for atrazine in Juanchito in October 2010 and for simazine from Juanchito to Paso de la Torre in May 2011 as well as for concentration below the limit of quantification in Mediacanoa. Simulations within a factor of two were observed at Puente Guayabal in June 2010 for atrazine and simazine by factors of 1.3 and 1.7; in the same station only for atrazine in October 2010 and May 2011 differing by factors of 1.2 and 2.0, respectively; and for Mediacanoa, in October 2010 atrazine was simulated within a factor of 1.2 and for simazine concentration measured below the limit of quantification, the model simulated a concentration above this limit by a factor of 1.7. Some good results were also obtained for total triazine concentrations, but in less sampling dates and stations than when looking at each individual herbicide. Good agreements for total triazines were only observed on days when both herbicides were well simulated.

Table 5-19 Simulated and measured atrazine, simazine and total triazine concentrations in μg/l for dates were samples were taken in June 2010, October 2010 and May 2011. Measured concentrations were provided by Sarria (2014). Highlighted values show the best model simulations.

Sampling Month-Year/ location	Day	Atrazine concentration[1]		Simazine concentration[2]		Triazine concentration	
		Measured	Simulated	Measured	Simulated	Measured	Simulated
June 2010							
Juanchito	9	ND	ND	ND	ND	ND	ND
P. Isaacs	10	ND	ND	ND	ND	ND	ND
P. Torre	10	ND	ND	ND	ND	ND	ND
Mediacanoa	10	0.481	0.018	ND	NQ	0.481	NQ
P. Guayabal	11	0.052	0.039	0.050	NQ	0.102	0.068
Anacaro	11	ND	0.039	ND	NQ	ND	0.067
October 2010							
Juanchito	26	ND	ND	0.112	ND	0.112	ND
P. Isaacs	11	ND	ND	ND	ND	ND	ND
P. Torre	11	ND	NQ	0.104	ND	0.104	NQ
Mediacanoa	25	0.052	0.043	NQ	0.051	0.052	0.094
P. Guayabal	25	0.058	0.070	ND	0.082	0.058	0.152
Anacaro	25	ND	0.131	ND	0.129	ND	0.259
May 2011							
Juanchito	10	ND	ND	ND	ND	ND	ND
P. Isaacs	11	0.224	ND	ND	ND	0.224	ND
P. Torre	11	ND	NQ	ND	ND	ND	NQ
Mediacanoa	12	ND	0.042	NQ	NQ	ND	0.072
P. Guayabal	12	0.088	0.044	0.344	NQ	0.432	0.076
Anacaro	12	ND	0.034	ND	NQ	ND	0.058

5.4.6 Uncertainty analysis

5.4.6.1 Grid cell resolution in AnnAGNPS

The model was used to evaluate the impact of cell resolution on runoff calculations. The resulting stream flow using CSA and MSCL values of 300 ha and 1000 m (i.e. double the original resolution) is shown and compared to the observed data in Figure 5-24. It was observed that the hydrograph of simulation with a higher grid resolution has fewer peaks, a smoother curve and underestimated stream flow compared to the original simulation. However, the linear regression analysis for the runoff showed only a slightly smaller model efficiency ($E = 0.68$ and $r^2 = 0.73$) than the original simulation ($E = 0.70$ and $r^2 = 0.73$) (Appendix, Figure A5- 2).

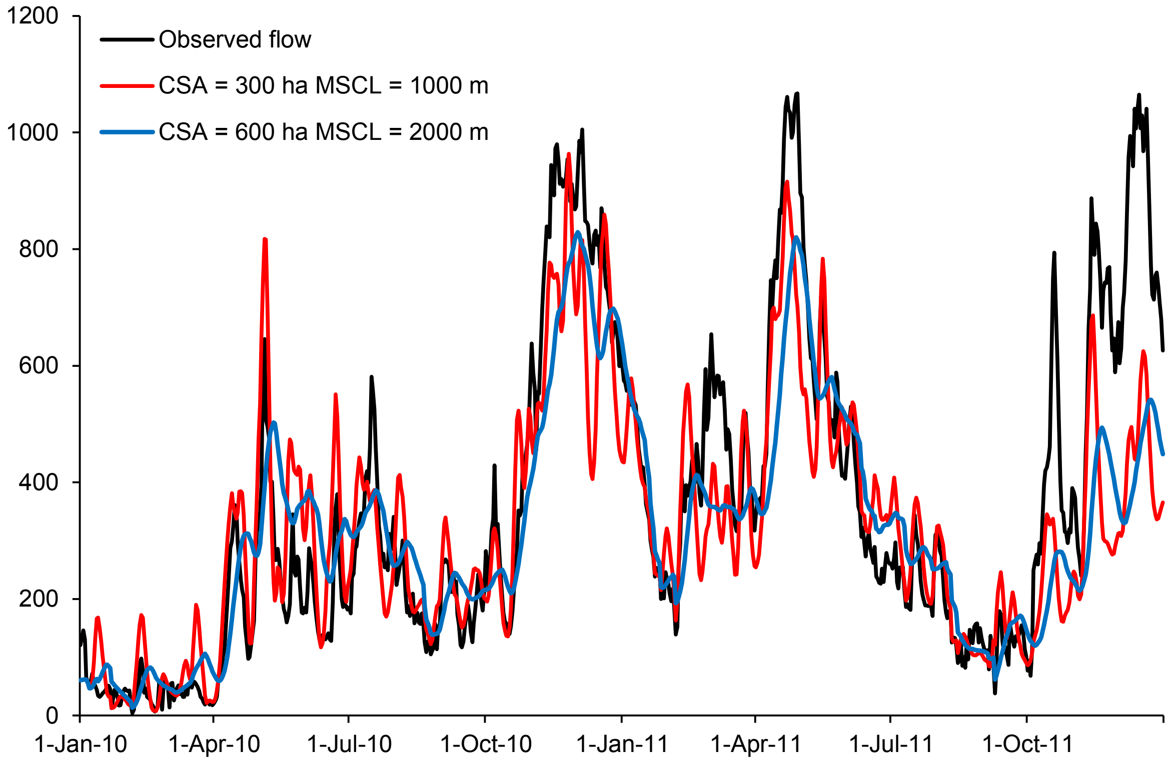


Figure 5-24 Stream flow calculation using CSA and MSCL of 300 ha and 1000 m compared to the original simulation (600 ha and 2000 m) and the observed flow at Anacaro station.

5.4.6.2 Pesticide sorption and degradation

The uncertainty in the simulation of triazine concentrations due to the use of average degradation and sorption values was analysed by the use of extreme values derived from field studies. The results from the simulations were compared to the simulation obtained using average parameters and to the observed concentrations (Table 5-20). The smallest concentrations were simulated when using the reported minimum degradation and maximum sorption values and the largest concentrations when using the maximum degradation and minimum sorption (i.e. when triazines were less persistent and mobile and when persistence and mobility were highest, respectively).

Table 5-20 Comparison of the observed and simulated total triazine concentrations using the average and extreme pesticide sorption (K_{oc}) and degradation (DT_{50}) input parameters.

Sampling location	Day	Measured (µg/l)	Avg. DT_{50} K_{oc} (µg/l)	Max DT_{50} Max K_{oc} (µg/l)	Min DT_{50} Min K_{oc} (µg/l)	Max DT_{50} Min K_{oc} (µg/l)	Min DT_{50} Max K_{oc} (µg/l)
June 2010							
Juanchito	9	ND	ND	ND	ND	ND	ND
P. Isaacs	10	ND	ND	ND	ND	ND	ND
P. Torre	10	ND	ND	ND	ND	ND	ND
Mediacanoa	10	0.481	NQ	ND	ND	0.048	ND
P. Guayabal	11	0.102	0.068	ND	0.044	0.105	ND
Anacaro	11	ND	0.067	ND	0.061	0.098	ND
Oct. 2010							
Juanchito	26	0.112	ND	ND	ND	ND	ND
P. Isaacs	11	ND	ND	ND	ND	ND	ND
P. Torre	11	0.104	NQ	ND	NQ	NQ	ND
Mediacanoa	25	0.052	0.094	0.088	NQ	0.123	ND
P. Guayabal	25	0.058	0.152	0.134	NQ	0.199	ND
Anacaro	25	ND	0.259	0.144	0.054	0.391	NQ
May 2011							
Juanchito	10	ND	ND	ND	ND	ND	ND
P. Isaacs	11	0.224	ND	ND	ND	ND	ND
P. Torre	11	ND	NQ	ND	NQ	0.042	ND
Mediacanoa	12	ND	0.072	ND	0.043	0.114	ND
P. Guayabal	12	0.432	0.076	NQ	0.045	0.119	ND
Anacaro	12	ND	0.058	ND	0.036	0.092	ND

Sorption and degradation parameters had contrasting effects between sampling periods. For instance, for the same degradation but varying the sorption, concentrations varied by an average factor of 15 in June 2010 and May 2011, but in October the differences in triazine concentrations were smaller, only varying by an average factor of 3.4. In contrast, at the same sorption and changing the degradation, the concentrations increased by an average factor of 2.8 in June 2010 and May 2011; however, in October 2010 this effect was larger with an average factor of 9.7.

The pesticide module in AnnAGNPS considers two fixed parameters that affect pesticide transport (Bingner et al., 2011): 1) the runoff interaction layer which corresponds to the top 1 cm of the soil where pesticides are available for surface runoff, and 2) the efficiency for pesticide extraction (Pantone and Young, 1996), described by the extraction ratio whose value ranges between 0.05 to 0.2 depending on the conditions for runoff and erosion and the tendency for pesticides to be transported in solution or attached to the soil (Leonard and Wauchope, 1980). These two parameters caused the effect that pesticide sorption had in the simulation of pesticide concentrations in October 2010. For example, Figure 5-25 shows the simulated concentrations for Anacaro station using the different combinations of extreme values for sorption and degradation for rainfall events during October 2010. Two pesticide emission peaks were observed during the month in response to the rainfall events; the first higher concentrations than the second because it took place soon after pesticide application on October 1st. For most of the month (from October 3rd to 28th), the combination of maximum degradation and minimum sorption values resulted in the largest pesticide concentrations. However, for the second pesticide emission near the sampling day on October 25th 2010 the difference between the simulated concentrations using maximum degradation and minimum sorption and maximum degradation and maximum sorption become smaller with time as the pesticide available in the runoff interaction layer for the first reduces while for the later simulation the concentration remains almost constant. At this time, when using minimum degradation and sorption values, less pesticide becomes available in the runoff interaction layer since most of it had already been exported in the previous peak and the remaining pesticides had either leached or degraded. On the other hand, for the simulation using maximum degradation and sorption values, the pesticide available for runoff in the interaction layer is more stable due to the restricted mobility and the limited degradation behaviour.

