# *Volcanogenic Sulfate and Fluoride deposition: Effects on organic and mineral soil gas fluxes and chemistry*

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# Abstract

This thesis focuses on the environmental effects of volcanic eruptions such as Eyjafjallajökull (2010) from which volcanic gases and ash particles can impact upon ecosystems located thousands of kilometres from the source. Currently very little is known about the impact of volcanic pollutants such as $SO_4$ and F on the carbon cycle. This study is a first step towards understanding the potential environmental impacts of volcanic eruptions on peatland and mineral soil C gas fluxes.

Ombrotrophic peat mesocosms sampled from the Northern Peninne uplands, UK, were dosed over 20 weeks with concentrations of $SO_4$-S (24.5 kg ha$^{-1}$) and F (13.5 and 135 kg ha$^{-1}$) simulating a distal Icelandic tephra deposit. Methane and $CO_2$ gas fluxes were measured at regular intervals, but no significant differences were observed for any of the treatments when compared to the controls. This result contrasts with previous studies, which reported a suppression of $CH_4$ emission with the addition of $SO_4$. It can be explained if $CH_4$ production has remained suppressed in the peat soils as a long-term consequence of heavy $SO_4$ loadings in the Pennines area prior to the reduction of $SO_2$ emissions from industrial sources in the 1970s. The mesocosm study results indicate that F deposition, at rates representative of tephra fallout does not interfere with C gas fluxes in peat soils, despite the well-established toxicity of F in the environment. However, F addition to a pristine peat soil in laboratory slurry experiments showed an increase in potential $CH_4$ production rates thus further research is recommended.

Addition of treatments containing high concentrations of F to peat mesocosms had a significant effect on soil solution chemistry. The addition of F increased the solubility of Al, Fe and acetate resulting in the accumulation of both species in solution near the peat surface. This build up of acetate, Al and Fe over the treatment period suggests that F breaks down organo-metallic compounds causing leaching of organic matter along with metal ions. This may

have important implications for microbial communities within the peat that are associated with decomposition of organic matter and carbon cycling.

After the 2010 eruption of Eyjafjallajökull, Iceland, a field experiment was carried out to assess the impact of tephra deposition on soil respiration from a grassland site. The results showed that the chemical effect of ash leaching resulted in a 30% reduction in ecosystem respiration. This study also highlighted the short-term physical effects of tephra deposition on the release of $CO_2$ from soil as the tephra layer impeded $CO_2$ release when wet.

This work provides a useful contribution to the scientific understanding of the effects of volcanic $SO_4$ and F on peatland ecosystems and the physical and chemical effects of ash deposition on soil respiration. Consideration of the impact of volcanic deposition on soil C fluxes in climate models is required in order to be able to fully appreciate how volcanism causes environmental changes.

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# Author's Declaration

This thesis is submitted in fulfilment of the PhD in Environmental Science at the Environment Department, University of York, Heslington, York, YO10 5DD. The material submitted is my own work unless otherwise stated.

# Chapter 1: Interactions of volcanic eruptions and peat soils with the carbon cycle

## 1.1Volcanic eruptions

Volcanoes in a non-eruptive state can emit gases passively semi-continuously. These systems represent a significant source of sulphur (S) (mainly sulphur dioxide ($SO_2$)) and halogens (hydrogen chloride (HCl) and hydrogen fluoride (HF)) to the troposphere, sometimes creating environmental and health hazards for local communities and ecosystems. Alternatively, volcanoes can produce explosive eruptions, injecting massive amounts of gas and tephra high in the troposphere and even up in to the stratosphere.  The Volcanic Explosivity Index (VEI) is a general indicator of the explosive character of an eruption (Newhall and Self 1982).  The VEI is a scale from 0-8, which describes the volume of tephra ejected and the height of the eruption column.  A VEI of 0 indicates a non-explosive eruption which ejects <10,000 $m^3$ of tephra with a column height of <100 m e.g. Kilauea.  A VEI of 8 represents a mega-colossal eruption that ejects >1000 $km^3$ of tephra with an eruption column height of > 50 km e.g. Toba (74,000 BP).

In the UK we are affected at regular intervals by Icelandic volcanism. During the 20th century there were 26 separate eruptions in Iceland of which the majority included some explosive activity. Large explosive eruptions producing more than 1 $km^3$ of volcanic ash occur in Iceland on average once every 1000 years (Thordarson 2007, Goodenough 2010).  Depending upon the weather conditions, ash can be transported to the UK. There is evidence of 10 Icelandic ash layers in UK lake sediments and peat soils (Blackford et al. 1992; Charman et al. 1995; Dugmore et al. 1995; Dwyer and Mitchell 1997; Pilcher and Hall 1992; Pilcher et al. 1995). Similarly, tephra layers from at least 16 volcanic events in Iceland that took place over the last millennium have been traced in locations across northern Europe (Wastegård and Davies 2009)

The 2010 eruption of Eyjafjallajökull in Iceland brought the potential impacts of volcanic eruptions into the media spotlight as ash plumes caused disruption and chaos across Europe with widespread closures of airports leading to thousands of stranded travellers (Brooker 2010). The eruption was relatively small in terms of the amount of ash emitted (0.14 $km^3$ (Global Volcanism Program 2011)), compared to other explosive eruptions in the recent past both in Iceland and throughout the world e.g. Tambora (150 $km^3$ (Stothers 1984)) (Goodenough 2010). The reason why this small eruption caused so much disruption was due to the weather conditions at the time. The Eyjafjallajökull ash plume travelled with the prevailing north-westerly wind and was carried southeast over mainland Europe eventually expanding to the North Atlantic Ocean and the eastern seaboard of Canada. The eruption plume reached approximately 10 km in height.

This thesis will focus on the environmental effects of volcanic eruptions such as Eyjafjallajökull from which volcanic gases and ash particles can impact upon ecosystems located thousands of kilometres from the source.

### 1.1.1 Volcanic eruptions and climate

Explosive volcanic eruptions typically emit large quantities of gases into the upper atmosphere with $H_2O$, $N_2$ and $CO_2$ being the most abundant. Both $H_2O$ and $CO_2$ are important greenhouse gases but they do not impact the greenhouse effect because their current atmospheric concentrations are so large that individual eruptions have a negligible effect (Robock 2000). The most important climatic effect of explosive eruptions is the emission of S species into the stratosphere such as $SO_2$ (Pollack et al. 1976; Rampino and Self 1984). These S species react with OH and $H_2O$ over a number of weeks in the stratosphere to produce $SO_4$ aerosols by the reaction:

$$SO_2 + OH^{\bullet} \rightarrow H_2SO_{4\,(l)}$$

The $SO_4$ aerosols are rapidly advected around the globe and can reside in the stratosphere for approximately 1 -3 years. After the eruptions of El Chichón (1982) and Mt Pinatubo (1991) it took 3 weeks for the aerosol clouds to circle the globe (Bluth et al. 1992; Robock and Matson 1983). These sulfate aerosol layers can cause perturbations in the earth's radiative balance causing warming in the stratosphere and cooling of the earths surface (Fig. 1.1). Sulfate aerosol particles are approximately the same size as visible light (radius ~0.5 µm) and have a single scatter albedo of 1, this causes them to scatter sunlight back into space (Robock 2000). This back scattering reduces the solar radiation reaching the earth's surface thus reducing surface temperatures. Although the direct flux of solar radiation is reduced, some of the incoming solar radiation is forward scattered which results in enhanced flux of diffuse radiation (Roderick et al. 2001). Sulfate aerosols absorb the terrestrial infra-red (IR) radiation, which results in a warming of the stratosphere (Stenchikov et al. 1998). At the top of the aerosol cloud the atmosphere is warmed by absorption of solar radiation in the near IR (Robock 2000).

The most recent and well-documented explosive volcanic event that caused global cooling due to the injection of $SO_4$ aerosols in to the stratosphere was the 1991 eruption of Mt Pinatubo in the Philippines. It has been estimated that this eruption injected 20 Mt $SO_2$ into the atmosphere (Bluth et al. 1992). A climate model simulation of the eruption period suggested a global climate cooling of 0.5°C in 1992 (Hansen et al. 1992). This is similar to the global cooling from Mt Agung 1963 (-0.5°C), the unknown volcanic eruption of 1809 (-0.6°C), Tambora in 1815 (-0.4- -0.7°C), El Chichon 1982 (-0.2°C) and Krakatau in 1883 (-0.3°C) (McCormick et al. 1995; Pinto et al. 1989). The lower surface temperatures caused by the eruption of Mt Pinatubo resulted in deeper vertical convective mixing of water in the Red Sea. This enhanced the supply of nutrients to the surface waters causing huge algal and phytoplankton blooms. These blooms covered large sections of the underlying coral reef leading to extensive coral death (Genin et al. 1995). The climate perturbation following Mt Pinatubo also impacted polar bear numbers in Hudson Bay. In the summer of 1992, cooler surface temperatures resulted in the ice on Hudson Bay melting one month later than usual. The extra time on the ice proved beneficial to the Hudson Bay polar bears as they were heavier and had healthier cubs with more bears being born that year compared to the years before and after (Robock 2003; Stirling 1997).

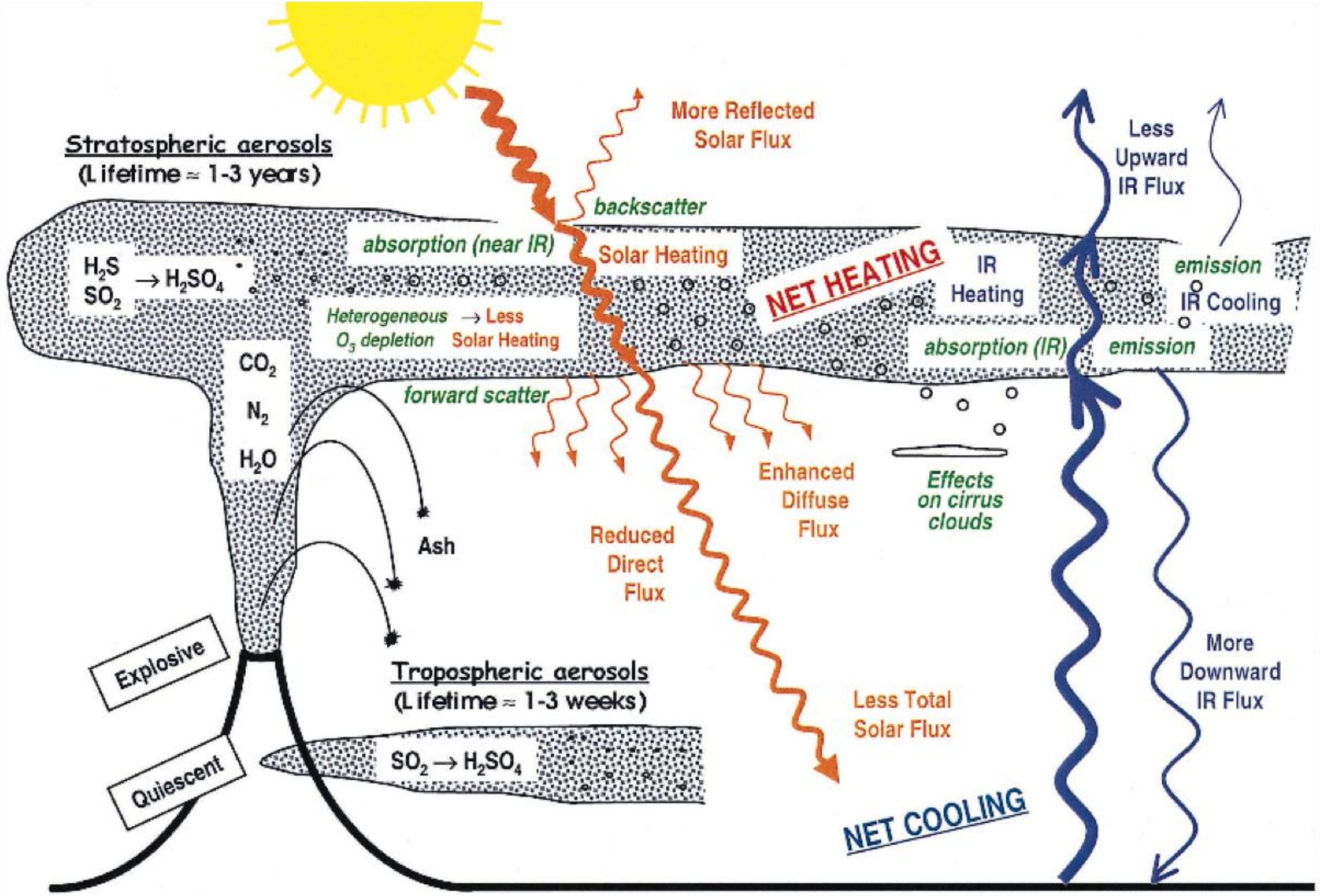


**Fig. 1.1** Diagram representing the effect of volcanic eruptions on the earth’s radiative balance. Taken from Robock (2000).

### 1.1.2 Volcanic eruptions and the carbon cycle

As large volcanic eruptions have significant effects on global climate it is reasonable to assume that they may also have indirect effects on the global C cycle, which is sensitive to temperature. Concentrations of atmospheric carbon dioxide ($CO_2$) have shown a gradual increase since measurements began (Keeling et al. 1976). Over time there have been occasional large deviations from this trend as measured $CO_2$ concentrations suddenly dip, which cannot be explained by anthropogenic emissions or El Nino events. These reductions in $CO_2$ coincide with large volcanic eruptions such as Mount Agung (1963) (Keeling et al. 1996), El Chichon (1982) (Jones and Cox 2001) and Pinatubo (1981) (Gu et al. 2003) (Fig. 1.2). The net loss of C from the atmosphere after the Pinatubo eruption is estimated to be 1.6 Pg (1.6 x $10^{15}$ g) (Sarmiento 1993). A decrease in atmospheric $CO_2$ cannot be directly linked to the injection of volcanic gases because volcanoes inject large quantities of $CO_2$ into the atmosphere. However, the observed decrease in $CO_2$ concentrations may be due to the indirect effects of changes in temperature, atmospheric composition and deposition of volcanic species in the environment. A number of hypotheses have been suggested to explain the decrease in atmospheric $CO_2$ in relation to volcanic eruptions (Sarmiento 1993), these will be outlined below.

Firstly, lower surface temperatures due to the formation of stratospheric aerosols may contribute to decreased respiration from soils and vegetation, therefore reducing $CO_2$ emissions from terrestrial ecosystems. Temperature is one of the main regulating factors of soil respiration (Luo and Zhou 2006; Rustad et al. 2000; Schlesinger and Andrews 2000), which accounts for a large portion of the total biosphere respiration and is the second largest flux from terrestrial ecosystems. Ecosystem respiration is an important source of $CO_2$ to the atmosphere, releasing 119 Pg C $yr^{-1}$ compared to just 6 Pg C $yr^{-1}$, which is released from anthropogenic combustion (Luo and Zhou 2006). Model experiments investigating the effects of the Pinatubo eruption (1991) on the global C cycle showed that lower surface temperatures and a change in precipitation patterns caused a decrease in global soil and plant respiration. Lower temperatures also enhanced gross primary productivity (GPP) in the tropics resulting in 7-8 Gt C to be removed from the atmosphere in the years after the eruption (Jones and Cox 2001).

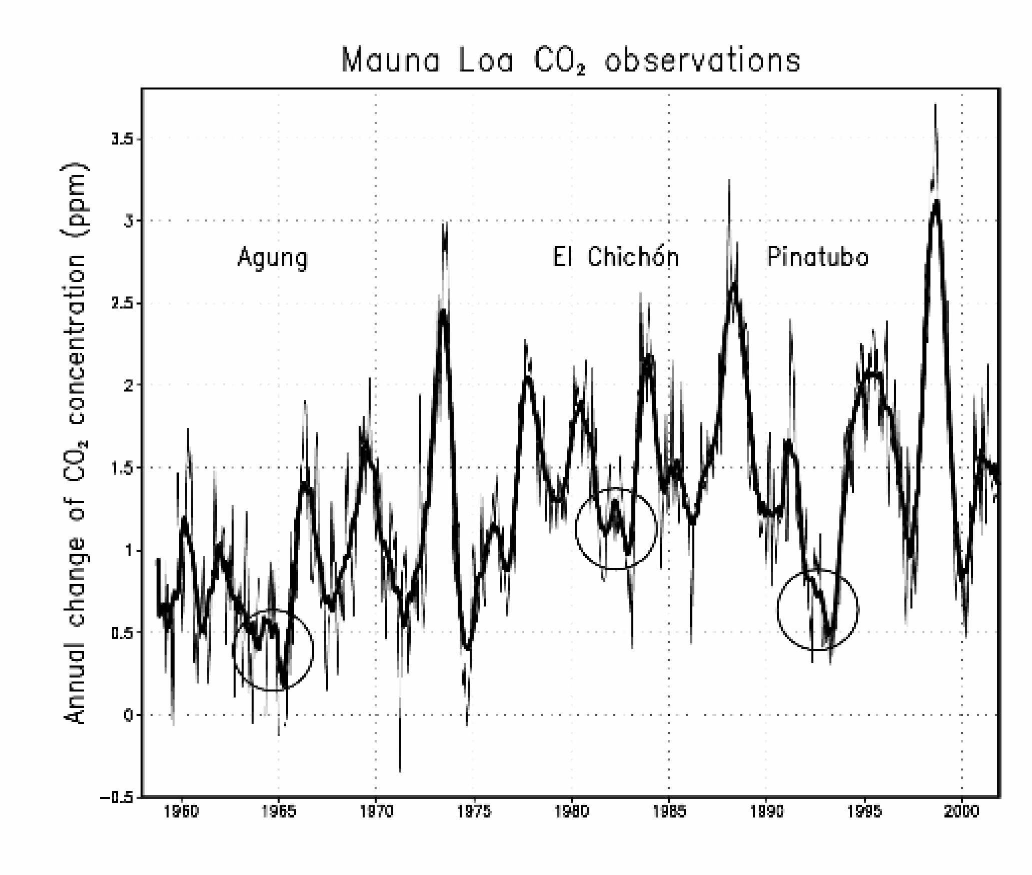


**Fig. 1.2** Carbon dioxide concentrations measured at Mauna Loa 1950-2000. Circles indicate variations in the usual upward $CO_2$ trend that coincide with large volcanic eruptions. Diagram from Robock (2003).

Secondly, it has been suggested that the reduction in $CO_2$ after large volcanic eruptions is due to stratospheric aerosols increasing diffuse solar radiation, which enhances photosynthesis and therefore $CO_2$ consumption (Baldocchi et al. 2002; Farquhar and Roderick 2003; Gu et al. 2003; Roderick et al. 2001). Vegetation is sensitive to changes in the diffuse faction of light as plant canopies can use this radiation more efficiently than direct beam radiation in photosynthesis (Goudriaan 1977). When light is diffuse, it exposes more lower leaves in the canopy as compared to direct light, which tends to only illuminate the leaves in the beam and produce a greater volume of shade elsewhere (Farquhar and Roderick 2003). An increase in the diffuse fraction of light by volcanic aerosols increased photosynthesis after the 1991 eruption of

Pinatubo which led to a greater consumption of $CO_2$ (Roderick et al. 2001). In a Harvard forest, photosynthesis was enhanced for two years after the Pinatubo eruption because of the increase in diffuse light caused by volcanic aerosols (Gu et al. 2003). Diffuse light conditions caused by aerosols have been reported to increase the $CO_2$ sink in forest and cropland ecosystems (Niyogi et al. 2004). However, a decrease in $CO_2$ was recorded at a grassland site (Niyogi et al. 2004) and there was no evidence of any increase in $CO_2$ uptake in a peatland ecosystem, which the authors suggest is due to the unique physiological character of the ecosystem (Letts and Lafleur 2005).

The third hypothesis is that chemical weathering of deposited volcanic tephra increases atmospheric $CO_2$ consumption. The weathering of silicate rock requires inputs of $CO_2$, which is withdrawn from the atmosphere to take place in the following reaction: $CaSiO_3 + CO_2 = CaCO_3 + SiO_2$ (Berner et al. 1983). This weathering reaction may be particularly intense in the first few years after deposition if large quantities of tephra have been lain down. Basalts from oceanic and volcanic arc islands weather at very high rates of ~100 t $km^{-2}$ $yr^{-1}$ (Louvat and Allegre 1997). Dessert et al (2003) estimated that $4.08 \times 10^{12}$ mol $yr^{-1}$ of $CO_2$ is consumed by the weathering of basalts. This represents approximately one third of the $CO_2$ consumption resulting from silicate weathering on the continents (Gaillardet et al. 1999).

Another possible reason for the decrease in atmospheric $CO_2$ concentrations may be due to volcanic ash (fine-grained tephra material < 2mm particle diameter) being deposited on marine environments. As ash from explosive eruptions can be transported thousands of kilometres from the source, a substantial fraction of the erupted ash is deposited over the open ocean. For example, during the 1991 eruption of Mt. Pinatubo, at least 3000 Tg of ash fell over the South China Sea (Wiesner et al. 1995). This ash may contain soluble surface Fe originating from gas-ash particle interactions in the eruption plume. Iron is a key micronutrient for phytoplankton growth in the surface ocean, and in some areas it limits marine primary productivity. Similar to aeolian deposition of mineral dust sources from semi-arid and arid areas, the addition of ash to the open ocean may alter the surface iron budget and promote phytoplankton growth

(Duggen et al. 2007; Jones and Gislason 2008). Following the August 2008 eruption of Kasatochi in the Aleutian subduction zone, marine primary productivity increased. Satellite data showed a significant phytoplankton bloom in the NW Pacific a few days after volcanic ash fallout (Langmann et al. 2010). It is estimated that iron fertilisation by the Kasatochi ash removed ~0.12 Pg C from the atmosphere (Hamme et al. 2010; Langmann et al. 2010). This is approximately 0.5 % of the 2 Pg C of anthropogenic $CO_2$ taken up by the ocean each year (Manning and Keeling 2006).

There is also evidence that volcanic eruptions can affect concentrations of atmospheric methane ($CH_4$). The eruption of Mt Pinatubo led to changes in $CH_4$ growth rates with sharp increases in 1991 and early-1992 in the tropics and high-southern latitudes (Dlugokencky et al. 1996). The growth rate of $CH_4$ is affected by changes in both $CH_4$ sources and sinks. The major sink for atmospheric $CH_4$ is the chemical oxidation by the hydroxyl radical (OH), which is formed through the photolysis of ozone ($O_3$) in the wavelength region 290-330 nm (Wuebbles and Hayhoe 2000). As stated above, UV radiation was absorbed by $SO_2$ emitted from the Pinatubo eruption and was scattered by $SO_4$ aerosols which led to a significant decrease in UV flux in the wavelength region 290-330 nm (Robock 2000). This resulted in lower atmospheric [OH] which reduced the $CH_4$ sink, enhancing $CH_4$ growth rates during 1991 and early-1992 (Dlugokencky et al. 1996).

In late-1992 and into 1993, there was a sharp decline in atmospheric $CH_4$ growth rates. The average trend for the Northern Hemisphere before the Pinatubo eruption (1983-1991) was $11.6 \pm 0.2$ ppbv $yr^{-1}$ but the increase in 1992 was only $1.8 \pm 1.6$ ppbv $yr^{-1}$ (Dlugokencky et al. 1994). The reason for the sharp decline is unknown (Wuebbles and Hayhoe 2000). Among the suggested possibilities is a decrease in anthropogenic $CH_4$ emissions (Dlugokencky et al. 1994) or reduced wetland $CH_4$ emissions (Hogan and Harriss 1994). Another explanation is that changes in stratospheric temperatures following the Pinatubo eruption caused an increase in stratospheric circulation causing greater exchange of gases between the troposphere and stratosphere. As the stratosphere contains lower mixing ratios of $CH_4$ this mixing could be responsible for the decrease in growth rate in the troposphere (Pitari and Mancini 2002; Schauffler and Daniel 1994).

### 1.1.3 Effects of volcanic deposition

Volcanoes are strong emitters of sulphur dioxide ($SO_2$), hydrogen chloride (HCl) and hydrogen fluoride (HF). Many release these compounds into the low atmosphere for prolonged periods of time, sometimes resulting in elevated deposition of acidifying compounds downwind, either dissolved in precipitation or directly in “dry” form (Aiuppa et al. 2001; Delmelle 2001; Delmelle et al. 2003). Others erupt violently and produce an acid plume laden with ash, which can be transported over great distances. It is known that such large volcanic eruptions can affect climate but also can cause local, regional and even global disruption of ecosystems (Grudd et al. 2000; Hall 2003; Robock 2003).

The Lakagigar (or Laki) fissure eruption which occurred in south-east Iceland in 1783-4 is considered to be one of the worst environmental disasters in recent history (Thordarson and Self 2002). Laki emitted 122 million tones of $SO_2$, 7 million tones of HCl and 15 million tones of HF into the upper troposphere and lower stratosphere over its eight month eruption period (Thordarson and Self 2002). Due to the presence of a high pressure system, the Laki plume was transported over most of Europe, creating one of the most catastrophic air pollution events of the past 250 years. Shortly after the start of the eruption, there were widespread reports of a so-called “dry fog” across Europe, which consisted of volcanic acidic gases and aerosols, including $SO_2$, HCl, HF and sulphuric acid ($H_2SO_4$).

The presence of the dry fog is held responsible for the occurrence of various health effects, including respiratory diseases and increased mortality across the UK and most of Europe (Stone 2004). In the UK alone, Whitham and Oppenheimer (2005) concluded recently that the poor air quality generated by the Laki plume caused 20,000 extra deaths. The Laki eruption plume is also reported to have been harmful to vegetation (Grattan 2005; Grattan and Brayshay 1995; Grattan and Charman 1994; Grattan and Pyatt 1994). The damage was described as burning, scorching, withering and drying with a wide range of colour changes (Grattan, 2005). It was noted that wildflowers disappeared, plants shed their fruit unripened and seed cases of cereal crops were empty (Demaree and Ogilvie 2001; Grattan and Pyatt 1999). Data collected by Dutch scientist Brugmans (1787) suggests that a wide range of critical plant processes such as photosynthesis, leaf formation, leaf retention, fruiting, flowering and seeding were affected by the acidic dry fog. There is also evidence of fish kills in Scotland (Grattan and Pyatt 1994, 1999). These accounts indicate that the Laki eruption caused severe effects on distal ecosystems.

Icelandic volcanism may have been responsible for widespread environmental impacts in the northern Atlantic region. In Scotland, a rapid decline in *Pinus Sylvestris* coincides with tephra deposition from Hekla-4 (Blackford et al. 1992). Payne and Blackford ( 2005) and Hotes et al. (2004) simulated the impacts of distal volcanic products upon peatland ecosystems looking at the link between distant volcanic activity and environmental change. They reported that key species such as *Sphagnum spp.* are highly sensitive to deposition of sulphur pollutants. According to Hogg *et al.* (1995), acid deposition can cause rapid species change with the more acid tolerant species out-competing the acid sensitive species. Some authors tentatively argued that deposition of the volcanic acid pollutants from the Laki plume was sufficient to induce acidification and leaching of base cations in sensitive soils of Scotland and Ireland (Grattan and Brayshay 1995; Grattan and Gilbertson 1994). The Scottish soils most sensitive to acidification from acid deposition are peats (White et al. 1995). Ombrotrophic peats are naturally acidic and they have a poor buffering capacity. The composition of peat itself may also be affected by acidification as plant decomposition and carbon flux is altered. It is therefore important to investigate the effect of volcanic deposition on the biological processes in the peat, which play a major role in the C cycle.

## 1.2 Peat soils

In active volcanic regions such as Alaska, Patagonia, Kamchatka and Iceland, peatlands are within the transport range of volcanic emissions. In Indonesia, 50-80% of the wet deposited sulfur (S) in peat swamp areas is of volcanic origin (Langmann and Graf 2003).