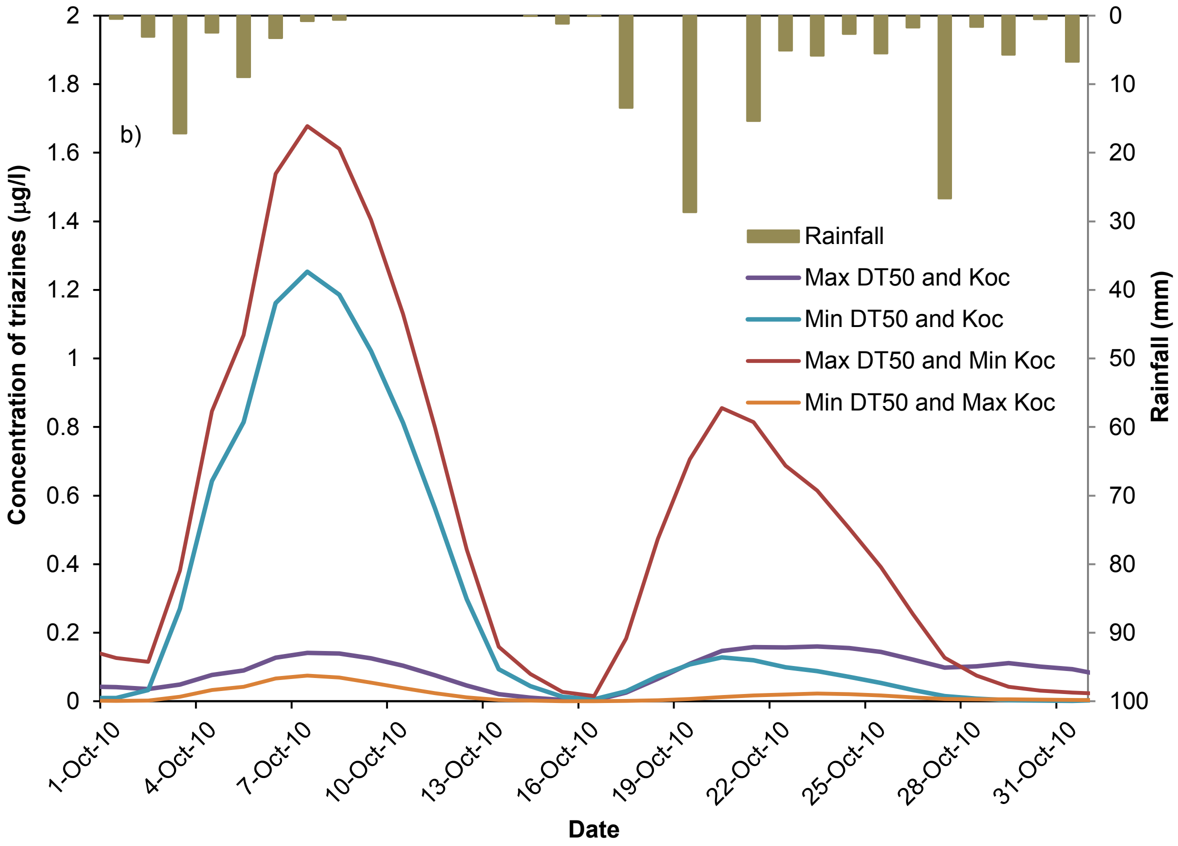


Figure 5-25 Simulated triazine concentrations using maximum and minimum values of degradation and sorption, together with the observed rainfall in October 2010 at Anacaro station.

Uncertainty in pesticide degradation and sorption had a big effect on pesticide concentrations in the sense that wide concentration ranges were obtained using extreme data (e.g. for Puente Guayabal in October 2010 concentrations varied from ND to 0.199 µg/l while the observed concentration was 0.058 µg/l) but these ranges of pesticide concentrations not always explain the difference between measured and simulated data; this is the case for the large concentrations observed at Mediacanoa in June 2010, Juanchito and Paso de la Torre in October 2010, Puerto Isaacs and Puente Guayabal in May 2011, as well as for the non-detection at the catchment outlet (Anacaro) in October 2010.

5.4.6.3 Pesticide usage

Pesticide application date

Table 5–21 shows the impact of uncertainty in the application date on triazine concentrations. When triazine applications were simulated on the 15th of each month the simulated concentrations were mostly not detected or very small values on days when samples were taken; this matches the measured data in most of the stations except for Mediacanoa and Puente Guayabal in June 2010, and Puerto Isaacs and Puente Guayabal in May 2011 when high concentrations were observed. In addition, in October 2011 the model simulated higher concentrations when applying pesticides on the 15th than on the 1st, which disagrees with the measured data.

Table 5-21 Simulated triazine concentrations applying herbicides on the 15th compared to the original simulation (1st) and the measured data. Highlighted cells show the best agreements with the measured data.

Sampling location	Day	Measured (μg/l)	1st (μg/l)	15th (μg/l)
June 2010				
Juanchito	9	**ND**	ND	ND
P. Isaacs	10	**ND**	ND	ND
P. Torre	10	**ND**	ND	ND
Mediacanoa	10	**0.481**	NQ	ND
P. Guayabal	11	**0.102**	0.068	ND
Anacaro	11	**ND**	0.067	ND
October 2010				
Juanchito	26	**0.112**	ND	ND
P. Isaacs	11	**ND**	ND	ND
P. Torre	11	**0.104**	NQ	ND
Mediacanoa	25	**0.052**	0.094	0.486
P. Guayabal	25	**0.058**	0.152	0.665
Anacaro	25	**ND**	0.259	1.03
May 2011				
Juanchito	10	**ND**	ND	ND
P. Isaacs	11	**0.224**	ND	ND
P. Torre	11	**ND**	NQ	ND
Mediacanoa	12	**ND**	0.072	ND
P. Guayabal	12	**0.432**	0.076	ND
Anacaro	12	**ND**	0.058	ND

Figure 5-26 also shows the effect of both frequencies of application on triazine concentrations in Anacaro station for the three sampling periods. Differences in pesticide concentrations are due to the availability of pesticides at the top 1 cm of the soil (runoff interaction layer). When rainfall took place soon after pesticides were applied, larger concentrations were simulated since pesticides were more available for runoff; then, a reduction in the availability for surface runoff took place since some of the pesticides would either have runoff or leached through the soil profile below the interaction layer. For the simulations in June 2010 and May 2011 (Figure 5-26 a and c, respectively) with an application on the 1st, when samples were taken between the 9th and 12th of each month, pesticides were simulated at high concentrations since they were in the soil for about ten days whereas for an application on the 15th, pesticides were in the soil for almost a month. However, for the simulation in October 2010 (Figure 5-26 b), when most of the samples were taken on the 25th and 26th, more pesticide was still available from the simulation using both application dates, but less available for the simulation on the 1st than for the 15th since the period until sampling was 25 and 10 days, respectively.

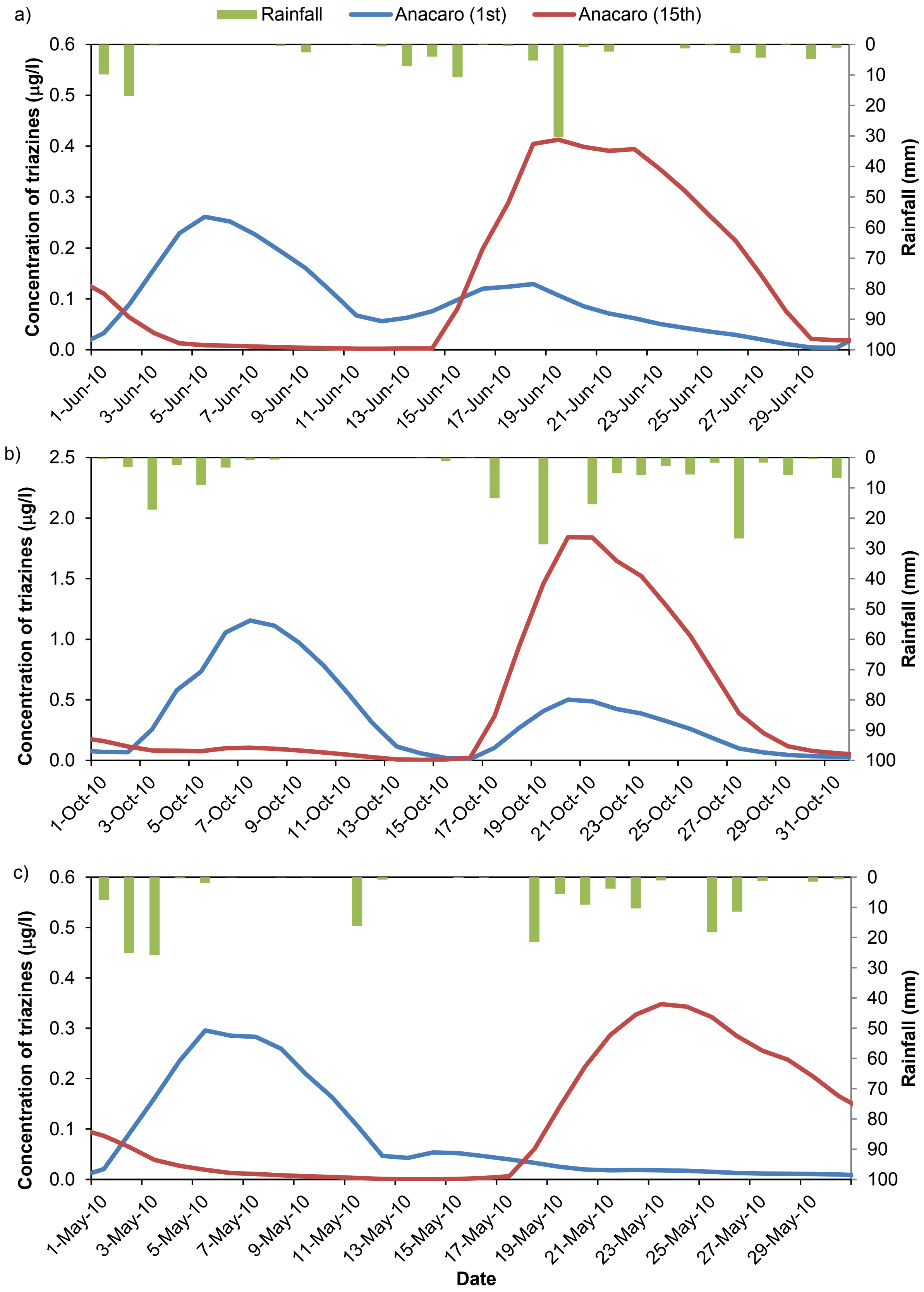


Figure 5-26 Comparison of simulated triazine concentrations with application dates on the 1st and 15th of every month for the three sampling periods: a) June 2010, b) October 2010 and c) May 2011 at Anacaro station.

Frequency of application in sugarcane

The uncertainty due to the assumption on average frequency of application to sugarcane along the catchment was tested by simulating applications every two months. Table 5-22 shows the effect that this change had on triazine concentrations compared to the initial simulation using a frequency of every month. Despite that the application rate to sugarcane for each application event was double that when applying every month, pesticide concentrations were generally smaller by up to two orders of magnitude on days when samples were taken, except for May 2011 when the model simulated higher concentrations by an average factor of 2.0. Application events were simulated for even months throughout the simulation period (i.e. January, March, May…), so no pesticide application was simulated for June and October 2010.

Table 5-22 Comparison of the simulated triazine concentrations with a frequency of application to sugarcane of every two and one month.

Sampling location	Day	One month (µg/l)	Two months (µg/l)
June 2010			
Juanchito	9	ND	ND
P. Isaacs	10	ND	ND
P. Torre	10	ND	ND
Mediacanoa	10	NQ	ND
P. Guayabal	11	0.068	ND
Anacaro	11	0.067	ND
October 2010			
Juanchito	26	ND	ND
P. Isaacs	11	ND	ND
P. Torre	11	NQ	ND
Mediacanoa	25	0.094	ND
P. Guayabal	25	0.152	NQ
Anacaro	25	0.259	NQ
May 2011			
Juanchito	10	ND	ND
P. Isaacs	11	ND	ND
P. Torre	11	NQ	0.050
Mediacanoa	12	0.072	0.141
P. Guayabal	12	0.076	0.149
Anacaro	12	0.058	0.112

5.4.7 Analysis of the areas of risk, practices and conditions for water contamination using AnnAGNPS

5.4.7.1 Areas of risk

Annual application of triazines per sub-basin area

The total annual triazine application per sub-basin area is shown in Table 5-23 along with the percentage area of sugarcane, maize, sorghum and total studied crops for each sub-basin. The maximum usage corresponded to the areas with a large percentage of crops; for example watersheds with over 1.5 kg/ha of triazine application such as 2, 3, 4, 5 and 9, have more than 40% of their area planted with the target crops with the majority being sugarcane. The visual distribution of the annual triazine application per watershed area across the study area is presented in Figure 5-27. These areas of high risk due to intensive triazine usage are mostly located in the top and middle part of the catchment.

Table 5-23 Pesticide annual application calculated for each sub-basin along with the percentage areas of target crops (sugarcane, maize and sorghum) and sub-basin areas in hectares.