### 1.2.1 Definitions and composition

Peat is a substance composed of the partially decomposed remains of plants with over 65% organic matter and less than 20-30% inorganic content (Charman 2002; Clymo 1983; Heathwaite et al. 1993). A peatland is an area where peat accumulates naturally at the surface in a layer of more than 30cm thickness (Joosten and Clarke 2002). Peatlands are generally 88-97% water, 2-10% dry matter and 1-7% gas (Heathwaite et al. 1993). The high water content is a key factor in the formation of peatlands as it limits decomposition resulting in the accumulation of organic matter. Oxygen diffuses ~10 000 times slower in water than in air, which exerts a severe limitation on the rate of decomposition of plant litter in waterlogged environments (Maltby and Proctor 1996). Peatlands are encompassed under the broad concept of wetlands and can be referred to as mires. Definitions of the main terms used in peatland literature can be found in Table 1.1. Peatlands are also classified by nutrient status. Ombrotrophic peatlands (bogs) receive water and nutrients from the atmosphere and so are generally acidic and nutrient poor. Minerotrophic peatlands (fens) receive inputs from groundwater and surface run-off making them more alkaline and nutrient-rich.

### 1.2.2 Global distribution of peat soils

There are approximately 4 million km$^2$ of peatlands worldwide, covering some 3% of the land surface containing 5000 to 6000 Gt of peat (Lappalainen 1996). Over 90% of peatlands are in the temperate and cold belt in the Northern Hemisphere with the remaining 10% in tropical and sub-tropical latitudes (Maltby and Proctor 1996). There is a strong northern bias in the distribution of peats across Europe with almost a third of the peatland resource concentrated in Finland and a quarter in Sweden (Montanarella et al. 2006). In Great Britain, the estimated total area of peatland is 17 549 km$^2$ with a further 31 070 km$^2$ of shallow peats and mineral soils with peaty surface horizons (Burton 1996). The global distribution of peat soils is presented in Fig. 1.3.

**Table 1.1** Definitions of the main terms used in peatland literature (Charman 2002)

| Term | Definition |
|---|---|
| Wetland | Land with the water table close to or above the surface or which is saturated for a significant period of time. Includes most peatlands but also ecosystems on mineral substrates, flowing or shallow waters. |
| Peatland | Any ecosystem where in excess of 30-40 cm of peat has formed. Includes some wetlands but also organic soils where aquatic processes may not be operating (e.g. drained or afforested peatlands). |
| Mire | All ecosystems described in English as swamp, bog, fen, moor, muskeg and peatland, but often used synonymously with peatlands. Includes all peatlands, but some mires may have a mineral substrate. |
| Fen | A mire which is influenced by water from outside its own limits. |
| Bog | A mire which receives water solely from rain and/or snow falling onto its surface. |
| Marsh | Loose term usually referring to a fen with tall herbaceous vegetation often with a mineral substrate. |
| Swamp | Loose term with very wide range of usage. Usually referring to a fen and often implying forest cover. |

### 1.2.3 Peatlands and the carbon cycle

Northern peatlands play a major role in the global C cycle. Although they cover only 2-3% of the world's total land surface (Rydin and Jeglum 2006), they store approximately one-third of the global soil C (455 Pg C) (Gorham 1991; Lappalainen 1996), which is more than half the atmospheric stock of $CO_2$ (Rydin and Jeglum 2006). Consequently, it is important to quantify processes that might influence exchanges of C, in its various forms, between peatlands and the atmosphere. Carbon enters the peatland system mainly as $CO_2$ by photosynthesis and is fixed in plant tissues until decay of dead plant material occurs. Some C is retained in the peat, some is transformed into $CO_2$ and $CH_4$ and some is exported as Dissolved Organic Carbon (DOC) and Particulate Organic Carbon (POC). The carbon cycle in peatlands is presented in Fig. 1.4. Most peatlands are diplotelmic, that is they consist of two distinct layers, the acrotelm and the catotelm (Ingram 1978). The acrotelm is the near surface oxygen rich layer where aerobic decomposition of organic matter by aerobic fungi and bacteria occurs. This layer is shallower than the catotelm and is the layer in which the water table fluctuates providing both aerobic and anaerobic conditions to support high rates of microbial activity. The catotelm is the oxygen-poor waterlogged layer situated below the acrotelm. Here the processes of decay are much slower with low rates of anaerobic microbial activity (Charman 2002; Ingram 1978).

Methane is an important greenhouse gas as it is 25 times more powerful than $CO_2$ on a molecule for molecule basis (IPCC 2007) and contributes 22% of the total climate forcing of all long-lived greenhouse gases (IPCC 2007; Lelieveld et al. 1998). Its atmospheric abundance has increased by a factor of ~2.5 since the pre-industrial era (IPCC 2001). Biogenic sources account for more than 70% of the global total $CH_4$ emission (Denman et al. 2007) with wetland soils being the main natural source producing an estimated 100-200 Tg year$^{-1}$ (Houghton 2004; Le Mer and Roger 2001). Although peatlands and wetlands are the largest biogenic source of $CH_4$ to the atmosphere, it is difficult to quantify the source strength accurately. There is uncertainty over the extent of the global peatland area and there are large variations in fluxes between the different types of peat and through the seasons (Shotyk 1989).

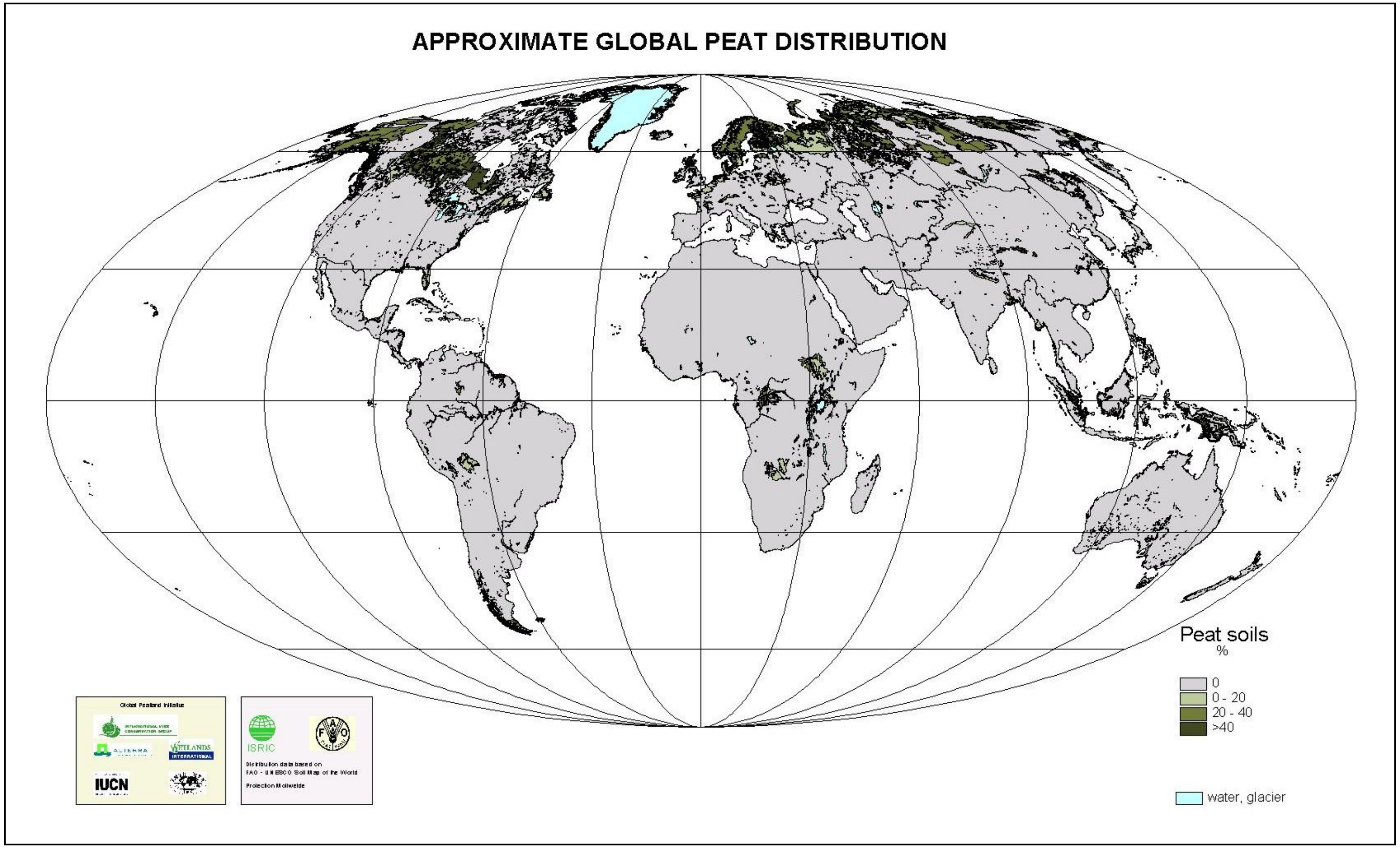


**Fig. 1.3** The global distribution of peat soils provided by Professor Joosten, University of Greifswald (personal communication)

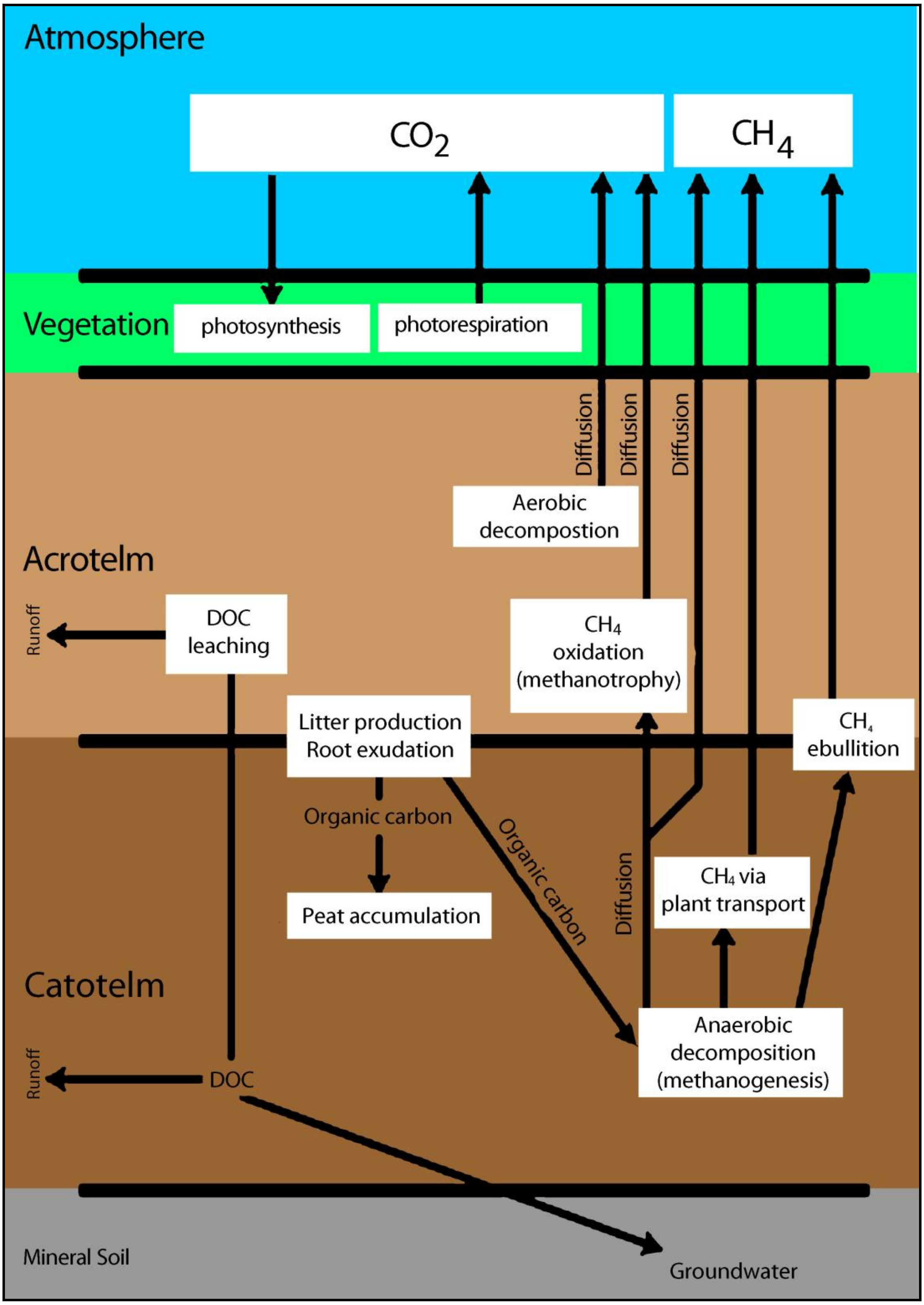


**Fig. 1.4** Overview of carbon cycling in peatlands (Redrawn from http://www.theses.ulaval.ca/2004/21536/21536001.png)

### 1.2.4 Methanogenesis in peatlands

Methanogenesis is the formation of methane by anaerobic microbes (methanogens). It occurs via the fermentation of organic matter in the catotelm and can be expressed by the following equation (Le Mer and Roger 2001):

$$C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4$$

Methanogens can only use a small number of simple compounds most of which only contain one C and therefore rely on other organisms for their substrates (Ferry 1993). This transformation of complex organic molecules into simpler compounds including organic acids and acetate, and finally into $CH_4$ and $CO_2$ requires the successive actions of four populations of micro-organisms (Le Mer and Roger 2001). The four stages are: hydrolysis, acidogenesis, acetogenesis and methanogenesis (Lai 2009). Methanogenesis requires strict anaerobiosis and low redox potentials (Eh <-200mV) (Le Mer and Roger 2001) and therefore can only take place in the waterlogged conditions of the catotelm. In environments where organic substrate is limiting methanogens must compete with other organisms for substrates. The hierarchy of competition is as follows: $Fe^{3+}$ reducers> $SO_4$ reducing bacteria> methanogens> acetogens (Zinder 1993).