Sub-watershed	Sugarcane (%)	Maize (%)	Sorghum (%)	Total crops (%)	Sub-basin area (ha)	Annual pesticide application (kg/ha)
1	22.8	0.3	1.0	24.0	67,640	0.89
2	39.4	0.3	0.6	40.3	74,215	1.52
3	38.9	1.1	1.3	41.4	41,028	1.52
4	55.3	0.1	0.8	56.1	25,146	2.13
5	39.5	1.3	1.1	41.9	32,224	1.55
6	14.6	0.1	0.6	15.2	51,308	0.57
7	1.3	0.1	0.0	1.4	37,510	0.05
8	27.1	0.4	1.7	29.2	141,946	1.07
9	58.3	12.6	10.5	81.4	2,867	2.52
10	1.4	0.7	0.1	2.2	90,456	0.06
11	22.5	3.8	2.1	28.4	24,383	0.94
12	4.0	0.5	0.7	5.1	66,071	0.17
13	0.3	2.2	0.1	2.6	15,216	0.04
14	13.7	0.0	0.0	13.7	63,475	0.53
15	11.7	4.0	6.0	21.7	130,315	0.57
Whole catchment	19.5	1.1	1.6	22.3	863,800	0.78

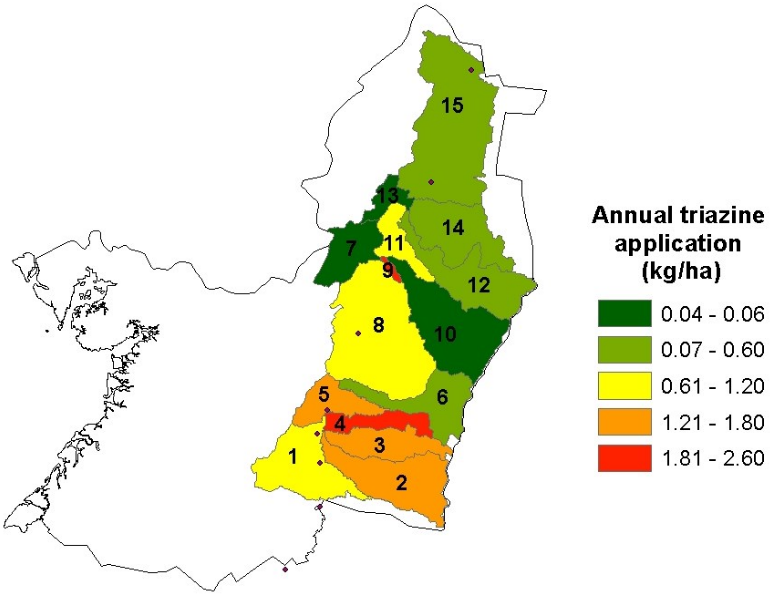


Figure 5-27 Map of pesticide application per area in kg/ha.

<u>Relative pesticide export to the River Cauca</u>

The results of the relative percentage of pesticide export to the River Cauca showed that export values ranged from 0.01 to 0.27% (Table 5-24). The average export value for the sub-watersheds was 0.07% and the highest relative pesticide export was for the sub-watershed located at the middle of the catchment (Figure 5-28). The total percentage loss at the catchment outlet during the simulation period was 0.04%.

Table 5-24 Relative percentage of pesticide export to the River Cauca.

Sub-watershed	Total pesticide export (kg)	Total pesticide export per area (10^{-3} kg/ha)	Relative pesticide export (% of applied)
1	30	0.44	0.025
2	86	1.16	0.038
3	11	0.26	0.009
4	12	0.48	0.011
5	18	0.55	0.018
6	100	1.95	0.172
7	10	0.28	0.273
8	119	0.84	0.039
9	3	1.06	0.021
10	22	0.24	0.186
11	8	0.34	0.018
12	10	0.16	0.047
13	1	0.07	0.084
14	25	0.39	0.037
15	53	0.41	0.036
Total	508	0.59	0.038

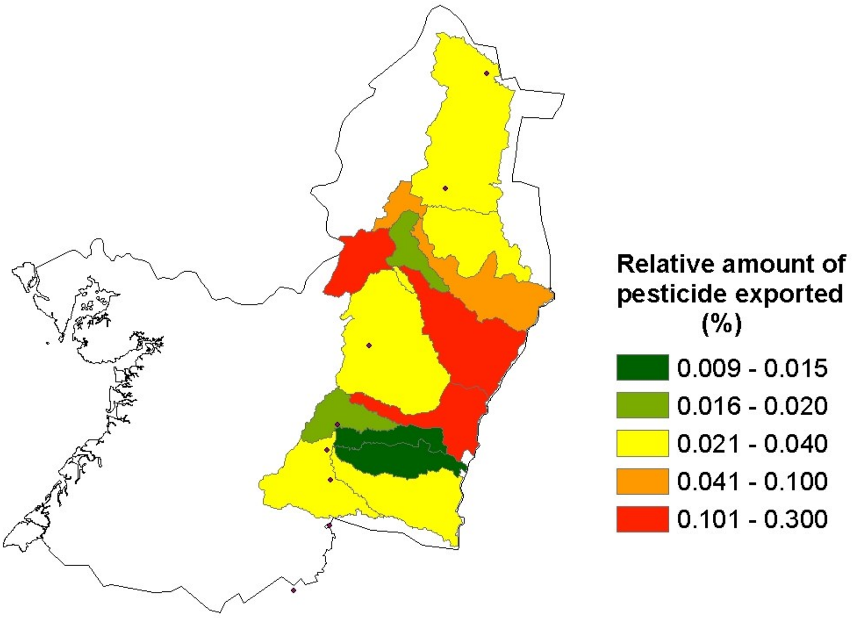


Figure 5-28 Map of the percentage of relative pesticide export to the river Cauca for the calculated watershed using ArcHydro.

5.4.7.2 Practices and conditions

The effect of improving drain conditions in the catchment on triazine emissions by reducing overland runoff was evaluated. A comparison between the resulting pesticide concentrations between this practice improvement and the original simulation (poor drain conditions) is shown in Table 5-25; the simulated concentrations show a 89% average reduction in pesticide emissions on days when samples were taken in 2010 and 2011 and a reduction of 78% of pesticide loads at the catchment outlet over the whole simulation period.

Table 5-25 Simulated concentrations improving the runoff behaviour in the crop (good drain conditions) compared to the original simulation (poor drain conditions).

Sampling Location	Day	Poor drain conditions (μg/l)	Good drain conditions (μg/l)
June 2010			
Juanchito	9	ND	ND
P. Isaacs	10	ND	ND
P. Torre	10	ND	ND
Mediacanoa	10	NQ	ND
P. Guayabal	11	0.068	ND
Anacaro	11	0.067	ND
October 2010			
Juanchito	26	ND	ND
P. Isaacs	11	ND	ND
P. Torre	11	NQ	ND
Mediacanoa	25	0.094	ND
P. Guayabal	25	0.152	ND
Anacaro	25	0.259	0.035
May 2011			
Juanchito	10	ND	ND
P. Isaacs	11	ND	ND
P. Torre	11	NQ	ND
Mediacanoa	12	0.072	NQ
P. Guayabal	12	0.076	NQ
Anacaro	12	0.058	NQ

5.4.7.3 Alternative for triazine pesticides

The alternative to triazine pesticides, mesotrione was tested in the catchment to simulate pesticide concentrations along the catchment and evaluate the effect of this replacement. Simulated mesotrione concentrations are compared to triazine simulations in Table 5-26. Pesticide emissions when samples were taken showed a reduction in the concentration by up to two orders of magnitude. Table 5-27 compares the calculated usage and simulated emission figures for triazines and mesotrione. The table also shows the potential reduction of these figures from the replacement of triazines with mesotrione. Important reductions in pesticide usage and export were observed (83.5 and 95.9%, respectively) as well as a reduction of 87.4% in pesticide loss along the catchment.

Table 5-26 Comparison of the simulated mesotrione and triazine concentrations for each sampling location.

Sampling Location	Day	Triazine (µg/l)	Mesotrione (µg/l)
June 2010			
Juanchito	9	ND	0.000
P. Isaacs	10	ND	0.000
P. Torre	10	ND	0.000
Mediacanoa	10	NQ	0.001
P. Guayabal	11	0.068	0.002
Anacaro	11	0.067	0.003
October 2010			
Juanchito	26	ND	0.000
P. Isaacs	11	ND	0.000
P. Torre	11	NQ	0.001
Mediacanoa	25	0.094	0.001
P. Guayabal	25	0.152	0.001
Anacaro	25	0.259	0.003
May 2011			
Juanchito	10	ND	0.000
P. Isaacs	11	ND	0.000
P. Torre	11	NQ	0.001
Mediacanoa	12	0.072	0.002
P. Guayabal	12	0.076	0.002
Anacaro	12	0.058	0.002

Table 5-27 Pesticide usage, export to the catchment outlet and percentage loss for mesotrione and triazines along the potential reduction of these figures from the hypothetical replacement of triazine herbicides with mesotrione.

	Mesotrione	Triazines	Potential reduction (%)
Average pesticide application per year over the whole catchment (kg/ha)	0.13	0.78	83.5
Pesticide exported at the catchment outlet (kg/2 years)	239	5,778	95.9
Pesticide loss (%)	0.11	0.85	87.4

5.5 Discussion

5.5.1 Stream flow simulation

AnnAGNPS was used to simulate the hydrology of the River Cauca in the Valle del Cauca as well as triazine emissions from non-point source pollution due to their application in maize, sorghum and sugarcane crops in the valley. AnnAGNPS is an improved GIS integrated version of the single event AGNPS model, capable of continuous simulation of spatially distributed watersheds and applicable to larger catchments. Since launch in 2005, several studies have applied and evaluated AnnAGNPS (Das et al., 2008; Shamshad et al., 2008; Polyakov et al., 2007; Shrestha et al., 2006; Baginska et al., 2003; Suttles et al., 2003; Yuan et al., 2001). Most of these studies have focused on sediment and nutrient transport and there are only a few that consider pesticide emissions (Zuercher et al., 2011; Heathman et al., 2008; Lively et al., 2002). Nevertheless, most of the studies have concluded that AnnAGNPS was good in predicting runoff volume while other outputs were only of moderate accuracy.

The Nash–Sutcliffe model efficiency (*E*) has been widely used to evaluate model performance. This method provides an indication of strength of correlation between the model simulation and the measured data by determining the relative magnitude of the residual variation compared to variance in the measured data (Nash and Sutcliffe, 1970). Criterion of acceptance for assessing hydrologic simulations is still a subjective process. Chiew et al. (1993) proposed results as being acceptable for an *E* value greater than 0.6 and the simulated mean flow to be within 15% of the measured mean flow; in contrast, Van Liew et al. (2003) classified flow results as highly satisfactory for *E* values equal to or greater than 0.75, satisfactory results between 0.36 and 0.75 and unsatisfactory for *E* smaller than 0.36.

The initial simulation of the stream flow was partially satisfactory according to the Van Liew et al. (2003) criterion ($E = 0.50$ and $r^2 = 0.729$), but the simulation showed under-estimation of runoff during periods of high flow by up to a factor of two. The Valle del Cauca Department, located in the pacific region of the country, is one of the most vulnerable areas to el Niño and la Niña phenomena in Colombia. In this country, the cold ENSO episodes (la Niña) are manifested with an increase in rainfall, resulting in a higher occurrence of river overflows, floods, landslides, torrential floods and windstorms, whereas, el Niño is characterized by a decrease in rainfall, increasing the occurrence of droughts and forest fires (IDEAM, 2001). El Niño began to manifest in May 2009, and the event reached its highest stage of development between late December 2009 and early January 2010 (IDEAM, 2010), causing very low observed flows at the beginning of the simulation period. Then, a period of neutralization by the gradual cooling of the waters of the Pacific Ocean was observed until the middle of 2011 when low ocean temperatures gave way to La Niña, reaching its maximum intensity at the end of the year; during this period La Niña caused extreme flow events that were greatly underestimated by the simulation using AnnAGNPS.

Other studies using the AnnAGNPS model found under-estimation of runoff (Shamshad et al., 2008; Sarangi et al., 2007; Mohammed et al., 2004; Suttles et al., 2003; Yuan et al., 2001). Runoff under-estimation in a 333-km^2 watershed in Georgia was due to inadequate representation of the land cover according to Suttles et al. (2003). Chahor et al. (2014) conducted a simulation with AnnAGNPS for a 207-ha agricultural watershed located in Navarre, Spain, observing seasonal over- (summer and autumn) and under-estimation (winter and spring) in the runoff. Yuan et al. (2001) found for a 82-ha watershed in the Mississippi delta that AnnAGNPS under-estimated runoff for periods of extreme rainfall events (rainfall over 80 mm per year) and this was attributed to a small culvert at the monitoring station which caused water accumulation leading to over-estimation in the observed runoff for large events by increasing the apparent flow depth at the monitoring point. However, since a similar behaviour was observed when La Niña phenomena took place in the Valle del Cauca, low response by the model in the simulation of runoff from extreme rainfall events is a more likely explanation for this behaviour.