There are two main groups of methanogens, which use different substrates to produce $CH_4$; these are hydrogenotrophic methanogens and acetotrophic methanogens (Conrad et al. 1989). Hydrogenotrophic methanogens use hydrogen to reduce $CO_2$ to $CH_4$ by the following reaction:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

Acetotrophic methanogens split acetate to form $CH_4$ and $CO_2$ (Ferry 1993):

$$CH_3COOH \rightarrow CH_4 + CO_2$$

Other trophic groups of methanogens have been identified, which can use substrates such as formate, methylated compounds (methanol, methylamines, dimethylsulfur) and primary and secondary alcohols (Le Mer and Roger 2001). Several studies have shown that the main methanogenic pathway in peatlands shifts from $H_2$ substrate in cool periods to acetate fermentation during the warmer growing season (Avery et al. 1999; Kelly et al. 1992). Further, the main pathway for $CH_4$ production in peat bogs is normally via $H_2$- and $CO_2$-dependant methanogenesis, whereas in fens, acetoclastic methanogenesis is often the predominant process (Chasar et al. 2000; Galand et al. 2005; Hornibrook et al. 1997; Kotsyurbenko 2010).

### 1.2.5 Factors controlling $CH_4$ emission from peatlands

In a review of $CH_4$ dynamics in mires, Shotyk (1989) stated that the over-riding control on $CH_4$ emission from peatlands is the presence or absence of an oxygenated surface layer suitable for $CH_4$ oxidising bacteria. The depth of this oxygenated layer is dictated by the water table level, which is regulated by temperature and precipitation (Kettunen et al. 1999). Methane is produced in the catotelm and is released into the atmosphere via three processes: diffusion through the peat column, ebullition and through the aerenchyma of vascular plants (Whalen 2005). As $CH_4$ is produced in the anaerobic catotelm it has to pass through the aerobic acrotelm where it can be oxidised to $CO_2$ by methanotrophic bacteria (Fig. 1.4). This methanotrophic oxidation can reduce the methane flux to the atmosphere by up to 90% (Dedysh et al. 1998; Segers 1998). *Sphagnum* mosses can also consume $CH_4$ through symbiosis with methanotrophic bacteria leading to highly effective in situ $CH_4$ recycling (Raghoebarsing et al. 2005).

Peatland $CH_4$ emissions are also regulated by temperature, pH, vegetation type and peat composition (Lai 2009) or by the presence of alternative electron acceptors enhancing competition for substrates (Abram and Nedwell 1978; Nedwell and Watson 1995; Van Bodegom and Stams 1999). Temperature has a major influence on $CH_4$ dynamics in northern peatlands (Lai 2009) as the growth of methanogens is temperature dependant. Methanogenesis is optimum between 30 ºC and 40 ºC (Le Mer and Roger 2001), it can operate at much lower temperatures but the process is slower (Zinder 1993). Seasonal differences in $CH_4$ emissions are often reported in field studies (Dise et al. 1993; Shannon and White 1994; Ward et al. 2007). pH can limit methanogenic activity in peat as methanogens have a pH optima near neutrality (Ferry 1993). When acidic peat was incubated at elevated pH levels, maximum rates of $CH_4$ production occurred at pH 6-7 (Goodwin and Zeikus 1987; Valentine et al. 1994; Williams and Crawford 1984).

Vegetation plays a major role in controlling $CH_4$ emissions from peatlands. Firstly, plants supply litter and root exudates as substrates for methanogens (Schutz et al. 1991). Secondly, the presence of vascular plants with aerenchyma provides a direct pathway for $CH_4$ transport to the atmosphere. The greater the density of these plants, the higher the $CH_4$ emission to the atmosphere. In a Canadian fen, over 90 % of the $CH_4$ emission was plant-associated transport (Whiting and Chanton 1992). However, the primary function of aerenchyma is to transport oxygen down to the rhizosphere, which encourages $CH_4$ oxidation. In a peat mesocosm study, soils vegetated with *Sphagnum* moss emitted more $CH_4$ than those with *Juncus* because the rhizosphere of the aerenchyma-containing *Juncus* peat had become oxidised (Roura-Carol and Freeman 1999). Thirdly, peat composition is dependant upon the plant species present and influences the type and quality of substrates available for methanogens. It is reported that an increase in cellulose content and a decrease in lignin to nitrogen ratio can increase the decomposability of the peat and therefore the $CH_4$ production potential (Lai 2009). Peat composition can also affect the availability of non-competitive substrates. Some substrates such as methanol (Oremland et al. 1982), methanethiol and dimethyl sulphide (Kiene et al. 1986) may be used by methanogenic archaea but are poorly used by sulfate reducing bacteria. Some low molecular weight hydrocarbons such as lactate, propionate and ethanol may be used preferentially over acetate by sulfate reducing bacteria (Elferink et al. 1998).

Further, emissions may be influenced by a change in the composition and flux of atmospheric deposition namely anthropogenic $SO_4$ and nitrate ($NO_3$) (Blodau 2002; Watson and Nedwell 1998). Recent studies indicate that acid rain $SO_4$ deposition decreases $CH_4$ emission in peatlands in the northern hemisphere due to a shift in microbial communities as $SO_4$ reducing bacteria out-compete methanogens for substrates (Dise and Verry 2001; Fowler et al. 1995; Gauci and Dise 2002; Gauci et al. 2004b; Granberg et al. 2001; Watson and Nedwell 1998). Sulfate reduction is energetically favourable to methanogenesis, so, $SO_4$ reducing bacteria are able to out-compete methanogens for substrates such as $H_2$ and acetate (Schimel 2004). Rates of $SO_4$ reduction increase with increasing S deposition up to deposition rates of around 15-20 kg S $ha^{-1}$ $y^{-1}$ (Gauci et al. 2004b), after which, $SO_4$ reduction rates asymptote towards a maximum suppression of ~ 40 % as $SO_4$ reduction becomes limited by factors other than sulphate supply.

## 1.3 Distal volcanic eruptions and the effects on peat soils

Volcanic eruptions can affect the composition and flux of atmospheric deposition, in particular $SO_4$, both on local and regional scales (Graf et al. 1998). In active volcanic regions such as Alaska, Patagonia, Kamchatka and Iceland, peatlands are within the transport range of volcanic emissions. In Indonesia, 50-80% of the wet deposited sulfur (S) in peat swamp areas was predicted to be of volcanic origin (Langmann and Graf 2003). Besides S species ($SO_2$ and $SO_4$), volcanic emissions also contain hydrogen fluoride (HF). Hydrogen fluoride is of particular interest as fluoride (F) is the most electronegative and reactive of all ions (Weinstein and Davison 2004). However, long-range transport of gaseous or particulate F in the volcanic plume is unlikely due to the short residence time of F in the atmosphere as compared to that of $SO_2$ (Harnisch 1999). Another means by which volcanogenic F and $SO_4$ can be co-added to peatlands is through tephra deposition. It is well established that tephra particles are coated with a variety of variable amounts of sulfate and halide salts, such as $CaF_2$, $CaSO_4$, $Na_2SO_4$) formed during interaction of the tephra material with the gas and aerosol phases of the eruption plume (Delmelle et al. 2007; Witham et al. 2005).

While the presence of tephra in peatlands is well documented in volcanic regions (Cronin et al. 1998; Haflidason et al. 2000; Hotes et al. 2006), there is also evidence for tephra in peatlands located far away from the source. Notably, tephra derived from past Icelandic eruptions is found in British peatlands (Blackford et al. 1992; Charman et al. 1995; Dugmore et al. 1995; Dwyer and Mitchell 1997; Pilcher and Hall 1992; Pilcher et al. 1995), and tephra layers from at least 16 volcanic events in Iceland that took place over the last millennium have been traced in locations across northern Europe (Wastegård and Davies 2009). Distal deposits are often diffuse and unevenly distributed due to rainfall patterns, wind direction and site-specific sedimentation processes (Davies et al. 2010). This can produce microscopic ash layers that are invisible to the naked eye (cryptotephras) (Payne and Blackford 2004). Although such layers are minute, they have the potential to release significant amounts of $SO_4$ and F upon exposure to water. This is due to the large surface area-to-volume ratio of the fine-grained ash material, which was advected for several thousands of kilometers in the atmosphere before being deposited.

The effect of F addition to peat soils has never before been assessed. Due to the toxic nature of F in the environment, it is likely to affect soil microorganisms and therefore have an effect upon the emissions of $CH_4$ and $CO_2$. Fluoride can affect microbial communities (Treshow 1965; Tscherko and Kandeler 1997) and has been reported to stimulate soil respiration (Van Wensem and Adema 1991). Methyl fluoride ($CH_3F$) is commonly used as an inhibitor of $CH_4$ oxidation in lab experiments and has been found to inhibit acetoclastic methanogenesis (Frenzel and Bosse 1996; Janssen and Frenzel 1997). If F was toxic to methanogenic populations this would result in decreased $CH_4$ production and therefore reduced $CH_4$ emissions to the atmosphere. However, if F was toxic to methanotrophs this would reduce $CH_4$ oxidation and therefore increase $CH_4$ emissions to the atmosphere. Fluoride can also be phytotoxic when taken up by plants (Fridriksson 1983; Grattan and Pyatt 1994; Vike 1999). One of the main transport routes of $CH_4$ to the atmosphere is through the aerenchyma of vascular plants (Whalen 2005). If F causes plant damage this could potentially reduce the flux of $CH_4$ from peatlands. Fluoride can also influence the mobility of other environmentally important elements like aluminium (Al), which may impact upon a range of soil processes (Elrashidi and Lindsay 1987; Romar et al. 2009). Fluoride behavior in mineral soils has been investigated in the vicinity of Al smelters, but its effect on peat soils has never before been assessed. In mineral soils, F addition leads to the dissolution of organic matter, Al and Fe and an increase in soil solution pH. However, peat soils behave differently to mineral soils as they are composed of organic matter and do not contain clay particles where anion exchange sites occur. Organic matter solids do contain exchange sites but very little is currently known about anion exchange interactions with organic matter. Due to its reactive nature, F addition may disrupt the complex biogeochemical cycling that occurs in peats. The presence of F may therefore be important when studying the effect of volcanic depositions on peatland ecosystem functioning.

A number of studies have investigated the effect of $SO_4$ deposition on $CH_4$ emissions from peat soils. These acid rain studies indicate that $SO_4$ deposition decreases $CH_4$ emission in peatlands in the northern hemisphere due to a shift in microbial communities as $SO_4$ reducing bacteria out-compete methanogens for substrates (Dise and Verry 2001; Fowler et al. 1995; Gauci and Dise 2002; Gauci et al. 2004b; Granberg et al. 2001; Watson and Nedwell 1998). More recently, Gauci et al (2008) investigated the potential link between volcanic activity and the release of $CH_4$ by peatlands. In this work, the impact of the Icelandic eruption of Lakagigar in 1783 on the Northern wetland $CH_4$ source was modeled based on responses observed in pristine (i.e. unpolluted) peats to simulated $SO_4$ deposition that was of a similar magnitude to volcanogenic $SO_4$ inputs from the Lakagigar eruption (Gauci et al. 2008; Gauci et al. 2004b). The results showed that the combined effect of cooling from volcanic aerosols with deposition of S on wetlands was sufficient to suppress $CH_4$ emissions by 14 % (from 160 to 137 Tg year$^{-1}$). Based on previous results (Gauci et al. 2005), the same authors argued that the volcanogenic $SO_4$ deposition on $CH_4$ fluxes may only decrease over decade-long timescales due to re-oxidation of reduced S-compounds in the peat soil. While these findings provide important insights into the environmental effects of volcanogenic emissions, the potential impact of F must also be assessed, in particular when considering the long-range transport of soluble $SO_4$ and F-bearing tephra. Fluoride readily displaces $SO_4$ on exchange sites (Rose 1998) in mineral soils and so may interact in the same manner in peat. If F displaces $SO_4$ on exchange sites this would increase soil solution $SO_4$ concentrations and therefore stimulate $SO_4$ reducing bacteria, increasing the competition for substrates with methanogens.

A greater understanding of the effects of volcanic deposition on C cycling in peatlands and mineral soils has important implications for evaluating the role of volcanic activity in influencing the terrestrial C cycle possibly affecting the release of powerful greenhouse gases to the atmosphere.

## 1.4Research objective

### 1.4.1 Overarching aims

The main objective of this thesis is to investigate the link between distal volcanic deposition and peatland ecosystem functioning, in particular the effects of F and $SO_4$ on the emissions of $CH_4$ and $CO_2$ and on soil biogeochemistry. To meet this objective, a mesocosm experiment was used to assess the effects of volcanic inputs of $SO_4$ and F on peatland ecosystems. Treatments of F and $SO_4$ were added both alone and in combination, at concentrations that could be leached from tephra deposited on the peat surface after a large volcanic eruption. This experiment is an important first attempt to characterise the behaviour of F in peatland ecosystems. Until now, the effect of F on peatland emissions of $CH_4$ and $CO_2$ has not been considered despite the reactive and toxic nature of F in the environment. The effect of $SO_4$ deposition on $CH_4$ emissions from peat soils is well researched but the co-addition of $SO_4$ with F at concentrations likely to be leached from volcanic tephra is a new idea to be tested. The effect of F addition on the chemistry of mineral soils has been tested previously but this is the first time that the effect of F on peat soil chemistry has been assessed. This experiment aims to improve the understanding of anion sorption behaviour in peat soils as currently very little is known.

The eruption of Eyjafjallajökull in Iceland (2010) provided an exciting opportunity to study the effects of volcanic ash deposition on soil respiration. Areas around volcanoes often receive heavy ash loadings during an eruption. These layers can persist in the environment for weeks and months after the eruption. However, the effect of ash layers on soil respiration has never before been assessed. As a first attempt to investigate this, a field-based experiment was carried out in Iceland to investigate the short-term physical and chemical effects of ash deposition on ecosystem respiration of an Icelandic mineral soil.