Sensitivity analysis is usually conducted to guide calibration efforts by identifying the parameters that are most likely to produce important variations in the output data. Several studies have performed sensitivity analyses for the ANGPS and AnnANGPS models. The selection of parameters for the analysis depends on the output to be calibrated; sensitivity analysis for the calibration of runoff flow included parameters related to the hydrology such as the runoff curve numbers, weather data, irrigation, tile drainage, land slope, Manning's "n" coefficient, hydraulic conductivity and erodibility factor. Studies have shown curve numbers as the most sensitive parameters in the simulation of runoff and these were often adjusted during calibrations (Das et al., 2008; Liu et al., 2008; Sarangi et al., 2007; Leon et al., 2004; Mohammed et al., 2004). In addition to the curve numbers, precipitation also has a great impact on model outputs (Das et al., 2008; Liu et al., 2008; Leon et al., 2004;

Mohammed et al., 2004) and to a lesser degree so do the Manning's "n" and hydraulic conductivity (Das et al., 2008). Further sensitivity analysis prior to model calibration was not considered necessary here as runoff from AnnAGNPS and AGNPS was successfully calibrated in most studies by modifying the curve numbers (Chahor et al., 2014; Parajuli et al., 2009; Taguas et al., 2009; Das et al., 2008; Shamshad et al., 2008; Licciardello et al., 2007; Polyakov et al., 2007; Sarangi et al., 2007; Shrestha et al., 2006; Baginska et al., 2003; Grunwald and Norton, 2000).

The process of model calibration usually involves the variation of uncertain and sensitive model input parameters over reasonable ranges of values until a satisfactory match between simulated and measured data is obtained. Calibration is needed to account for unmeasured, unknown or unrepresented conditions or processes, and for uncertainty in the input parameters. The non-random pattern in the residuals for the uncalibrated simulation for the Valle del Cauca was also an indicator that the model was not capturing some explanatory information which needed to be improved by model calibration. After calibration, model validation is generally undertaken to demonstrate that the calibrated model is an adequate representation of the physical system for independent measurements.

Curve numbers are generally equally adjusted for all cover types in most of the studies; however, Chahor et al. (2014) found over-estimation of the runoff during summer and autumn seasons and under-estimation throughout winter and spring, so CN were calibrated by adjusting their values by seasons; this approach noticeably improved the runoff simulation (from E = -1.52 to E = 0.75). For the River Cauca, calibration of the CN was only carried out for crops and pasture cover types since these areas account for approximately 83% of the catchment and most of the uncertainty in the input parameters was thought to arise from these land covers where more assumption and simplifications were made. Shamshad et al. (2008) used a similar methodology to calibrate the CN for a 125-km^2 watershed in Malaysia, applying adjustments of 2% each time and using the observed versus simulated flow plot and statistical parameters that included r^2 and E to evaluate the best results.

Best calibration in the current study based on E was found when increasing the CN by 14% (E = 0.71), however, a decrease in r^2 was observed after an 8% adjustment. Therefore, the most suitable calibration was thought to result from an increase of 10% in the CN, in order to improve model performance without sacrificing linear correlation with the observed data and to avoid over-calibration of the model. However, four sets of CN between 8 and 14% were tested in model validation to confirm this decision. Model validation was carried out for the same watershed but for a different period of time (2008 – 2009). The best validation results were indeed obtained for an increase of the CN by 10% (E = 0.63 and r^2 = 0.64). This result showed the importance of using more than one statistical parameter to evaluate the calibration process. Model calibration improved the simulation of runoff (from E = 0.50 to E = 0.70) without affecting the linear correlation between the observed and simulated values (r^2 = 0.73); however, some under-estimation was still observed for the runoff in December 2011 by a factor of 1.5. The validated runoff simulation was still classified as satisfactory according to the criterion of Van Liew et al. (2003).

Calibrated parameters are not always by themselves plausible values (Ramireddygari et al., 2000), as in this case for the calibrated runoff numbers which were higher than typical values for the cover types; however, model calibration accounted for defined uncertainties which made the calibrated curve numbers descriptive of the field conditions in the model. The stream flow results suggest that the model was suitably representative of the study area and AnnAGNPS can simulate runoff with reasonable accuracy under Colombian conditions. Similar modelling performance was observed in other studies. Mohammed et al. (2004) observed under-estimation of flow by 14% after calibration (E = 0.73 and r^2 = 0.87). Parajuli et al. (2009) compared simulations using AnnANGPS and SWAT for watersheds in Kansas; model efficiency for the simulation of runoff after calibration was better for AnnAGNPS than SWAT (0.69 and 0.56, respectively) while results for model validation were similar for both models (0.47 for AnnAGNPS and 0.48 for SWAT).

5.5.2 Pesticide simulation

Hydrology calculations are independent in AnnAGNPS, whereas pesticide transport is flow-dependent (Bingner et al., 2011). Inconsistencies in the flow can greatly affect the carrying capacity for pesticide loads, so it is particularly important to ensure accurate runoff simulations before analysing pesticide emissions. After calibration and validation of the simulated stream flow, AnnAGNPS was used to simulate atrazine and simazine concentrations in the Valle del Cauca. Lack of detailed information about pesticide usage in the catchment was the main limitation in the simulation, so data from pesticide labels in Colombia and other assumptions were needed to fill gaps in input requirements. The model was run assuming a 50% usage of each herbicide (atrazine and simazine), but results were analysed for total triazines to reduce uncertainties on the relative use of the two compounds. The model achieved results of the same order of magnitude as the measured data and closely matched some of the observed concentrations for the stations along the catchment. However, the pattern of non-detections was not completely caught by the model such as detecting high concentrations upstream and simulating concentrations below the LOD downstream, or never detecting concentrations at the catchment outlet.

Studies of the AnnAGNPS model for pesticide emissions are scarce; only a conference abstract (Lively et al., 2002) and two published papers (Zuercher et al., 2011; Heathman et al., 2008) were found in the literature; in all cases, atrazine was the pesticide simulated in agricultural watersheds in the USA. Lively et al. (2002) tested the modelling capacity of AnnAGNPS to simulate atrazine loads in a small watershed in Springfield, Illinois. The study showed great inconsistencies between the observed and simulated atrazine concentrations even after extensive calibration and validation; the authors concluded that the model might not be appropriate to accurately simulate atrazine losses. Heathman et al. (2008) applied the AnnAGNPS and SWAT models to simulate monthly and annual stream flow as well as atrazine emissions in the Cedar Creek watershed in Northeast Indiana. Results from an uncalibrated simulation using AnnAGNPS showed poor simulations for all outputs, with model efficiency coefficients of 0.13, -2.06 and -0.64, respectively; atrazine concentrations were 100 times smaller than the observed data. SWAT achieved better simulations of the stream flow but also could not accurately simulate atrazine concentrations. Zuercher et al. (2011) also applied AnnAGNPS to the Cedar Creek watershed, as well as to a subcatchment (Matson Ditch). The model evaluation was undertaken using more detailed monitoring data than Heathman et al. (2008). Runoff was satisfactorily simulated for both catchments after model calibration. The authors identified an error in the coding of the pesticide routine in AnnAGNPS model version 3.57, specifically a discrepancy in runoff units which was responsible for pesticide under-simulations in previous studies. After correction of the model code, atrazine simulations were successfully calibrated and validated. No sensitivity analysis was applied prior to calibration; pesticide concentrations were calibrated by adjusting the percentage of pesticide applied to soil and foliage as well as the percentage of wash off from foliage. The unsatisfactory simulation of the pesticide concentrations for the Rio Cauca was thought to arise predominantly from uncertainties in pesticide usage parameters in the model.

In this study, an issue regarding the pesticide output from the AnnAGNPS model was observed. The model simulates pesticides mass dissolved in water and attached to soil particles in the runoff water. The expected behavior of atrazine is to be mostly dissolved in water but the opposite was observed in the model output. The pesticide mass attached to soil was on average 99.7% of the total pesticide of the total simulated runoff (soil particles and water). This is very likely to be due a bug in the model. This issue was discussed with the developers of the model but it was not addressed by them and no satisfactory response was received (Binger, 2014). In this study, the pesticide mass dissolved in the runoff was used in the calculations but the model requires further assessment of the pesticide module.

5.5.3 Uncertainty analysis

The major difficulty for the parameterization of the model was the lack of some of the required input parameters in the model, particularly information related to weather, soil and pesticide usage. A range of approaches was applied to fill these gaps in the information. It was necessary to pre-calculate actual evapotranspiration in the area using available pan evapotranspiration class A for Univalle station and a crop factor for sugarcane since some of the weather parameters required by AnnAGNPS were not available (solar radiation) or only existed as average monthly (wind speed) or average historical monthly data (sky cover). Precipitation is known to be a very sensitive parameter in the model (Das et al., 2008; Liu et al., 2008; Leon et al., 2004; Mohammed et al., 2004). In addition, an accurate spatial and temporal representation of the rainfall has been found to be important for runoff simulation models particularly at large-scales (Berndtsson and Niemczynowicz, 1988; Troutman, 1983; Beven and Hornberger, 1982; Osborn et al., 1979; Osborn and Laursen, 1975; Dawdy and Bergmann, 1969). In this study, precipitation data from six different meteorological stations along the catchment were used which is expected to reduce model uncertainty due to the rainfall data.

The AnnAGNPS model has been tested for tropical conditions with satisfactory results for catchments up to 125 km^2 (Shamshad et al., 2008; Polyakov et al., 2007; Sarangi et al., 2007) but it has not been tested at the scale of the Valle del Cauca. The model developers suggest the use of the model in agricultural watersheds with size up to 3,000 km^2 (Bosch et al., 2001). The studied catchment exceeds this limit by 3 times (8,638 km^2). Simulation of large catchments can imply an increased number of grid cells which cannot be easily handled by the system capacity or can require the use of computer clusters. Thus, the maximum catchment size in a grid-based model is determined by the maximum number of cells that can be simulated with the available computer specifications. More detailed grids require a more comprehensive description of the catchment but do not always imply an improvement in the simulation. Bhuyan et al. (2003) applied AGNPS coupled to GIS to five sub-watersheds of the Cheney Reservoir watershed in Kansas. Good results were observed for most of the sub-watersheds except for the largest one (1,223 km^2). The authors suggested avoiding the use of average input data by the division of watersheds when the information is available. However, this was not an option for the Valle del Cauca since more detailed information was unavailable.

The effect of the grid cell size in the simulation of the runoff and pesticide load was tested by running an additional simulation with doubled resolution. A slightly lower performance compared to the original simulation as well as a smoothing of the runoff peaks in the hydrograph were obtained. However, differences were very small and the simulated flow was only 1.92% higher than in the original simulation. Sensitivity analyses for AnnAGNPS and AGNPS show that grid size, generally exhibits little or no sensitivity for runoff simulations (Leon et al., 2004; Haregeweyn and Yohannes, 2003; Vieux and Needham, 1993; Panuska et al., 1991), but can affect outputs such as sediment yield (Vieux and Needham, 1993; Panuska et al., 1991). For example, Haregeweyn and Yohannes (2003) found no significant improvement in the runoff simulation using AGNPS when increasing the resolution from 100 to 200 m grid size. A slightly better performance using AGNPS in the simulation of peak flow was observed by Leon et al. (2004) with a 2-km grid size than with a more detailed 1-km grid but differences were not significant.

Uncertainty regarding the use of average pesticide sorption and degradation input data was tested by using extreme values for these parameters reported in pesticide databases (maximum and minimum data). The simulations showed the large impact that both parameters have on the simulation of pesticide emissions; particularly the pesticide half-life showed slightly higher sensitivity for pesticide concentrations than the organic carbon normalized soil-water partition coefficient (K_{oc}). However, these effects were small compared to sensitivity analyses carried out for leaching models used in Europe for pesticide registration (MACRO, PRZM, PELMO and PESTLA; Dubus et al. (2003a)) where sorption- and degradation-related parameters were the inputs with the largest influence on the prediction of pesticide loss.

Other parameters that have shown great impact on the pesticide simulations were the size of the interaction layer for surface runoff, located in the top 1cm of the soil profile (Pantone and Young, 1996; Leonard and Wauchope, 1980) and the extraction ratio which depends on the runoff and erosion conditions as well as the physicochemical tendency of pesticides to be transported in solution or attached to the soil (Leonard and Wauchope, 1980). Both parameters determine the availability of pesticide for surface runoff and have fixed values in the model which cannot be modified by the user. Larger pesticide sorption and degradation values would increase the pesticide residence time in the interaction layer which enables their availability for surface runoff for a longer period of time.

Uncertainty analyses related to pesticide usage in the catchment were carried out by testing different values of frequency of application to sugarcane and the application date for all crops. When assuming that the annual application of triazines to sugarcane to the whole area was spread into six applications (i.e. every two months) instead of 12 (i.e. every month), the concentrations varied according to the presence or absence of an application event in the month. For months when applications were not simulated a reduction in pesticide concentrations by up to two orders of magnitude was observed on days when samples were collected; however, for months with simulated pesticide applications, triazine concentrations almost doubled values obtained with a monthly frequency of application. In addition, the middle value of the recommended range of application rates reported in pesticide labels were used for each crop in the model. The uncertainty in the application rate can also cause over-estimation of triazine concentrations if pesticides are not applied or are applied at a lower rate in some of the crops. However, the uncertainty due to the application dates showed the largest impact on pesticide export evidencing that the assumption of uniform application for each crop type could be a major cause for the discrepancies between observed and simulated triazine concentrations in some of the stations; the application date in sugarcane is thought to be particularly uncertain as this crop is planted on a continuous rotation in the catchment. The uncertainty in the application date was assessed by an additional simulation applying the triazines on the 15th of each month rather than the 1st of each month. It was found that for most of the days when discrepancies between the original simulation and the measured pesticide concentrations occurred, the additional simulation achieved better results; there were six exceptions (Mediacanoa in June 2010, Juanchito, Paso de la Torre and Anacaro in October 2010 and Puerto Isaacs and Puente Guayabal in May 2011). The impact of the interaction layer depth and the extraction ratio (fixed parameters in the model) was also observed for this analysis due to the residence time of pesticide in the soil since application until sampling; longer periods would reduce pesticide availability for surface runoff due to pesticide infiltration to deeper layers and degradation. Results suggest that assuming uniform application dates was a big constraint in the simulation.

Results from all the uncertainty analyses showed that the simulated ranges of pesticide concentrations did cover some of the pesticide concentrations observed in the measured data but these uncertainties did not explain all discrepancies in the simulation. The large concentrations that were not covered by the model and the uncertainty analyses are very likely to be caused by point-source pollution from handling pesticides or cleaning spraying equipment since they were always simulated at very small concentrations and they occurred during recession flow without association to any runoff event or change in the flow.

Finally, most model evaluations assume absolute quality of the measured data; nevertheless monitoring data are prone to error (Baginska et al., 2003) due to different sources of uncertainty in sampling collection, handling and analysis. In this study, errors were found in the calculations of the reported concentrations which were suspected not to be referred to the volume of the samples used in the analysis. In addition, single samples from each sampling location were collected which pose an important source of uncertainty due to temporal variability in the concentrations during the day and between sampling dates; integrated sampling techniques would provide more reliable data than grab samples (Holvoet et al., 2007b). The restricted amount of monitoring data was a limiting factor for the assessment of pesticide simulations. There could be differences in the magnitude of pesticide emissions for specific days but it is also important to assess the model performance in the simulation of the overall pattern of pesticides throughout the year. Other studies with limited amount of catchment information have opted for carrying out continuing studies to set up more reliable databases (Shamshad et al., 2008). However, the model as it stands can be used for a comparative assessment of the areas of risk, practices and conditions that can contribute to surface water pollution in the Valle del Cauca.

5.5.4 Analysis of the areas of risk, practices and conditions for water contamination using AnnAGNPS

Risk maps can be used when targeting water protection measures (Brown et al., 2007; de Snoo et al., 2006). These maps should be clear and objective so that they could be used to support decision making. Risk maps were calculated based on two different indicators, one about pesticide usage and the other about pesticide export to water. The first map (Figure 5-27) showed the amount of pesticide applied per area which depends on the crop area; larger crop area will imply more pesticide applied. The second (Figure 5-28) about the relative percentage of pesticide exported to the River Cauca combines both pesticide application as well as the watershed conditions responsible for pesticide emissions; this calculation showed moderate pesticide losses in most of the watersheds with an average export value of 0.07% which should be addressed by policy makers and environmental agencies in the area.

The AnnAGNPS model was designed to assist with determining Best Management Practices (BMPs). Studies that used the model for this purpose concluded that the model was suitable for gross estimation and comparative assessment of BMPs (Baginska et al., 2003; Bhuyan et al., 2003). For the Valle del Cauca, a comparative assessment to study the impact of improving soil management conditions in the studied crops was undertaken by changing the calibrated runoff curve numbers to their equivalent for good hydrological conditions (keeping the 10% increase in curve numbers from model calibration). The improvement in the runoff conditions for the studied area showed a reduction of 78% in pesticide loads at the catchment outlet. A variety of BMPs that can help to reduce pesticide emissions due to overland flow which can also be evaluated in the model include crop management to minimize the use of pesticides in agricultural production, reforestation, the use of buffer zones along the river banks and management of riparian and wetland areas.

5.5.5 Alternative to triazine pesticides

Despite efforts in BMPs, triazine pesticides are relatively mobile, persistent and pose a high risk for groundwater and surface water contamination. An analysis by Ackerman (2007) showed that atrazine is not the only viable solution for maize production as many organizations have claimed. Italy and Germany have not seen a decrease in maize yield since atrazine was banned in 1991, and yield figures are comparable to data from the US where atrazine is still in use (Ackerman, 2007). A chemical alternative to replace the use of atrazine is mesotrione, a triketone herbicide, with a short half-life, crop selectivity, wide application window and low toxicity (US EPA, 2001). Mesotrione is available on the market as a single active ingredient produced by Syngenta (Callisto®) and DuPont (Mesotrione 50WG) or as mixed formulations with other herbicides (e.g. with S-metolachlor in Lumax® or with glyphosate and S-metolachlor in Halex®).

The effect of replacing triazine herbicides was evaluated by the simulation of mesotrione emissions in the calibrated model in the Valle del Cauca. Modelling results showed a 94% reduction in the total mass of pesticide applied. In addition, the transport of pesticide to surface water was predicted to be reduced by 96% expressed on a mass basis or by 87.4% when expressed as a proportion of the total pesticide applied. Additional tests related to yield performance and cost impacts should be made to ensure the viability of this chemical alternative under Colombian conditions. Based on pesticide usage to maize in this study and listed prices per gallon from a supplier in the US (AG Chemical Solutions Inc., 2014), the cost of mesotrione ($86/ha) per application would be six times higher than atrazine ($15/ha). Some farmers in the US have begun replacing atrazine with mesotrione (Land Stewardship Project, 2009). Different studies have tested and compared mesotrione weed performance in maize against that of atrazine, and most of them have demonstrated equal or better results on yields (Armel et al., 2003), weed control (Hartzler and Owen, 2013; Stephenson et al., 2004; Armel et al., 2003; Johnson et al., 2002) and reduced development of weed resistance (Armel et al., 2003). In contrast, other studies claimed that a ban on atrazine would reduce yield by about 1 to 6% in the USA (Coursey, 2007; Fawcett, 2006). The alleged negative economic impact that a ban on atrazine would have on crop production in the USA seems to be the main reason for still allowing its usage in this country (Coursey, 2007; Fawcett, 2006) despite the proven high potential of water pollution. Other studies consider that a cost-benefit approach instead of only looking at the economic impacts would be the best way to determine whether the triazine herbicides should be banned (Ackerman et al., 2014; Ackerman, 2007).

5.6 Conclusions

This modelling study was useful to determine the minimum site-specific data requirements to simulate triazine emissions from maize, sorghum and sugarcane in the Valle del Cauca. One of the major difficulties in the application of the model was the lack of information about the catchment. A combination of field data, modelling and assumptions were used to estimate some of the input parameters. This approach resulted in a good hydrological simulation of the River Cauca. Triazine concentrations were not always well simulated compared to the measured data though good results were observed for some stations and monitoring days. Uncertainty analysis of some of the input parameters could not explain all discrepancies in the simulation and showed that a particular uncertainty of great impact in the simulation was the assumption of uniform pesticide application. The use of a more realistic application schedule is expected to considerably increase the modelling performance in the simulation of pesticide transport but the data for such a large and complex catchment would be difficult to obtain and would require the participation of farmers and sugarcane mills. In addition, the lack of more detailed pesticide monitoring data as well as inconsistencies and uncertainty in some of the observed concentrations was a major constraint more in depth evaluation of model performance.

Despite discrepancies in the pesticide simulation, the model was suitable to be used to identify some of the risk areas and to evaluate the possible reduction of pesticide emissions by implementing BMPs in the area. Modelling results confirm that the intensive use of triazine herbicides in the Valle del Cauca and the lack of pesticide application control pose a high risk to water bodies in the region which is exacerbated by the lack of monitoring data. BMPs were predicted to reduce emissions by around 78% but the risk of pesticide pollution would remain high because of the extensive agriculture in the area and the high persistence and mobility of triazine herbicides. The best solution appeared to be a switch to other herbicides such as mesotrione. A simulation of this pesticide following the recommended usage, showed an 87% reduction in pesticide loss of total pesticide applied from early weed control in maize, sugarcane and sorghum crops in the catchment. In addition, catchment management including a pesticide monitoring programme combined with pesticide modelling has shown to be the most viable and efficient approach to control pesticide contamination in the area.

6 Solute fate modelling at the catchment-scale

There is a wide range of models for the simulation of transport of contaminants in rivers. The level of complexity of these models ranges from very simple screening tools which require a very limited amount of input data to complex models with extensive input data requirements. Simple screening models (e.g. Fugacity Level III (Mackay et al., 1985b), SimpleBox (van de Meent, 1993) and dynamic flow analysis (Morf et al., 2007)) can give an initial estimate of the environmental partitioning and expected order of magnitude of chemical concentrations in the environment but they cannot reflect the spatial and temporal dynamics of pollutants in real river/stream systems in the same way as more complex models (Leu et al., 2004; Neumann et al., 2002; Kreuger, 1998). Generally models range in level of complexity from empirical to more sophisticated physically-based models. However, an increase in the level of complexity does not necessarily imply an increase in reliability in predictions (Grunwald and Frede, 1999). The level of complexity of a fate model should be selected according to the modelling purpose, available data, geographical scale and output resolution required. Moreover, factors influencing the transport of pollutants in the environment are not the same for different locations. The simplest model that suits all these factors would be the best choice to avoid unnecessary over-parameterisation. Parameter parsimony has the advantage that if a successful fit in the model is achieved without a large number of parameter to adjust then confidence would increase that the important drivers controlling the fate of solutes are covered (Jorgensen, 1984).

Modelling the fate of relatively new contaminants such as brominated flame retardants has the limitation of data availability and applicability of models in contrast to other well studied contaminants such as pesticides. The global lack of information on the usage of BFRs generates great uncertainty in model input parameters and model evaluation. For instance, special attention has been focused into the remaining commercially available PBDE, decabromodiphenyl ether but statistics about its consumption at the country level are scarcer in both industrialised and developing countries.

Pesticides are well-known contaminants and information about their fate continues to grow. There are about 300 active ingredients of pesticides registered in Europe (Bielza et al., 2008). Pesticide regulations tend to become stricter over time and the process of registration of new ingredients requires a large number of studies to ensure safety standards for the environment and humans. It is estimated that the process from developing to getting approval for a new active ingredient can take about 9 years and costs approximately £140 million (CPA, 2007). Despite restrictions and regulations, monitoring studies have found a wide range of active ingredients in surface water at concentrations that are above the permitted standards (Pesticide Forum, 2012). Pollution of water bodies by diffuse transport of pesticides occur in both industrialised and developing countries. However, different challenges for pesticide management are faced in the two contexts due to variation in agricultural practices and environmental conditions.

In the UK, the Catchment Sensitive Farming programme has been deploying intensive pesticide management strategies since 2006 to reduce diffuse emissions including pesticides from agricultural practices (CSF, 2011). The strategy includes training for farmers and regular monitoring of surface water. Since the programme started, a considerable amount of data has been generated for pesticide concentrations from priority catchments. The design of the monitoring programmes as well as the interpretation of results and trends is a complex task that this programme has faced (CSF, 2012). Monitoring results show that the rate of detections has been very low compared to the total number of samples collected. In addition, there is uncertainty in the level of impact of the programme on reducing pesticide diffusion to surface water due to changes in rainfall and flow during the period of the programme. The dynamics of pesticides depend on many environmental, usage and climate factors. Mathematical fate models offer a holistic approach that can help to understand the dynamics of pesticides.