### 1.4.2 Specific hypotheses

The peat mesocosm experiment was designed to investigate the following research hypotheses:

*The effect of F and $SO_4$ addition on peat soil chemistry*

- The addition of F will result in an increase in F concentrations in soil, soil solution and plant material.
- Fluoride will behave in the same manner as reported in mineral soils i.e. addition of F will increase the solubility of Al and Fe resulting in elevated concentrations of these metals in the soil solution. It will result in an increase in soil solution pH as F replaces –OH on exchange sites. It will increase DOC concentrations in solution due to the breakdown of organo-metallic compounds or the inhibition of microbial species.
- The addition of $SO_4$ will result in an increase in $SO_4$ or S concentrations in soil, soil solution and plant material.
- The addition of $SO_4$ will result in a lowering of soil solution pH as $SO_4$ replaces H ions on exchange sites increasing concentrations in solution
- The addition of F in combination with $SO_4$ would lead to no change in pH as the two effects cancel each other out.

*The effects of F and $SO_4$ treatments on peat soil $CH_4$ emissions*

- Increased F in soil solution will become toxic to methanogens thereby reducing production rates. It will also be toxic to methanotrophs, reducing $CH_4$ oxidation rates. If F reduces both $CH_4$ production and oxidation there will be no overall effect on measured $CH_4$ emissions.
- Increased $SO_4$ in soil solution will stimulate a population of $SO_4$ reducing bacteria to outcompete methanogens for substrates thus reducing $CH_4$ emissions.
- Co-addition of F and $SO_4$ will lead to a reduction in $CH_4$ emissions.

*The effects of F and $SO_4$ treatments on peat soil net ecosystem exchange*

- An increase in soil solution F will decrease ecosystem respiration due to toxicity. Increased plant uptake of F will cause plant damage and reduce photosynthesis rates therefore reducing $CO_2$ uptake. A decrease in ecosystem respiration and photosynthesis would result in no overall effect on net ecosystem exchange during the daytime when both processes occur. There would be an overall decrease in $CO_2$ release to the atmosphere at night due to reduced respiration rates.

- The addition of $SO_4$ would have no effect on respiration or photosynthesis rates and therefore there would be no overall effect on net ecosystem exchange.

- The co-addition of $SO_4$ and F would have the same effect as if F was added alone.

*The effect of volcanic ash deposition on ecosystem respiration from an Icelandic mineral soil*

The research hypotheses of the field-based experiment carried out in Iceland to investigate the short-term physical and chemical effects of ash deposition on ecosystem respiration of a mineral soil are;

- Ash deposition has a physical effect on the soil environment due to a physical blockage and an increase in soil moisture levels, impeding the transport of $CO_2$ and thus reducing ecosystem respiration.

- Ash deposition has a chemical effect upon soil microorganisms either through direct toxicity of leachates containing metals (e.g. Al, Fe, Cu) or a decrease in pH, which would reduce ecosystem respiration.

- The burial of vegetation under the ash layer would lower photosynthesis rates and therefore substrate supply to microbes, which could reduce ecosystem respiration.

## 1.5 Thesis structure

- Chapter 2: Effects of volcanic deposition on peat soil chemistry
- Chapter 3: The effects of volcanic deposition on peatland carbon gas fluxes
- Chapter 4: The use of incubation experiments to assess the effects of volcanic deposition on potential methane production and oxidation
- Chapter 5: The effect of volcanic ash deposition on ecosystem respiration from an Icelandic soil
- Chapter 6: Conclusions

# Chapter 2: Effects of volcanic deposition on peat soil chemistry

## 2.1 Introduction

Many studies have investigated the environmental effects of industrial F emissions. In Europe, the problem was particularly acute in the vicinity of aluminium smelters and brick kilns (Arnesen et al. 1995; Divan Junior et al. 2008; Domingos et al. 2003; Franzaring et al. 2006; Gilbert 1985; SkjelkvÂle 1994; Vike 1999; Wenzel and Blum 1992). In areas receiving large quantities of F pollution, changes in vegetation, soil chemical composition and physical properties were noticed (Arnesen et al. 1995; Arneson 1998; Divan Junior et al. 2008; Haidouti 1991; Wenzel and Blum 1992). In the vicinity of Al smelters where F contamination of soils is high, there have been reports of increases in soil F concentrations in the surface layers and increased pH and Al and Fe concentrations in soil solution (Elrashidi and Lindsay 1987; Omueti and Jones 1977; Polomski 1985; Polomski et al. 1982; Romar et al. 2009; Wilke 1987). A number of other studies have also found that F addition to soils results in an accumulation of organic matter (Elrashidi and Lindsay 1987; Rao and Pal 1978; Tscherko and Kandeler 1997). It is therefore possible that inputs of F and $SO_4$ from volcanic tephra deposition may influence the chemistry of peatlands located thousands of kilometres from the pollution source. This alteration in chemical composition may have subsequent effects upon microbiological organisms and processes.

To investigate the effect of volcanic deposition upon peat soil chemistry, peat soil mesocosms were collected from Moor House - a bog area in the northern Pennine uplands of the UK. These mesocosms were returned to the University of York where pore water samplers were inserted to monitor soil water chemistry as the mesocosms were dosed with small weekly additions of

$SO_4$ and F for twenty weeks to simulate the effects of leaching a layer of ash deposited on the peat surface after a large Icelandic eruption.

Previous studies have investigated the effect of F behavior in mineral soils, but its effect upon peat soils has never before been assessed. In mineral soils, F addition leads to the dissolution of organic matter, Al and Fe and an increase in soil solution pH. However, peat soils behave differently to mineral soils as they are composed of the partially decomposed remains of plants with over 65% organic matter. The Moor House soils are characterised by a low ash content (3.2% dry weight, (Gorham 1961)) and belong to the ombrotrophic peat group. (Shotyk 1988). These peats receive all nutrient inputs from precipitation and atmospheric deposition, so the only input of mineral material is from the deposition of soil dust from the surrounding environment on the surface of the bog (Charman 2002; Clymo 1983; Shotyk 1988). Therefore, sorption of F on mineral surfaces is expected to be minimal. Organic matter solids do contain exchange sites, but very little is currently known about anion exchange interactions with organic matter.

The objective of this chapter is to test the following hypotheses:

- The addition of F will result in an increase in F concentrations in soil, soil solution and plant material.
- Fluoride will behave in the same manner as reported in mineral soils i.e. addition of F will increase the solubility of Al and Fe resulting in elevated concentrations of these metals in the soil solution. It will result in an increase in soil solution pH as F replaces –OH on exchange sites. It will increase DOC concentrations in solution due to the breakdown of organo-metallic compounds or the inhibition of microbial species.
- The addition of $SO_4$ will result in an increase in $SO_4$ or S concentrations in soil, soil solution and plant material.
- The addition of $SO_4$ will result in a lowering of soil solution pH as it replaces H ions on exchange sites increasing concentrations in solution

## 2.2 Methodology

### 2.2.1 Sampling site and mesocosm collection

*Sampling site*

The site chosen for peat sampling was an area of blanket bog at the Moor House National Nature Reserve (NNR), Upper Teesdale, which is situated in the northern Pennine uplands of the UK (Fig. 2.2). This site is an Environmental Change Network (ECN) site, a UNESCO Biosphere Reserve and a European Special Protection Area. It was studied intensively as part of the International Biological Programme in the 1960's and as the lead site for NERC's Terrestrial Initiative in Global Environmental Research (TIGER) in the 1990's. Research was enabled due to the opening of the Moor House field station in 1952. The ECN have equipment on site to monitor meteorology, atmospheric chemistry and precipitation chemistry on a daily basis. The ECN have compiled information gathered by different organisations at the site to form a meta-database, which can be used by researchers.

The sampling site was located at OS grid: NY76097 33047, which is an extensive area of peat located in a valley bottom surrounded by gentle sloping hills (Fig. 2.1). The underlying bedrock consists of Lower Carboniferous sequences of interbedded limestone, sandstone and shale overlain by glacial boulder clay (Johnson and Dunham 1963). This clay impedes drainage allowing blanket peat to develop. A peat deposit of up to 3 m thickness covers 90% of the reserve (Holden and Burt 2003). The dominant vegetation at the site was *Sphagnum* spp. and *Eriophorum* spp. The blanket peat at this site has built up predominantly from the breakdown of *Sphagnum* moss. The water table was within 30 cm of the peat surface. Mean annual temperature at the site is 5.9 ºC. Mean annual rainfall is 2136 mm (values calculated from summary data on http://www.ecn.ac.uk/Database/index.html).

Background non-marine S deposition was 5.19 kg ha$^{-1}$ y$^{-1}$ (total oxidised non-sea salt S) in 2006 (CEH pollutant deposition data from http://www.uk-pollutantdeposition.ceh.ac.uk/data). Historically this site received heavy loads of

S pollution from coal combustion and industrial sources.  However, due to the decline of heavy industry in the 1970's and the use of cleaner energy sources, S emissions in the UK have decreased by 91% from 1970 to 1997 and are still steadily declining.

**Fig. 2.1** Photograph of the area of blanket bog at Moor House where peat soil mesocosms were sampled.

*Mesocosm collection*

Thirty intact peat cores were excavated from the site on 3rd July 2008 in PVC tubes (diameter 20 cm, depth 40 cm).  The sampling location for each core was chosen carefully where the peat had similar vegetation.  When the appropriate site had been selected, a serrated knife was used to cut vertically down around the core through the surface vegetation.  A piece of wood was placed on top of the core and a large mallet used to drive the core into the bog until the top rim was at the same level as the surface vegetation.  The cores were then carefully excavated avoiding damage to the vegetation.  The bottom of each core was sealed using a PVC cap and then they were transported upright in bags back to the University of York.

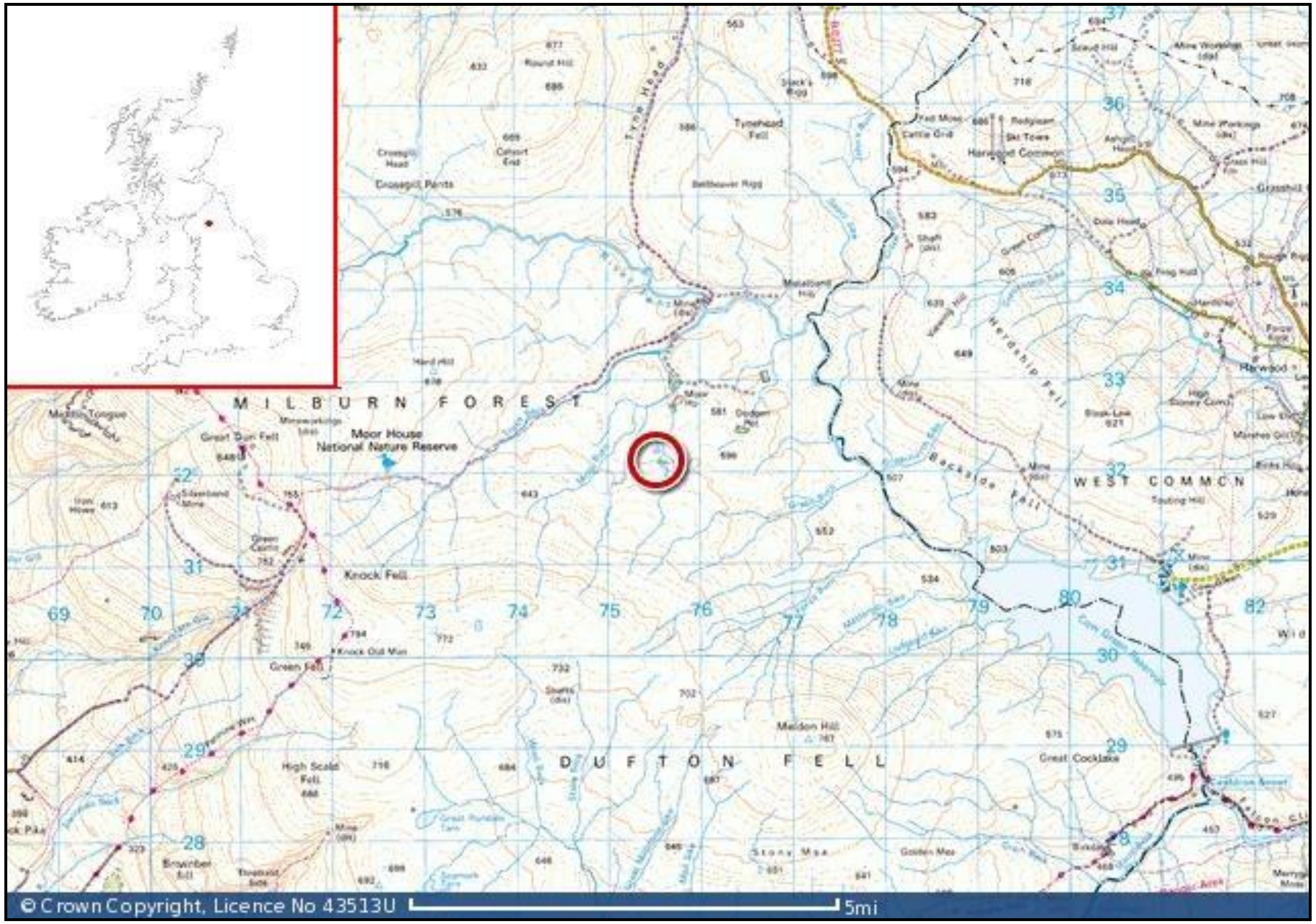


**Fig. 2.2** Map of the sampling site at Moor House in the northern Pennine uplands, where peat soil mesocosms were excavated for this experiment. Adapted from Multimap (www.multimap.com).

### 2.2.2 Experimental design

*Experimental setup*

The experiment was set up in the walled garden at the University of York (Fig. 2.3). The bottom of each mesocosm was sealed using a silicon sealant to prevent loss of pore water. Each mesocosm was placed into a 25 litre bucket and then the bucket was filled with water to help buffer against changes in temperature. The average daytime temperature measured at the experiment site between October 2008 – October 2009 was 15°C (Fig. 3.6). The cores were not covered so that they could receive natural precipitation. A rain gauge was installed at the site to collect rainwater, which was analysed alongside pore water samples for background levels of F and $SO_4$. The average monthly precipitation May – Sept 2009 was 57 mm. At times where there was little precipitation, the cores were topped up with deionised water to keep the water table in a fixed position at the surface.

**Fig. 2.3** Photograph of the experimental setup in the walled garden at the University of York. Intact peat mesocosms were placed in buckets under natural conditions for the duration of the experiment.

### 2.2.3 Treatment loads and application

Treatments were added to the mesocosms as small weekly additions for 20 weeks. This was to simulate the effects of leaching a layer of ash deposited on the peat surface after a large Icelandic eruption. If ash is deposited on the surface of the soil it is leached with every precipitation event. This means that the soil receives small regular pulses of F and $SO_4$ rather than one large dose. Fluoride is adsorbed onto ash particles in the plume and concentrations increase with decreasing particle grain size; therefore the finest ash particles have the greatest concentrations of F (Oskarsson 1980). Fine ash travels longer in the plume than coarse tephra and therefore has a greater contact time with the plume gas and so greater adsorption of F onto the ash surface can occur. Due to the increased adsorption onto fine ash, the heaviest loadings on the environment are likely to be at some hundreds of kilometres from the vent (Witham et al. 2005). This means that tephra from Icelandic eruptions deposited on the UK or Scandinavia could have high concentrations of F and $SO_4$ adsorbed onto the surface, which may be readily leached.

*Preliminary experiment to evaluate conditions for the main experiment*

A preliminary ash leaching experiment was carried out to decide upon realistic treatments to be applied to the mesocosms. The ash emanating from the 1970 eruption of Hekla, Iceland, was chosen to estimate the quantity of F, which may be released from the deposit upon exposure to rainwater. This ash was chosen as it was fresh i.e. it had not been exposed to water previously, it is known to contain F and $SO_4$ and is a representative sample of ash which is likely to be deposited in the UK from an Icelandic eruption. The ash used was a fine size fraction and so is likely to be the fraction that could be deposited over distant peatlands. The ash was leached with deionised water ten times using a continuous flow pump (Watson Marlow 205S) with a flow rate of 0.1 ml $min^{-1}$. The ash to water ratio was 1:4 which represents an ash layer of 1.2 mm deposited on the surface of each mesocosm which is leached by 200 ml of precipitation.

Volume of ash = mesocosm surface area x ash layer thickness = $0.027\ m^2$ x $0.0012\ m = 3.24 \times 10^{-5}\ m^3$ (surface area = $\pi\ (0.0935)^2 = 0.027\ m^2$).

$$\text{Mass of ash} = \text{volume} \times \text{density} = 3.24 \times 10^{-5}\ \text{m}^3 \times 1500\ \text{kg m}^{-3} = 49\ \text{g}$$

(density of ash = 1500 kg $m^{-3}$).

At Moor House the average daily rainfall rate (March- September 2008) over the surface area of the mesocosm would be 7.3 mm, which equates to approximately 200 ml per mesocosm. The results of the preliminary experiment in Fig. 2.4 show that approximately 90% of the $SO_4$ is leached in the first rainfall event followed by very low concentrations after every other pulse of water. However, F concentrations in the leachate remain consistently high after every rainfall event. The subsequent mesocosm treatments were designed to follow the pattern of these results, starting with very high $SO_4$ in the first pulse followed by much lower concentrations.

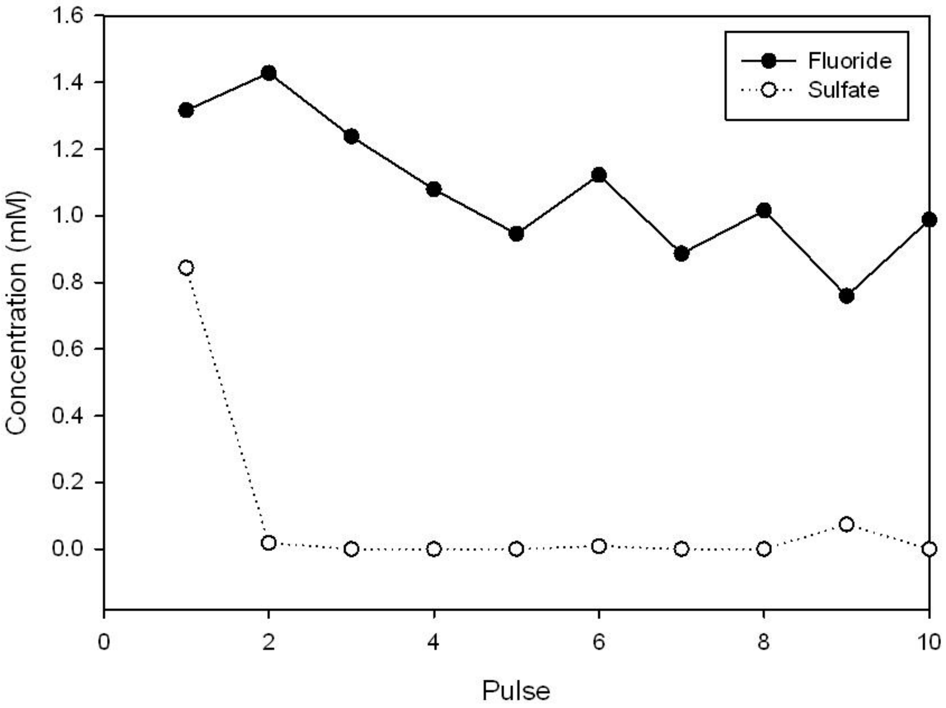


**Fig. 2.4** Concentrations of F and $SO_4$ in leachate when volcanic ash from the Hekla 1970 eruption was leached ten times during the preliminary ash leaching experiment.

*Treatment application*

Five treatments were applied to the mesocosms; these were: Control (deionised water), Sulfate, Sulfate + High Fluoride, Sulfate + Low Fluoride and High Fluoride alone. There were six replicates of each treatment. The treatment groups were chosen according to $CH_4$ emission rates (see Section 3.2.1). The total deposition rates of F and $SO_4$ for each treatment can be found in Table 2.1. Treatments were added as $Na_2SO_4$ and NaF. The concentrations of the treatment solutions added to the mesocosms over the 20 weeks are reported in Table 2.2. The $SO_4$-treated mesocosms received one large pulse of $SO_4$ in the first week and then this was followed by very low concentrations of $SO_4$ in subsequent weeks. This is what was observed in the preliminary ash leaching experiment. The mesocosms treated with high F received their highest dose in the first week followed by a slightly lower dose in subsequent pulses. Fluoride concentrations in the low F treatment were ten times lower than the high F treatment to represent other volcanoes with ash which is not so rich in F. Treatments were added in 200 ml of deionised water, which was poured evenly onto the mesocosms to ensure coverage of soil and vegetation. This volume of solution was chosen as it is the average rainfall per day (May – September) at the Moor House NNR sampling site (Values calculated from summary data on http://www.ecn.ac.uk/Database/index.html). Treatments were applied on the same day each week at approximately the same time. The first treatments were added on 12th May 2009.

**Table 2.1** Treatments applied to mesocosms over 20 weeks

| **Treatment name** | **Deposition rate (kg ha$^{-1}$) over 20 weeks** | |
|---|---|---|
| | $SO_4$-S | F |
| Control | Deionised water | |
| Sulfate | 24.5 | - |
| Sulfate + High Fluoride | 24.5 | 135 |
| High Fluoride | - | 135 |
| Sulfate + Low Fluoride | 24.5 | 13.5 |

**Table 2.2** Concentrations (μmol) of $SO_4$ and F in weekly treatment solutions (200 ml) added to peat soil mesocosms over the treatment period.

| Week | Application Date | Treatment (μmol) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | High F | High F + $SO_4$ | | Low F + $SO_4$ | | $SO_4$ | Control |
| | | | F | $SO_4$ | F | $SO_4$ | | |
| 1 | 12/05/2009 | 1430 | 1430 | 1770 | 140 | 1770 | 1770 | DI |
| 2 | 19/05/2009 | 950 | 950 | 120 | 100 | 120 | 120 | DI |
| 3 | 26/05/2009 | 950 | 950 | 10 | 100 | 10 | 10 | DI |
| 4 | 02/06/2009 | 950 | 950 | 10 | 100 | 10 | 10 | DI |
| 5 | 09/06/2009 | 950 | 950 | 10 | 100 | 10 | 10 | DI |
| 6 | 16/06/2009 | 950 | 950 | 10 | 100 | 10 | 10 | DI |
| 7 | 23/06/2009 | 950 | 950 | 10 | 100 | 10 | 10 | DI |
| 8 | 30/06/2009 | 950 | 950 | 10 | 100 | 10 | 10 | DI |
| 9 | 07/07/2009 | 950 | 950 | 10 | 100 | 10 | 10 | DI |
| 10 | 14/07/2009 | 950 | 950 | 10 | 100 | 10 | 10 | DI |
| 11 | 21/07/2009 | 950 | 950 | 10 | 100 | 10 | 10 | DI |
| 12 | 28/07/2009 | 950 | 950 | 10 | 100 | 10 | 10 | DI |
| 13 | 04/08/2009 | 950 | 950 | 10 | 100 | 10 | 10 | DI |
| 14 | 11/08/2009 | 950 | 950 | 10 | 100 | 10 | 10 | DI |
| 15 | 18/08/2009 | 950 | 950 | 10 | 100 | 10 | 10 | DI |
| 16 | 25/08/2009 | 950 | 950 | 10 | 100 | 10 | 10 | DI |
| 17 | 01/09/2009 | 950 | 950 | 10 | 100 | 10 | 10 | DI |
| 18 | 08/08/2009 | 950 | 950 | 10 | 100 | 10 | 10 | DI |
| 19 | 15/08/2009 | 950 | 950 | 10 | 100 | 10 | 10 | DI |
| 20 | 22/08/2009 | 950 | 950 | 10 | 100 | 10 | 10 | DI |

### 2.2.3 Soil solution sampling

To enable the collection of soil solution, Rhizon Soil Moisture Samplers (Eijkelkamp Agrisearch Equipmat, Giesbeek, the Netherlands) were inserted into the mesocosms before the experiment began. The Rhizon sampler consists of a 10 cm porous polymer tube connected to a 10 cm PVC tube and a luer-lock connector. Two samplers were inserted into each mesocosm, one to collect solution from the top 10 cm of the peat and one at a depth of 30 cm. The first was inserted vertically through the top of the mesocosm. A metal rod was used to make a hole through the soil to prevent damage to the Rhizon sampler that was then pushed through. To collect solution at 30 cm, a hole was first drilled into the PVC mesocosm shell. The Rhizon sampler was inserted into a rubber stopper (Suba-seal 14 mm) and then with the aid of the metal rod, horizontally into the peat core. The stopper was pushed through the drilled hole and sealed with silicon sealant to prevent leakage. Tygon tubing was attached to the sampler to extend it as the mesocosms were placed in buckets of water.

Soil solution was sampled at monthly intervals before treatments began from January to April 2009 to examine background chemical properties. After treatments began, mesocosms were sampled on a fortnightly basis. Solution was collected using a 60 ml syringe connected to the Rhizon sampler. The syringe was held open to create a vacuum, which draws the soil solution through the sampler and into the syringe. When the syringes had filled, they were disconnected from the samplers and labelled in preparation for analysis.

### 2.2.4 Soil solution analysis

Soil solution samples were returned to the laboratory immediately after sampling and filtered using 0.2 µm syringe filters (Nalgene Surfactant-free cellulose acetate membrane in acrylic housing). The pH was then measured using a glass/calomel electrode and pre-calibrated Thermo Orion pH meter (model 420A+). Samples were then stored in a fridge until other analyses were completed which was always within 14 days of collection. Concentrations of dissolved organic carbon (DOC) were measured using a TOC analyser (LiquiTOC, ElementarAnalseneysteme, Hanau, Germany).

Anion concentrations (F, $CH_3COO$, CHOO, Cl, Br, $SO_4$ and $PO_4$) in soil solution were measured by Ion Chromatography using a Dionex ICS 2000 fitted with an AS18 column coupled with an AS40 automated sampler. A potassium hydroxide (KOH) eluent was used with a gradient of 1 to 38 mM over 40 minutes to produce the best possible peak resolution of F and acetate (Flow rate: 0.25 ml/min; Suppressor current: 24 mA; Column temperature: 30 ºC). However, when the samples contained high concentrations of F and acetate, these peaks overlapped meaning that absolute concentrations of these species were difficult to determine. In these cases, samples were diluted and re-run through the Ion Chromatograph to obtain better peak separation and more accurate quantification.

To determine concentrations of Al, Fe, Ca, Na, Mg, K, Mn, P, S, Si, and Zn, 6 ml samples were acidified with 60 µl of nitric acid (70%) and then frozen (L.

Van den Berg *personal communication*). Samples were sent for analysis by inductively coupled plasma- atomic emission spectroscopy (ICP-AES) (IRIS Intrepid II, Thermo Electron Corporation, Franklin, MA) at Radboud University Nijmegen, the Netherlands. These elements were chosen as they are either key nutrients or micronutrients, the concentrations of which may be affected by the addition of $SO_4$ or F and may impact upon soil microorganisms.

### 2.2.5 Chemical speciation modelling

The chemical speciation of mesocosm soil solution was modelled using the CHemical Equilibria in AQuatic Systems model (CHEAQS PRO) (Available to download from http://home.tiscali.nl/cheaqs/index.html) (Verweij, 2010). Although this model was designed for aquatic systems it also calculates complexation by organic matter using three different models (Tippings' model V, Wham-W and Tippings' 6). It has not been used for peat soils previously but may be useful to suggest the likely speciation of ions present in solution. Concentrations of all measured species and the solution pH were inputted into the model. The output gives the proportion of each species expressed as a percentage. The soil solution chemical speciation over time was modelled for one mesocosm from each treatment group to identify differences between treatment groups and changes over time.