6.1 Hydrology simulation

There is a wide range of fate models that have been used to simulate pesticide loss at the catchment-scale. However, a much smaller number of models are able to simulate pesticide emissions accounting for all the routes of entry to water. Most models are specialised in a few emission routes which could be a problem when the river network receives pesticide pollution from other important pathways. Designing modelling frameworks by coupling models has been shown to be a useful approach in tackling this issue (Zhu et al., 2013; Stenemo et al., 2005; Arheimer and Olsson) but care must be used when models are run separately and there is no feedback between them (Stenemo et al., 2005); disagreements in water and pesticide balance between models can cause under- or over-estimation of water flow and pesticide loads. For instance in the present study, field-scale models that simulate each route were coupled in attempt to simulate pesticide loss via drain flow and surface runoff for the Wensum catchment; the best results were obtained when coupling MACRO with PRZM but high over-estimation of runoff and pesticide emissions were observed particularly for soils with drainage systems since PRZM does not include drainage flow in the water flow description.

Field-scale models can be used to simulate small to medium-scale catchments, with reduced spatial variability of the weather data and on a daily time-step resolution. Field-scale models have been used to simulate catchment-scale processes with fairly good results (Tediosi et al., 2012; Beulke et al., 2009; Lindahl et al., 2005; Wilcox et al., 1990) despite not accounting for the effect of the river system in the simulations. In the present study, there was no major difference between simulations from a modelling framework composed of field-scale models and from a catchment-scale model when monitoring applied from a medium-scale catchment in Eastern England. This suggest that in-stream processes did not have significantly impact on the simulation of pesticides at the catchment outlet; this result contrasts with other studies that consider that the interaction of pesticides with sediments in the river system can influence the pattern of pesticide emissions (Holvoet et al., 2005). The use of field-scale models to simulate catchment-scale processes implies major challenges that need to be addressed when defining the conceptual model; the model should include the most important sources of flow over the catchment in order to satisfactorily simulate the river flow including baseflow to simulate low-flow periods.

The accurate simulation of periods of low-flow is particularly important for pesticides that are applied during spring and summer, when the models are not able to simulate small drain flow peaks after long, dry periods. Different sources of uncertainty can affect the simulation of low-flow periods such as uncertainty in the rainfall data. A common challenge in hydrological modelling is to obtain accurate rainfall data (Bardossy and Das, 2008; Kouwen et al., 2005; Mehta et al., 2004) since it is the main driver controlling the accuracy of hydrological simulation. Rainfall gauge measurements are subject to uncertainty and under-estimation of rainfall from rain gauge measurements is common during low intensity precipitation and high winds (Wang et al., 2008; Ciach, 2003; Nystuen et al., 1996). As errors in rainfall measurements are variable over time, the impact on water flow simulation varies during the hydrological year, as was observed in the present study; a great impact was particularly observed during low-flow periods depending on the sensitivity of the model by affecting the timing of flow recovery at the end of low-flow periods.

Owing to the complex nature of rainfall uncertainty, model calibration from this source of uncertainty can only be achieved by the use of more accurate measurements. Other hydrological models such as rainfall-runoff models used for flood forecasting have also been affected by rainfall uncertainty (Moulin et al., 2009; Bardossy and Das, 2008; Sun et al., 2000). Different models to estimate errors in rainfall measurements have been developed for rainfall-runoff models but no significant improvements in hydrology simulations have been achieved, even after intensive calibration, good quality rainfall data and long datasets (Moulin et al., 2009). Meteorological services should be aware of the limitations of uncertainty in rainfall data for the efficient use of hydrological models, and measures should be taken to deliver rainfall data along with information about the confidence intervals generated in real time. This information would be useful for applying probabilistic approaches that could improve hydrological simulations.

Spatially distributed catchment-scale models are more comprehensive tools, developed to assess medium to large-sized catchments, taking spatial and temporal variations into account to simulate diffuse pollution (Borah and Bera, 2003). Simple watershed models like SPIDER (Renaud et al., 2008) are useful when the spatial distribution of some of the input factors is available but the variability of the rainfall is small since the model only allows a single rainfall dataset. SPIDER can also be used to simulate relatively large catchments like the Wensum as long as the amount of fields and ditch/stream blocks does not affect the stability of the model. Stability issues were found when more than 45 fields and 25 ditch blocks were exceeded in the model set up. More complex watershed models like AnnAGNPS and SWAT simulate water quality responses to management practices including specific land-management operations, crop rotations and mitigation measurements in the catchment. These models allow high spatial variability of virtually any parameter including weather data. They can be used to evaluate the effect of best management practices on pesticide diffuse emissions as well as to gain insight into which measures would be most effective (Holvoet et al., 2007b).

The evaluation of model results involves the assessment of model performance by considering the degree of fit of pesticide simulations against measured data. The first step in the evaluation normally consists in the evaluation of the hydrology simulation. Model calibration may be required to meet good simulation standards. The identification of target parameters to calibrate the model hydrology can be carried out by analysing the water balance. Water budgets that are normally calibrated in fate models are those related with evapotranspiration or soil description (Zuercher et al., 2011; Grunwald and Norton, 2000; Besien et al., 1997; Singh et al., 1996). Evapotranspiration is an important process which greatly affected the simulated hydrographs in the present study, particularly during periods of low-flow. Studies have observed that a small over-prediction of the evapotranspiration can greatly under-estimate or miss small but important drain flow peaks during spring and summer (Lindahl et al., 2005; Besien et al., 1997). In addition in the present study, disagreements in evapotranspiration apart from causing a general under-estimation of the flow also caused delays in flow recovery during winter periods, under-estimating pesticide emissions. Calibration of evapotranspiration can be achieved by adjusting crop growth parameters in the model (Lindahl et al., 2005). Other options are to introduce pre-calculated evapotranspiration data or use an alternative evapotranspiration model.

6.2 Simulation of pesticide losses

Since pesticide emissions in models are dependent on water flow, a good hydrological simulation is important for the prediction of reliable pesticide loads. Moreover, a small deviation in the simulation of water flow generally affected pesticide results to a much greater extent. Model performance is usually evaluated by application of different statistical and visual approaches. The Nash-Sutcliffe model efficiency is a widely used statistical for model evaluation which provides an indication of the correlation between observed and simulated data (Nash and Sutcliffe, 1970). However, in the present study MACRO achieved better overall model performance in the simulation of hydrology in the Wensum than SPIDER but the latter was generally better at the simulation of pesticide emissions. The reason was that SPIDER was able to simulate water flow better than MACRO at key times such as at the beginning of the winter periods and SPIDER includes a description of interlayer flow (lateral sub-surface flow). Pesticide loss via interlayer flow normally contains less pesticide loss than drain flow (Carter, 2000). This agrees with model simulation from SPIDER; when drain flow occurred, emissions from this route were dominant but interlayer flow was important when drain flow was not the main driver for pesticide loss particularly for pesticides applied during spring and summer periods. Interlayer flow is normally simulated by the kinematic storage model of Sloan and Moore (1984) and SWAT and AGNPS include this approach in their simulations. Lateral movement of water and residual pesticide below the soil surface can be triggered by small rainfall events when antecedent soil moisture is large (Kahl et al., 2008; Ng et al., 1995).

Simulation of hydrology is a well-known process and satisfactory results are generally obtained with adequate weather and soil description. However, more complex challenges are faced when modelling pesticide emissions at the catchment-scale. The accuracy of the simulation of pesticide emissions is affected by different sources of uncertainty (Larsbo and Jarvis, 2005; Dubus et al., 2003b; Dubus and Brown, 2002; Sohrabi et al., 2002). Different approaches can be undertaken in order to reduce the level of uncertainty in pesticide results. Better simulations can be achieved by an improvement in some of the input parameters such as using site-specific experimental data on pesticide sorption and degradation as well as accurate information on application dates and pesticide usage but this information is seldom available (Boithias et al., 2014; Gericke et al., 2010; Holvoet et al., 2005; Dubus et al., 2003b). Model sensitivity can be a good initial guide to identify parameters that require special attention (Holvoet et al., 2005; Dubus et al., 2003a; Dubus and Brown, 2002; Fisher et al., 1997). However, the impact on the simulation has shown to be more pesticide-specific than model related (Boithias et al., 2014; Lindahl et al., 2005) and would depend on pesticide properties and usage patterns (Boithias et al., 2014). These observations are in agreement with results from the present study and were common to pesticide simulations obtained using contrasting models and different environmental and climate conditions. Pesticide fate models require accurate and detailed input parameters in order to provide more certain results. For instance, pesticides degradation is a critical parameter, particularly for solutes with small half-lives.

Uncertainty analyses showed that pesticide application date was the most critical input parameter common to most pesticides and all models. These results agree with the findings of other studies (Boithias et al., 2014; Boulange et al., 2012; Holvoet et al., 2005). Holvoet et al. (2005) suggested that application date had greater impact than application rate and rainfall errors to simulate atrazine emissions based on a sensitivity analysis for SWAT. In the present study, for an 8,000-km watershed in south-west Colombia, the simulation of triazine herbicides (atrazine and simazine) using AnnAGNPS was affected by pesticide availability in the runoff interaction layer which was mainly influenced by the application date, pesticide sorption, degradation rate and timing of rainfall event. This finding is in agreement with a study by Boithias et al. (2014) who carried out a sensitivity study for SWAT using plausible ranges of application dates for two contrasting pre-emergence herbicides; the authors showed that the effect of the application date was a pesticide-specific factor influenced by their bioavailability and hence by sorption and degradation. When comparing results between models in the present study, it was found that the parameters that influence bioavailability would also be different between modelling approaches. For preferential flow models, the availability for pesticide loss would depend on the leaching potential of pesticides to reach tile drains where degradation showed more influence than sorption. However, in runoff models pesticide sorption was more important than degradation in the availability of pesticides in the runoff interaction zone.

In principle, the application date should be a relatively easy parameter to obtain since it does not require significant financial investment compared to other input parameters such as pesticide sorption and degradation. However, this is a most socio-politically sensitive parameter and in some cases it is almost impossible to gain access to this information. For instance, the only state in the US that requires farmers to supply details of pesticide application and holds a detailed database on pesticide usage is California. California is recognised for having the most comprehensive pesticide usage reporting programme in the world (CDPR, 2013a). All pesticide use must be reported monthly to county agricultural commissioners, who then report the data to the Department of Pesticide Regulation (DPR) of the state of California (CDPR, 2013b). Reports include date, location, crop and rate of application. Pesticide reporting is not restricted to agricultural use but includes a broad range of pesticide usage; the only exceptions are home-and-garden use and most industrial and institutional uses. Data gathered since 1990 can be accessed by the public as summary reports or a full database in text and GIS formats. Specific data for one county or for a specific location can also be obtained by request to the DPR.

In Europe, farmers are required by law to keep records of pesticide treatments as part of good agricultural practices under the EU regulations 852/2004 and 183/2005 (EC Regulation, 2005, 2004) which came into force in the UK in January 2006 (DEFRA, 2006). Farmers must complete detailed forms which include the pesticide application rate and date. This is kept by the farmers, owners or contractors for an unestablished period of time

(DEFRA, 2006) but this information is not accessible to the public so the information is not fully exploited to tackle pesticide pollution. Therefore, pesticide usage information exists but it is not available to be used in catchment management programmes including the CSF or other research activities. If available, this information would be greatly beneficial to understand the dynamics of pesticides at the catchment-level in the UK by reducing uncertainty in fate model.

6.3 Fate modelling in Colombia and the UK

In the present study, different fate models were used to study the dynamics of pesticides in the UK and Colombia. In the UK, preferential flow has shown to be an important emission source in areas with heavy clay soils where field drains are present (Beulke et al., 2001a; Harris and Catt, 1999; Besien et al., 1997; Johnson et al., 1996; Brown et al., 1995a; Brown et al., 1995b; Haria et al., 1994; Harris et al., 1994)., including the present study for the Wensum. In Colombia, runoff was the most important emission pathway although soils with artificial draining systems were present in a catchment in the south-west of the country with intensive sugarcane cropping. The findings of the current study are consistent with those of Alavi et al. (2007) who showed that preferential flow was not significant in tropical soils after applying two leaching models to tropical soils (S1D DUAL (Ray et al., 2004; Vogel et al., 2000) and MACRO 4.3 (Jarvis et al., 1991)); the finding was attributed to reduce soil moisture. The presence of clay soils, torrential tropical rainfall (short-lasting high magnitude events) and poor pesticide management practices may also enhanced pesticide runoff in these regions.

Surprisingly, a preliminary modelling study using AnnAGNPS for the Cauca along with the use of a series of parameterisation models and assumptions was sufficient to fill the gaps of the scarcer amount of catchment-specific detailed information to achieve a satisfactory simulation of stream flow with rather little calibration. Calculation of runoff by AnnAGNPS, based on the empirical SCS curve number technique (Soil Conservation Service, 1972), was applicable to tropical conditions in Colombia. The applicability of models based on the curve number approach was previously shown by Perez and Paez (2010) using GLEAMS in a hilly region to the south of our study area in Colombia with comparable model performance for the simulation of runoff. In contrast, the application of PRZM (also based on curve numbers) in the UK showed high over-estimation in the runoff for the Wensum even for soils without preferential flow; these results suggest that the use of

PRZM in the UK would require calibration to reduce over-estimations. Calibration of curve numbers was required for Colombia in the present work but to reduce runoff under-estimation due to poor hydrological conditions in the catchment.

In general, pesticide fate models require climate, soil chemical and hydraulic properties, land use, physicochemical pesticide properties and pesticide usage. Differences in the availability and accessibility of these data were observed in Colombia and in the UK. In addition, the availability of monitoring data is a fundamental part of model evaluation, calibration or validation. The main challenge from applying fate models in Colombia was the paucity of both input and measured data. Databases from the government in Colombia are generally difficult to access; information for public access is insufficiently detailed or payment for access is necessary. Some improvements in the accessibility of the information have been made recently, but in most cases it is necessary to directly contact the relevant institution to get access (by email or phone calls). However, the Institute of Hydrology, Meteorology and Environmental Studies of Colombia (IDEAM) has a user-friendly and time-efficient web page for requesting different meteorological and hydrological parameters from a large number of stations across the country (IDEAM, 2011b). Some of the stations are no longer operational and only have historic data. Daily data of most of the measurements can be accessed but information with higher resolution (i.e. hourly data) is normally unavailable. This would be a limitation mainly when hourly precipitation data are required to model runoff events occurring from heavy rain in short periods of time.

The input data required for pesticide modelling in the UK is considerably more accessible and is generally open to the public or freely available for education and research purposes. For example, the Meteorological Office in the UK provides data for academic and research purposes after requesting access online from the British Atmospheric Data Centre (BADC) (UK Meteorological Office, 2012). A good amount of data is available in this database in different resolutions up to an hourly time-step. However, not all meteorological stations carried out measurements of all the required parameters for hydrological models so a mixture of information from different stations would need to be used; this can cause problems to simulations, particularly for precipitation data which is a very sensitive input parameter for the simulation of both water flow and pesticide losses (Arnaud et al., 2011; Obled et al., 1994). Regional pesticide usage statistics from DEFRA (2009) can also be useful information when site-specific pesticide usage is not available but this will add uncertainty in the model. If pesticide usage data are difficult to access in industrialised countries, they are more difficult to obtain in developing countries like Colombia where neither statistics are generated by the government nor is reporting on usage required by farmers.

Differences in pesticide usage between temperate and tropical conditions are due to different factors including climate, socio-economic conditions and crops (Bloomfield et al., 2006). In temperate regions like the UK, pesticide usage follows a uniform crop cycle in the whole country during the year and the period of application for a given crop can be restricted to a few months during the year. In contrast, in tropical regions periods for pesticide application can be more extended and some pesticides can be applied at any time during the year. This is the case for tropical crops such as sugarcane which can be in juxtaposition with several crops at different crop stages. In terms of mathematical modelling this difference implies that there is more uncertainty in the application dates in the tropics than in temperate regions which makes it more challenging to identify typical application dates.

Agricultural farming in Europe poses high pressure on farmers who have to deal with a great amount of paperwork to buy and use pesticides. Pesticide management practices have also reduced arable land by the installation of artificial detention ponds, ditches, wetlands and buffer strips. These practices reduced pesticide loss in temperate regions but pesticide pollution continues to occur and despite great efforts there are continuing difficulties observed in complying with European standards. Management practices can be more cost-effective when implemented using pesticide fate models.

6.4 Recommendations for future research

More information about the consumption of relatively new contaminants like BFRs at the country scale should be generated in order to produce more accurate calculations of emission and better risk assessments. More modelling studies at the catchment-scale using measured emission and removal information would help to understand the dynamics of these contaminants in river systems.

Model uncertainty is not only related to model predictive capacity but also to accurate parameterisation which is highly dependent on data accessibility and data quality. More studies into the combined effect of uncertainties in fate modelling as well as in pesticide-specific uncertainty effects would help to gain more understanding into the impact on simulations. The present study investigated the effect of a few sources of uncertainty; however, a full uncertainty analysis is recommended in future studies to provide a broader picture of their impact on simulations. For instance, a probabilistic approach using Monte Carlo analysis (Press, 1988) or the Bootstrap Method (Efron and Tibshirani, 1993) can help to gain insight into confidence intervals and uncertainty estimates of pedotransfer functions to derive hydraulic properties without collecting large quantities of data (Schaap et al., 2001).

The quality of rainfall data is crucial for hydrological modelling. Meteorological services should increase the amount of stations recording finer temporal resolution such as hourly rainfall data. They should also consider the delivery of rainfall information along with confidence intervals generated during measurements, based on the intrinsical error of the instrument, the method and other climate parameters such as wind and rainfall intensity. The addition of error information to rainfall data would be greatly beneficial for different areas such as flood forecasting and river quality modelling at the catchment-scale.

Further research is required to simulate summer flow using preferential flow models like MACRO and SPIDER. Real field moisture data can be used to study and assess water budgets during this period to improve simulations. In addition, more research in developing runoff models applicable to UK conditions is necessary; available runoff models are focused on runoff generated from short, intense rainfall events while runoff in the UK is often caused by excess runoff after soil saturation.

Studies into the applicability of fate models in tropical regions have shown successful results for runoff models (Bannwarth et al., 2014; Perez and Paez, 2010; Polyakov et al., 2007). Field assessments for the generation of curve numbers based on local conditions in the tropics would provide valuable information for runoff modelling as well as to identifying deviations in the behaviour of this empirical approach in these regions. Further model application should be done to study the applicability of other fate models particularly those describing other pesticide emission pathways. In addition, the generation of databases on soils and pesticide properties in tropical regions would reduce uncertainty from using input parameters generated in temperate regions.

Modelling results cannot be accepted as reliable without assessing model performance against real data. Composite samples of water should be used as a better representation of river quality data. Particularly, more long-term monitoring programmes are required in tropical regions to evaluate model results. Fate models can assist in the design of cost-efficient monitoring programmes and management practices.

Regulations for the control of pesticide use as well as training to farmers and pesticide agronomists are urgently needed in tropical countries to reduce both point and diffuse sources and pesticides. The implementation of licenses for individuals or organisations before buying and using pesticides and the generation of usage records can also help environmental authorities to gain more control on pesticide usage (CDPR, 2013b; EC Regulation, 2004).

Further work is necessary to generate databases related to pesticide usage in both industrialised and developing countries. Examples like the DPR database in California show that this can be accomplished and would be very beneficial to governmental agencies, policy makers, scientists, farmers and other interested parties (CDPR, 2013b). Specific areas in which detailed pesticide usage data would be beneficial include i) risk assessment to increasing their credibility by using real information and avoiding incorrect assumptions; ii) pesticide management programmes by access to up-to-date data for assessment of management practices, identification of the most successful strategies for pesticide management and pesticide usage trends; iii) epidemiological studies and other public health issues; iv) site-specific usage data combine with GIS information to help identify and resolve potential conflicts over pesticide pollution to the environment and potential risk to endangered species; v) identification of areas susceptible to diffuse pollution of pesticides; vi) calculation of emissions of volatile organic compounds (VOCs) generated from pesticide application.

6.5 Concluding comments

The present study was designed to determine the dynamics of contrasting environmental contaminants in a temperate and a tropical region by extrapolation of models and practice from temperate regions to Colombian conditions. Drivers of pesticide pollution differed between the two regions due to differences in geographical, usage and climatic factors. The present study confirms previous findings and contributes additional evidence that suggests fate models developed in temperate regions are applicable to developing countries but differences in input parameters should be considered. Constraints in data availability were observed in both countries for relatively new contaminants such as BFRs but also for pesticides which have been investigated over several decades; the study was limited by the lack of more accurate information. More accurate pesticide fate models are increasingly necessary to assist in design and evaluation of pesticide management programmes; however, the results of this research indicate that more work should be carried out for improving input data quality in particular rainfall data and pesticide usage to reduce model uncertainty.

Appendix

Appendix material for Chapter 2:

Table A2– 1 Estimated amount of EEE containing decaBDE in sales, stock and and accumulated WEEE for 2010 in Colombia.

Articles	**Production**	**Imports**	**Exports**	**Apparent consumption**	**Stock**	**WEEE accumulated**
	(10^6 units)					**(10^3 tonnes)**
Category 1: Large household appliances						
Refrigerators[a]	1.2	0.24	0.7	0.74	8.8	130
Washing machine[a]	0.06	0.7	0.027	0.73	5.1	49
Category 3: Information and communication technologies						
Desktop computer (incl. mouse and keyboard)[b]	NA	0.9	NA	0.9	3	84
Laptop computer[b]	NA	1.5	NA	1.5	1.5	
Mobile phone[b]	NA	2.70[c]	NA	2.7	42.02[c]	11
Category 4: Consumer electronics						
Television (CRT)[a]	0.25		NA	0.25	18	60
Television (LCD)[a]		1.5	NA	1.5		
DVD/VCR[a]	NA	1.75	NA	1.75	8.6	9
Average audio equipment[a]	0.4	8	NA	8.4	41	70

[a]Blaser (2009); [b]Ott (2008); [c](INCP, 2011)

Table A2– 2 Average weight for different articles containing decaBDE (UNEP, 2012).

Articles	Weight (kg)	Source
Category 1: Large household appliances		
Refrigerators	70	DIAN (2009)
Washing machine	45	DIAN (2009)
Category 3: Information and communication technologies		
CRT monitor	14.1	Laffely (2007); Zumbuehl (2006)
LCD monitor	4.7	Ecoinvent Centre (2010); SWICO Recycling Guarantee (2006)
Desktop computer (incl. mouse and keyboard)	9.9	Eugster et al. (2007)
Laptop computer	3.5	Ecoinvent Centre (2010); SWICO Recycling Guarantee (2006)
Mobile phone	0.1	UNEP (2012)
Category 4: Consumer electronics		
CRT TVs Colombia	22	DIAN (2009)
LCD TVs Colombia	19.2	DIAN (2009)
DVD	3	Blaser (2009)
VCR	4.2	Blaser (2009)
Average audio equipment	1.86	Blaser (2009)

Table A2– 3 Total polymer fractions in some EEE/WEEE applications (Waema and Mureithi, 2008).

Category/Article		Total polymer fraction $f_{Polymer}$ [in % by weight]		
		Minimum	Maximum	Mean
3	ICT equipment without monitors	26%	58%	42%
3	CRT monitors	13%	38%	30%
4	Consumer equipment without monitors	21%	26%	24%
4	CRT-TVs	15%	38%	30%

Table A2– 4 Total polymer fractions and decaBDE concentrations in relevant EEE categories (Waema and Mureithi, 2008).

Relevant EEE	Total polymer fraction (mean) $f_{Polymer}$ [in % by weight]	DecaBDE content (mean) in plastics $C_{DBDE;Polymer}$ (%)
WEEE category 3 (without CRTs)	42%	4.2 - 6.3
CRT computer monitors	30%	3.0 – 4.5
WEEE category 4 (without CRTs)	24%	2.4 – 3.6
CRT-TVs	30%	3.0 – 4.5

Table A2– 5 Production, import, export and estimated apparent consumption figures of carpets in Colombia (DANE, 2010).