### 2.2.6 Soil and vegetation analysis

At the end of the experiment, peat soil samples were taken at 0-10 and 10-20 cm from each of the Control mesocosms and from three of each treatment group. The soil was sorted to remove large roots and stones and was oven dried at 105 °C for 24 hours and then finely ground. Samples of *Eriophorum vaginatum* shoots and *Sphagnum* moss were collected from three mesocosms per treatment on the same day. Vegetation samples were oven dried at 70 °C for 48 hours and then finely ground.

The soil and vegetation samples were sent for acid digestion and ICP-AES analysis at the Radboud University Nijmegen, the Netherlands to determine concentrations of Al, Fe, Ca, Na, Mg, K, Mn, P, S, Si, and Zn. The digestion method used was based upon Sandroni (2003). Samples were homogenised and 200 mg of each was digested with 4 ml $HNO_3$ (65%) and 1 ml $H_2O_2$ (30 %) using an Ethos D microwave labstation (Milestone srl, Sorisole, Italy). Digests were diluted ten times and concentrations of elements were determined by ICP-AES.

Total F analysis of the ground soil and vegetation samples was carried out using a method adapted from McQuaker and Gurney (1977). Approximately 0.25 g of the prepared sample was weighed into a nickel crucible. To this, 3 ml of 17 M sodium hydroxide (NaOH) was added. The crucible was then placed in a furnace at 150ºC. After one hour, the temperature was increased to 300ºC and then was slowly increased further to 600ºC over 20 minutes where it remained for one hour. The furnace was turned off and the crucibles left to cool for two hours. Next, the crucibles were placed on a warming plate set at 70ºC and 10 ml of deionised water was added. The solution was stirred for ten minutes until the entire fusion residue was in suspension and 35 ml of deionised water was added. The pH of the solution was adjusted to within the range of pH 4-9 by adding 3 ml of concentrated hydrochloric acid (HCl). The solution was then diluted to 50% with TISAB IV (TISAB IV is made from 84 ml concentrated HCl, 242 g TRIS (tris(hydroxymethyl)aminomethane) and 230 g sodium tartrate diluted to 1 l with deionised water (Thermo-Scientific 1997)) which complexes with Al and Fe thereby releasing F which was previously bound to these elements. Fluoride concentration was then measured using an ion selective electrode (Thermo Scientific Orion Fluoride ion selective electrode).

### 2.2.7 Statistical analysis

*Soil solution analysis*

To compare the effects of treatments on soil solution chemistry, the chemical composition data were split into two groups prior to statistical analysis. These were pre-treatment concentrations (14/01/2009 to 16/04/2009) and post-treatment concentrations (18/05/2009 to 14/09/2009). ICP analysis was only carried out for one sampling date pre-treatment and so pre-treatment chemical composition data for Al, Fe, Ca, Na, Mg, K, Mn, P, S, Si, and Zn is only based on samples collected on 16/04/2009. These species were analysed differently from the other pre-treatment variables using univariate analysis of variance (U-ANOVA).

All data were first tested for normality using the Kolmogorov-Smirnov tests of normality ($p > 0.05$) and for homogeneity of variances with Levene’s test of equality of error variances ($p > 0.05$). Of the pre-treatment data, only pH, Cl, Al and Mg met these requirements. The other variables were log-transformed which considerably improved the normality and homogeneity of variances of all apart from Mn, P and S, which were ranked and tested non-parametrically. Of the post-treatment data, only pH and DOC were normally distributed with equal variances, so the other variables were log transformed. Transformation did not improve normality and equality of variances of the F, Mn or $NH_3$ post-treatment and so the data were summed across the treatment period to provide a cumulative value for each mesocosm. These data were then ranked and analysed non-parametrically.

Repeated-measures multivariate analysis of variance (RM-MANOVA) (Pillai’s trace) was used to analyse the effects of the treatments on the untransformed and log transformed chemical species concentrations, with sampling date as the within-subject factor and treatment as the between-subjects factor. This method also allowed examination of within treatment variability (time effect and interactions between time and treatment (time times treatment)). Post Hoc comparisons (Tukey HSD) were included if treatment was a significant factor ($p<0.05$) or to test if concentrations in the soil solution of the treatment mesocosms were significantly different from concentrations in Control mesocosms (Dunnett t-tests).

As pre-treatment data for Al, Fe, Ca, Mg, K, Si, and Zn were only available for one sampling date, the RM-MANOVA was unsuitable and was replaced with U-ANOVA instead. Treatment was a fixed factor with the species concentration as the dependant variable. This test was followed by Post Hoc comparisons (Tukey HSD and Dunnett t-tests as above) if treatment effect was a significant factor.

Pre-treatment Mn, P and S and post-treatment F and Mn were analysed non-parametrically using the Kruskal Wallis test to assess whether concentrations of the species in the treatment mesocosms were significantly different to the Control concentrations. If the test revealed a significant result, it was followed by a series of Mann-Whitney tests to test the treatment groups against the Controls to investigate what the significant differences were.

*Soil analysis*

The data were tested for normality and homogeneity of variances using the Kolmogorov-Smirnov test of normality and Levene's test of equality of error variances ($p > 0.05$). At 0-10 cm, Ca, Fe, Mg and P concentration data met these requirements and at 10-20 cm, Ca, Fe, Mg, P, S, Al and K data were also normally distributed and variances equal. These data were analysed using U-ANOVA as above. Many transformations were carried out to the data that did not meet the requirements of the Kolmogorov-Smirov and Levene's tests but none improved the normality or homogeneity of variances and so these data were ranked and analysed non-parametrically using the same methods as for the soil solution data.

*Vegetation analysis*

Concentrations of chemical species in sedges and mosses were tested for normality and homogeneity of variances using Kolmogorov-Smirnov and Levene's tests ($p > 0.05$). If data were normally distributed and variances equal, U-ANOVA was performed as above and was followed by Post Hoc comparisons. If the normality of variance requirements were not met, the Mann-Whitney non-parametric test was used instead.

All statistical analysis was performed with SPSS Statistics 17.0.

## 2.3 Results

### 2.3.1 Soil solution

#### 2.3.1.1 Pre-treatment

Analysis of mesocosm soil solutions sampled before treatments began highlighted significant differences in concentrations of acetate, Ca, Fe, Mg and Mn between treatment groups (Table 2.3). At 10 cm, the High Fluoride designates had significantly higher Mg concentrations than the Sulfate + Low Fluoride designated mesocosms. At 30 cm there were significant differences in acetate concentration with higher concentrations of acetate in the mesocosms allocated to receive Sulfate than the High Fluoride and Sulfate + Low Fluoride designate mesocosms. There were lower Ca concentrations in the Sulfate + Low Fluoride than the Sulfate + High Fluoride designates. Concentrations of Fe in the Sulfate designate mesocosms were significantly greater than the Control and Sulfate + Low Fluoride designates. The High Fluoride designates had significantly higher Mn concentrations than Control designates.

**Table 2.3** Summary of mean Pre-treatment soil solution chemical composition, RM-ANOVA and Post Hoc comparisons (continued on following two pages)

| Variable | Sampler position | Treatment group | Mean amount in solution (µmol $l^{-1}$) (±Std dev) | Between subjects effects[a] (treatment) | Tukey HSD Post Hoc comparison |
|---|---|---|---|---|---|
| pH | 10 cm | Control | 5.05 (0.55) | F= 1.523<br>*P*= 0.227 | |
| | | High F | 5.33 (0.42) | | |
| | | Sulfate + High F | 5.18 (0.53) | | |
| | | Sulfate + Low F | 4.77 (0.41) | | |
| | | Sulfate | 5.05 (0.44) | | |
| | 30 cm | Control | 4.88 (0.38) | F= 0.141<br>*P*= 0.965 | |
| | | High F | 4.95 (0.21) | | |
| | | Sulfate + High F | 4.95 (0.33) | | |
| | | Sulfate + Low F | 4.92 (0.32) | | |
| | | Sulfate | 4.93 (0.37) | | |
| SO$_4$ | 10 cm | Control | 12.69 (18.35) | F= 0.712<br>*P*= 0.590 | |
| | | High F | 7.04 (9.96) | | |
| | | Sulfate + High F | 16.19 (47.48) | | |
| | | Sulfate + Low F | 5.86 (6.25) | | |
| | | Sulfate | 8.93 (10.54) | | |
| | 30 cm | Control | 4.15 (4.62) | F= 1.485<br>*P*= 0.238 | |
| | | High F | 6.04 (8.61) | | |
| | | Sulfate + High F | 3.52 (2.42) | | |
| | | Sulfate + Low F | 5.83 (5.03) | | |
| | | Sulfate | 5.95 (5.85) | | |
| F | 10 cm | Control | 24.34 (28.40) | F= 1.123<br>*P*= 0.368 | |
| | | High F | 39.51 (72.57) | | |
| | | Sulfate + High F | 26.13 (20.27) | | |
| | | Sulfate + Low F | 14.09 (10.77) | | |
| | | Sulfate | 27.46 (32.04) | | |
| | 30 cm | Control | 18.38 (10.60) | F= 2.28<br>*P*=0.09 | |
| | | High F | 26.57 (7.02) | | |
| | | Sulfate + High F | 23.08 (6.37) | | |
| | | Sulfate + Low F | 16.81 (6.62) | | |
| | | Sulfate | 26.49 (11.20) | | |
| Ca | 10 cm | Control | 221.79 (292.07) | F= 1.378<br>*P*=0.27 | |
| | | High F | 333.25 (233.78) | | |
| | | Sulfate + High F | 304.38 (198.54) | | |
| | | Sulfate + Low F | 122.20 (91.11) | | |
| | | Sulfate | 225.54 (238.95) | | |
| | 30 cm | Control | 87.24 (30.08) | F= 3.004<br>*P*=0.04 | SO$_4$+LF<br>Vs<br>SO$_4$+HF<br>*P*= 0.04 |
| | | High F | 152.47 (47.09) | | |
| | | Sulfate + High F | 126.95 (55.88) | | |
| | | Sulfate + Low F | 79.63 (36.47) | | |
| | | Sulfate | 116.55 (38.27) | | |

| **Variable** | **Sampler position** | **Treatment group** | **Mean amount (μmol $l^{-1}$) (±Std dev)** | **Between subjects effects[a] (treatment)** | **Tukey Post Hoc comparison** |
|---|---|---|---|---|---|
| Fe | 10 cm | Control | 367.02 (578.22) | F= 1.24<br>*P*=0.32 | |
| | | High F | 527.08 (614.28) | | |
| | | Sulfate + High F | 535.13 (474.59) | | |
| | | Sulfate + Low F | 150.38 (117.29) | | |
| | | Sulfate | 371.28 (403.42) | | |
| | 30 cm | Control | 60.66 (25.02) | F= 4.223<br>*P*= 0.01 | Control Vs $SO_4$ *P*= 0.03<br>$SO_4$+LF Vs $SO_4$ *P*= 0.04 |
| | | High F | 98.59 (23.85) | | |
| | | Sulfate + High F | 99.71 (36.30) | | |
| | | Sulfate + Low F | 62.44 (14.83) | | |
| | | Sulfate | 112.18 (34.95) | | |
| Al | 10 cm | Control | 12.60 (7.63) | F= 0.673<br>*P*= 0.617 | |
| | | High F | 19.50 (8.84) | | |
| | | Sulfate + High F | 15.44 (8.52) | | |
| | | Sulfate + Low F | 20.11 (13.29) | | |
| | | Sulfate | 14.31 (9.77) | | |
| | 30 cm | Control | 20.47 (15.18) | F= 0.893<br>*P*= 0.483 | |
| | | High F | 18.66 (6.51) | | |
| | | Sulfate + High F | 16.82 (11.05) | | |
| | | Sulfate + Low F | 15.43 (4.36) | | |
| | | Sulfate | 23.44 (9.32) | | |
| DOC | 10 cm | Control | 7016.56 (4248) | F= 0.71<br>*P*= 0.59 | |
| | | High F | 8186.96 (7019) | | |
| | | Sulfate + High F | 10685.41 (8366) | | |
| | | Sulfate + Low F | 7560.22 (5203) | | |
| | | Sulfate | 9687.74 (8630) | | |
| | 30 cm | Control | 4805.47 (3518) | F= 1.127<br>*P*= 0.367 | |
| | | High F | 4765.45 (2419) | | |
| | | Sulfate + High F | 4904.19 (2055) | | |
| | | Sulfate + Low F | 2997.14 (1158) | | |
| | | Sulfate | 4944.37 (3691) | | |
| Mg | 10 cm | Control | 58.78 (55.35) | F= 0.89<br>*P*= 0.484 | |
| | | High F | 80.27 (50.61) | | |
| | | Sulfate + High F | 69.99 (43.18) | | |
| | | Sulfate + Low F | 36.30 (17.47) | | |
| | | Sulfate | 54.20 (42.87) | | |
| | 30 cm | Control | 28.04 (9.18) | F= 3.752<br>*P*= 0.016 | HF Vs $SO_4$+LF *P*= 0.033 |
| | | High F | 42.99 (6.94) | | |
| | | Sulfate + High F | 38.81 (14.30) | | |
| | | Sulfate + Low F | 25.66 (5.18) | | |
| | | Sulfate | 39.13 (9.91) | | |