Year	Production	Imported	Exported	Apparent consumption
			(tonnes)	
1999	33,112	20,403	8,316	45,199
2000	36,208	20,971	9,502	47,677
2001	40,446	23,908	10,667	53,687
2002	45,807	27,953	12,424	61,335
2003	50,957	25,546	13,591	62,912
2004	51,489	25,840	15,925	61,403
2005	62,917	29,726	17,164	75,480
2006	63,370	34,574	19,039	78,905
2007	69,009	30,110	21,580	77,539
2008	77,415	36,962	25,168	89,209
2009	96,142	45,673	33,738	108,078
2010*	90,411	41,589	30,064	101,936

*Estimate (Bautista, 2010)

Appendix material for Chapter 5:

Table A5– 1 Crop values of root mass, canopy cover and canopy droplet fall height used in the model (Renard et al., 1997).

Number of days after planting	Root mass in the top 100 mm of soil (kg/ha)			Canopy cover fraction			Rain fall height (m)		
	Sugar cane	Maize	Sorghum	Sugar cane	Maize	Sorghum	Sugar cane	Maize	Sorghum
15	334	56.	56	0.05	0.05	0.05	0.031	0.031	0.031
30	135	202	202	0.20	0.10	0.10	0.061	0.152	0.152
45	336	392	392	0.35	0.50	0.50	0.061	0.305	0.305
60	359	594	594	0.35	0.80	0.80	0.061	0.518	0.457
75	359	941	896	0.35	1.00	1.00	0.061	0.762	0.601
90	359	1188	1188	0.35	1.00	1.00	0.061	0.914	0.671
105	359	1188	1188	0.35	1.00	0.90	0.061	0.914	0.671
120	359	1188	1188	0.35	1.00	0.70	0.061	0.914	0.671
135	359			0.35			0.061		
150	359			0.35			0.061		
165	359			0.35			0.061		
180	381			0.40			0.152		
195	448			0.60			0.305		
210	740			0.90			0.396		
225	1121			1.00			0.457		
240	1345			1.00			0.457		
255	1345			1.00			0.457		
270	1345			1.00			0.457		
285	1345			1.00			0.457		
300	1345			1.00			0.457		
315	1345			1.00			0.457		
330	1345			1.00			0.457		
345	1345			1.00			0.457		

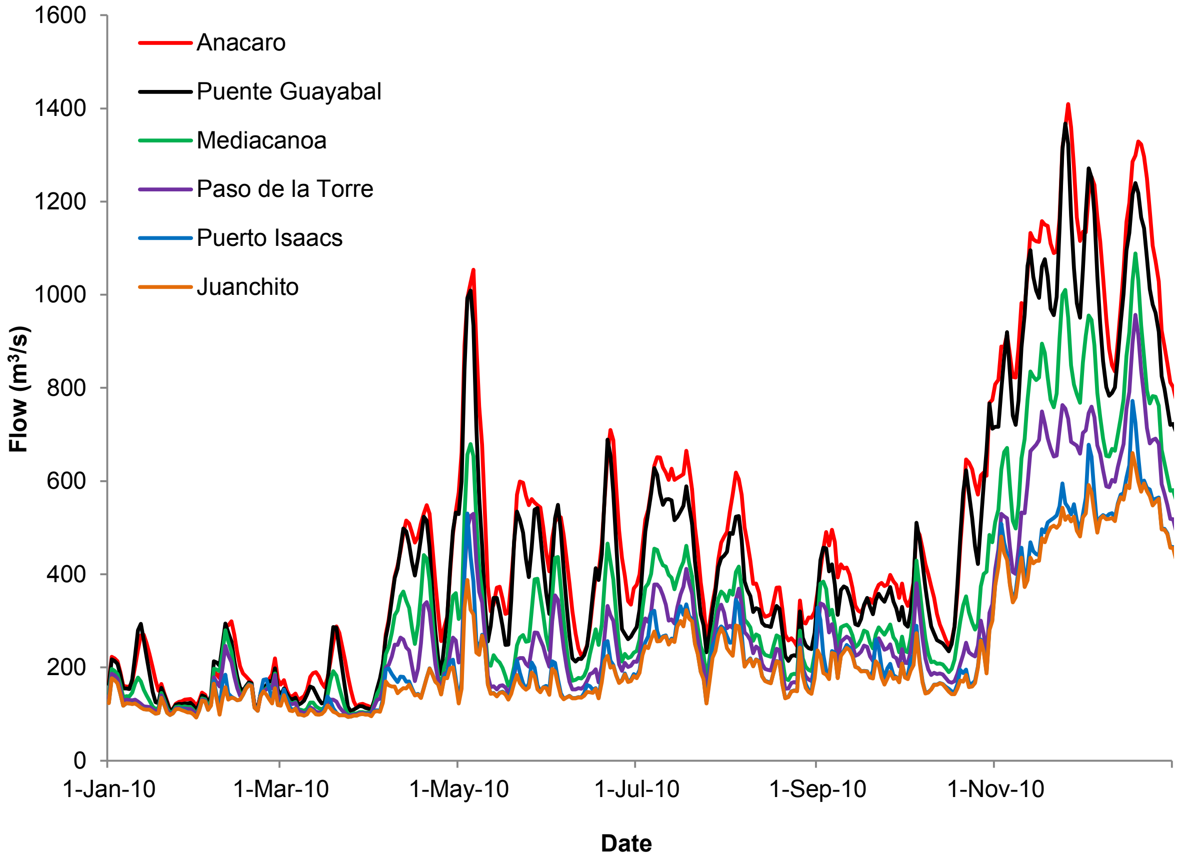


Figure A5- 1 Simulated stream flow for the different monitoring stations along the River Cauca.

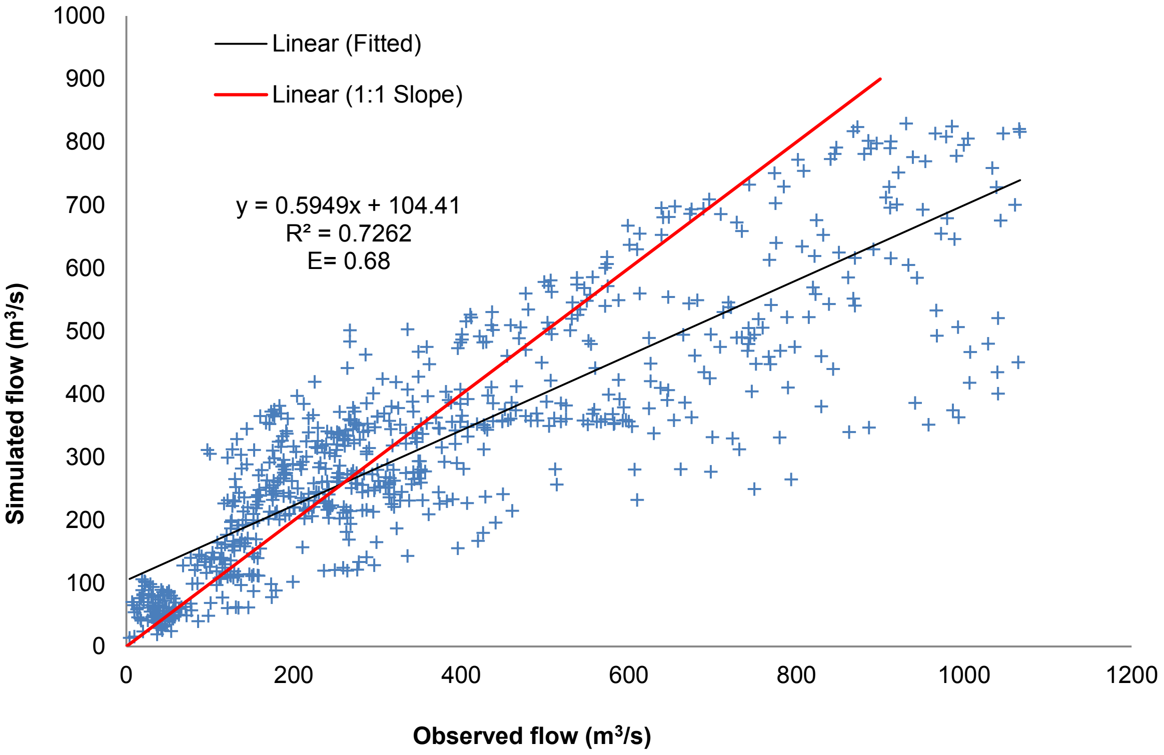


Figure A5- 2 Plot of simulated versus observed flow together with the one-to-one line slope (red line) and the linear fit (black line) for the simulation with CSA = 300 m, MSCL = 1000. The plot also shows the equation fitted to the linear model, the coefficient of determination and the Nash–Sutcliffe model efficiency coefficient.

List of acronyms

AnnAGNPS: Annualized Agricultural Non-Point Source pollution model

ALPHA: van Genuchten’s alpha

ASCALE: Effective diffusion pathlenght

ATTEN: Attenuation factor for solar radiation in a crop canopy

BADC: British Atmospheric Data Centre

BFI: Baseflow index

BFRs: Brominated flame retardants

BMPs: Best management practices

CANCAP: Canopy interception capacity

CFORM: Form factor that controls the rate of increase of leaf area between emergence and maximum leaf area

CRT: Cathode ray tube

CRITAIR: Critical soil air content for root water uptake

CSA: critical source area

CSF: Catchment Sensitive Farming programme

CTEN: Boundary soil water tension

CVC: Corporación Autónoma Regional del Valle del Cauca

DecaBDE: Decabromodiphenyl ether

DrWPAs: Drinking Water Protected Areas

DEM: Digital elevation model

DEGMAL: Degradation rates for liquid phase in the macropores

DEGMAS: Degradation rates for solid phase in the macropores

DEGMIL: Degradation rates for liquid phase in the micropores

DEGMIS: Degradation rates for solid phase in the micropores

DRAINDEP: Drain depth (primary drainage system)

EEE: Electrical and electronic equipment

EXPB: Exponent in the degradation water response function.

FAWC: Root adaptability factor

GIS: Geographical information system

GRAD: Hydraulic gradient values controlling the flow from the bottom boundary

GREAT-ER: Geography-referenced Regional Exposure Assessment Tool for European Rivers model

GW: Groundwater mixing model

HBCDs: Hexabromocyclododecanes

HMAX: Maximum crop height

HRU: Hydrological response units

IDEAM: Institute of Hydrology, Meteorology and Environmental Studies of Colombia

IDMAX: Day of maximum leaf area/rood depth

IDSTART: Day of crop emergence

IHARV: Day of harvest

KSATMIN: Saturated hydraulic conductivity (mm h^{-1});

KSM: Boundary hydraulic conductivity (mm h^{-1});

LAIHAR: Leaf area of harvest

LAIMIN: Leaf area index at ZDATEMIN

LAIMAX: Maximum leaf area index (unitless)

LCD: Liquid-crystal display

LOD: Limit of detection

LOQ: Limit of quantification

MSCL: Minimum source channel length

N: van Genuchten's N

OctaBDE: Octabromodiphenyl ether

OSR: Oilseed rape

PBDEs: polybrominated diphenyl ethers

PCBs: Polychlorinated biphenyls

PentaBDE: Pentabromodiphenyl ether

POPs: Persistent organic pollutants

POP-PBDEs: PBDEs listed in the POPs listed in the Stockholm Convention

PRZM: Pesticide root zone model

Q: Water flow

RI50: The solar radiation that reduces stomatal conductance by 50%

ROOTINIT: Root depth at ZDATEMIN

ROOTMAX: Maximum root depth

RPIN: Root distribution

RUSLE: Revised Universal Soil Loss Equation

RZWQM: Root zone water quality model

SPACE: Drain spacing

SPIDER: Simulating pesticides in ditches to assess ecological risk

STP: Sewage Treatment Plant

SWAT: Soil and Water Assessment Tool

TBBPA: Tetrabromobisphenol-A

TOPAZ: Topographic parameterization program

TPORV: Total porosity

TREF: Reference temperature.

TRESP: Exponent in the temperature response function.

WEEE: waste EEE

WFD: Water Framework Directive

WHAT: Web-based hydrograph analysis tool

WILT: Wilting point

XMPOR: Boundary water content

ZDATEMIN: Day number for intermediate crop development stage between emergence and maximum leaf area

ZHMIN: Crop height at ZDATEMIN

ZN: Tortuosity/Pore size distribution factor for macropores

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