| Variable | Sampler position | Treatment group | Mean amount ($\mu mol\ l^{-1}$) (±Std dev) | Between subjects effects[a] (treatment) | Tukey Post Hoc comparison |
|---|---|---|---|---|---|
| Cl | 10 cm | Control | 118.79 (61.37) | F= 2.640<br>*P*= 0.060 | |
| | | High F | 194.01 (60.18) | | |
| | | Sulfate + High F | 156.58 (60.89) | | |
| | | Sulfate + Low F | 116.42 (38.80) | | |
| | | Sulfate | 168.06 (72.23) | | |
| | 30 cm | Control | 126.52 (82.20) | F= 2.510<br>*P*= 0.070 | |
| | | High F | 205.86 (46.18) | | |
| | | Sulfate + High F | 133.04 (44.79) | | |
| | | Sulfate + Low F | 137.41 (39.11) | | |
| | | Sulfate | 182.17 (56.46) | | |
| Acetate | 10 cm | Control | 9.47 (12.24) | F= 4.223<br>*P*= 0.010 | $SO_4$ Vs HF<br>*P*= 0.019<br>$SO_4$ Vs $SO_4$+LF<br>*P*= 0.011 |
| | | High F | 7.14 (9.58) | | |
| | | Sulfate + High F | 17.40 (39.51) | | |
| | | Sulfate + Low F | 8.56 (13.74) | | |
| | | Sulfate | 32.41 (40.73) | | |
| | 30 cm | Control | 3.60 (6.31) | F= 2.260<br>*P*= 0.090 | |
| | | High F | 5.09 (7.76) | | |
| | | Sulfate + High F | 6.65 (6.77) | | |
| | | Sulfate + Low F | 3.17 (5.25) | | |
| | | Sulfate | 9.55 (14.96) | | |
| Mn | 10 cm | Control | 70.37 (107.71) | H= 7.31<br>*P*= 0.12 | |
| | | High F | 12.70 (12.16) | | |
| | | Sulfate + High F | 38.93 (64.25) | | |
| | | Sulfate + Low F | 0.82 (0.26) | | |
| | | Sulfate | 14.34 (32.46) | | |
| | 30 cm | Control | 1.68 (1.56) | H= 13.17<br>*P*= 0.01 | Control Vs HF<br>*P*= 0.04 |
| | | High F | 4.93 (2.42) | | |
| | | Sulfate + High F | 3.21 (2.62) | | |
| | | Sulfate + Low F | 0.84 (0.34) | | |
| | | Sulfate | 1.62 (0.78) | | |
| P | 10 cm | Control | 2.16 (1.83) | H= 1.75<br>*P*= 0.78 | |
| | | High F | 5.67 (9.69) | | |
| | | Sulfate + High F | 1.53 (0.56) | | |
| | | Sulfate + Low F | 1.63 (1.09) | | |
| | | Sulfate | 1.68 (0.33) | | |
| | 30 cm | Control | 10.17 (22.18) | H= 1.45<br>*P*= 0.84 | |
| | | High F | 2.03 (1.40) | | |
| | | Sulfate + High F | 1.54 (0.70) | | |
| | | Sulfate + Low F | 5.03 (0.70) | | |
| | | Sulfate | 1.82 (0.65) | | |

[a] *P* values were generated using RM-ANOVA. *P* values < 0.05 indicates a significant treatment effect. Mn and P data were analysed non-parametrically using a Kruskal-Wallis test followed by a Mann-Whitney U test as a post hoc comparison.

#### 2.3.1.2 Post-treatment

There was a significant effect of time for all cations and anions determined at $p<0.05$ in all cases. Interactive effects between treatment and time (treatment x time) were observed for acetate (10 cm), Al (10 cm), Na (10 cm), P (30 cm) and K (30 cm). A summary of the average concentrations of all of the chemical species measured over the treatment period and their significance is presented in Table 2.4.

*Fluoride*

Concentrations of F increased significantly in the mesocosms which received the Sulfate + High Fluoride and High Fluoride treatments at both 10 and 30 cm depth ($p<0.001$ and $p< 0.01$ respectively). One month after treatments began, concentrations of F started to increase in the soil solution samples at 10 cm (Fig. 2.5). At 30 cm, concentrations of F were generally lower and more variable over time when compared to the dataset for samples collected at 10 cm. There were no significant differences in F concentration in soil solution between the Sulfate + Low Fluoride mesocosms and the controls at either depth.

The results of Spearman's rho correlations indicate that F was significantly correlated with pH, Na, Ca, acetate, Al, Fe and Mn at 10 cm (Table 2.5). At 30 cm, the relationships between F and other chemical species change, as F concentrations are not related to Na, Al or Fe but instead to $SO_4$, Mg and Si. The significance of the relationship between F and acetate becomes lower with depth but the correlation of F with Ca and Mn becomes stronger with depth.

Chemical speciation modelling of soil solution collected at 10 cm showed that the majority of F present in solution was in the form of alumino-fluoride (Al-F) complexes (Fig. 2.6). In mesocosms receiving the Sulfate + Low Fluoride treatment, Al-F complexes accounted for 97% of the F speciation and this did not change over time. The speciation of F in the Sulfate + High Fluoride and High Fluoride treated mesocosms did however change over time. Over 95% of F was in the form of Al-F species at the start of the experiment but as time progressed more free F became available in solution. On the last sampling date the proportions of F complexed with Al were ~59 and ~85% in mesocosms receiving

Sulfate + High Fluoride and High Fluoride treatments, respectively. At 30 cm down the soil profile, over 95% of the F present in solution was in the form of Al-F complexes, and this composition did not change over time.

**Table 2.4** Summary of average soil solution chemical parameters for each treatment group over the post-treatment period.

| | Mean concentration (μmol $l^{-1}$) (±Std dev) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 10 cm | | | | | 30 cm | | | | |
| | Control | $SO_4$ | $SO_4$+Low F | $SO_4$+High F | High F | Control | $SO_4$ | $SO_4$+Low F | $SO_4$+High F | High F |
| **pH** | 4.6 (0.6) | 4.7 (0.4) | 4.4 (0.4) | 5.0 (0.5) | 5.2 (0.3) | 4.5 (0.3) | 4.6 (0.2) | 4.6 (0.3) | 4.7 (0.3) | 4.8 (0.2) |
| **DOC** | 5046 (2830) | 7216 (4886) | 6887 (3785) | 7550 (4779) | 6254 (3989) | 5815 (1783) | 6162 (2454) | 4130 (1498) | 5945 (1432) | 5386 (2173) |
| **F** | 9.4 (11.5) | 9.5 (10.5) | 7.8 (9.2) | 84.4 (87.6) *** | 54.9 (63.1) *** | 11.1 (9.5) | 16.2 (12.5) | 11.3 (11.9) | 17.3 (17.7)** | 20.1 (14.3)** |
| **$SO_4$** | 25.2 (49.3) | 42.3 (74.3) | 46.4 (86.7) | 52.9 (116.2) | 9.3 (97.5) | 13.0 (14.9) | 18.0 (36.7) | 14.0 (25.5) | 25.8 (71.7) | 38.0 (139.1) |
| **Acetate** | 11.4 (32.6) | 12.8 (27.5) | 7.2 (21.5) | 29.2 (29.3) *** | 21.3 (32.5)* | 4.3 (4.6) | 4.2 (3.7) | 4.0 (4.4) | 6.2 (6.1) | 5.8 (4.4) |
| **Formate** | 5.7 (6.7) | 9.6 (11.9) | 12.3 (13.2) | 32.9 (13.2)** | 26.4 (16.2)** | 10.9 (11.2) | 13.1 (13.3) | 7.9 (6.8) | 16.8 (11.6) | 14.2 (11.6) |
| **Cl** | 61.4 (56.6) | 108.4 (77.2) | 81.7 (44.3) | 123.9 (84.6) | 122.6 (9.4) | 90.8 (50.6) | 144.1 (57.1) | 119.1 (80.9) | 125.0 (60.9) | 170.75 (58.9) |
| **Al** | 11.5 (7.7) | 13.7 (9.9) | 20.4 (12.7) | 39.2 (18.4) *** | 35.4 (19.8) *** | 27.5 (12.7) | 28.2 (8.3) | 19.4 (4.6) | 25.9 (11.0) | 25.3 (6.8) |
| **Ca** | 142.7 (157.9) | 190.8 (152) | 141 (87.8) | 240.4 (176.6) | 264.4 (171.2) | 123.1 (40.4) | 143.6 (43.3) | 95.1 (29.8) | 185.3 (80.1) | 177.1 (75.9) |
| **Fe** | 139.8 (255.0) | 269.6 (290) | 159 (147) | 479.8 (530.6) | 432.1 (458.6) | 93.2 (37.7) | 122.7 (43.0) | 79.9 (26.2) | 156.1 (74.6)* | 122.2 (30.1) |
| **K** | 7.1 (13.2) | 5.3 (6.2) | 5.6 (6.9) | 5.1 (6.8) | 7.4 (14.1) | 5.9 (8.6) | 4.7 (5.0) | 5.0 (5.9) | 4.9 (8.7) | 5.32 (6.2) |
| **Mg** | 36.2 (31.0) | 46.0 (25.7) | 39.6 (14.1) | 48.9 (31.8) | 62.8 (37.9) | 38.7 (10.8) | 44.6 (12.2) | 31.5 (7.2) | 53.9 (19.1) | 55.4 (14.1) * |
| **Na** | 61.4 (42.7) | 102.6 (62.7) | 108.7 (41) | 242.5 (130.5) ** | 159.4 (98.6) | 115.7 (32.7) | 144.3 (41.5) | 106.8 (31.1) | 116.5 (88.5) | 134.2 (80.7)* |
| **P** | 4.6 (1.1) | 1.9 (0.9) | 1.6 (0.8) | 1.7 (0.8) | 3.4 (5.5) | 1.6 (1.1) | 1.9 (0.9) | 1.6 (0.8) | 1.7 (0.8) | 3.4 (5.5)* |
| **S** | 49.7 (42.9) | 75.4 (70.6) | 83.5 (76.7) | 88.1 (114.4) | 76.0 (96.7) | 47.3 (17.3) | 48.9 (39.2) | 38.8 (24.5) | 59 (74.3) | 68.8 (136.7) |
| **Si** | 42.9 (36.9) | 72.1 (61.9) | 65.5 (34.1) | 78.4 (48.0) | 78.6 (65.1) | 110.3 (60.5) | 125.4 (66.1) | 101.7 (49.0) | 105.2 (55.1) | 123.4 (72.3) |

Values are the mean of six replicates over the treatment period. Starred values are results which are significantly different from the control values as calculated using Dunnett's 2-sided t-test or by the Mann-Whitney U test (F, Mn, Si, Zn). * indicates $p<0.05$, ** indicates $p<0.01$ and ***indicates $p<0.001$

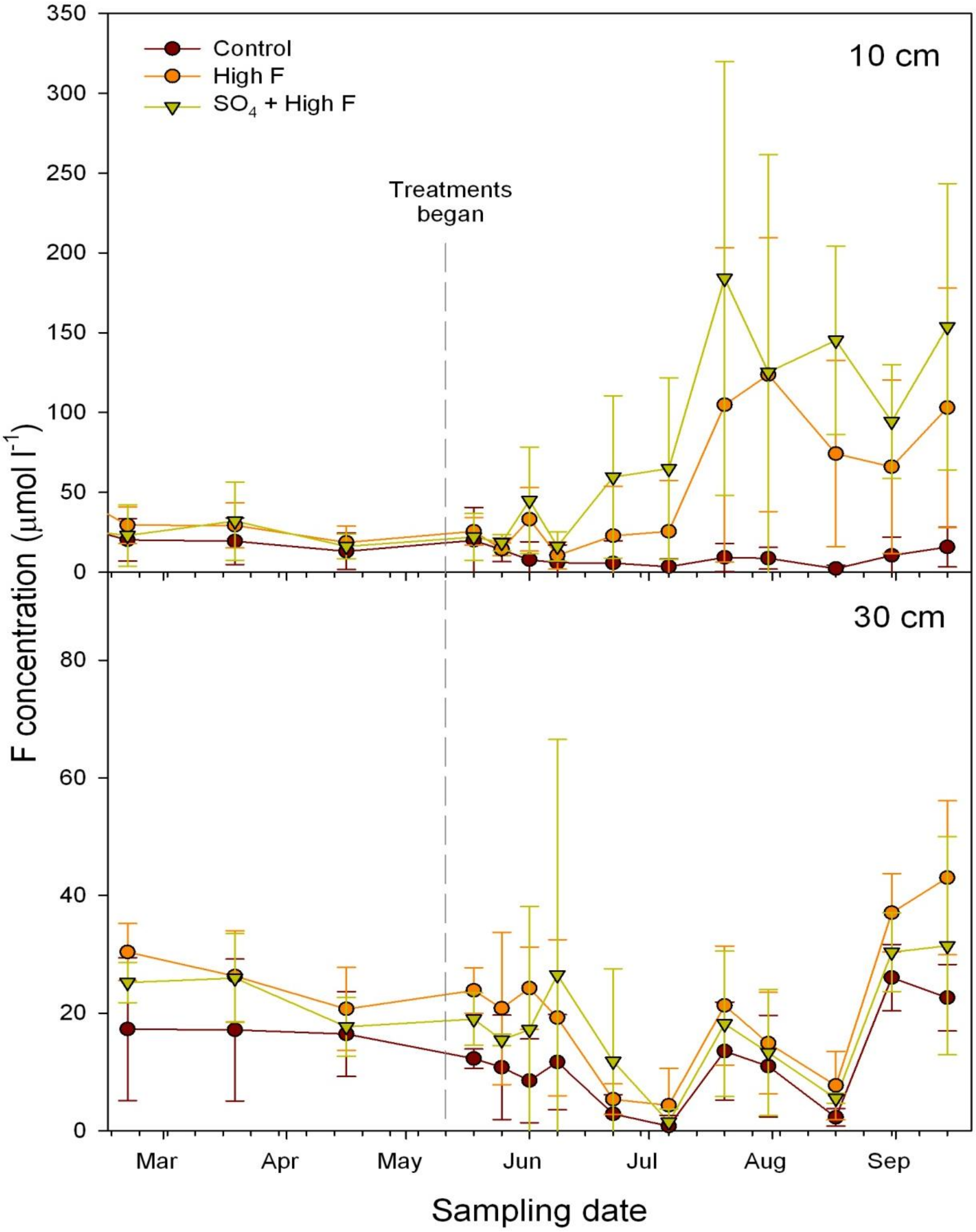


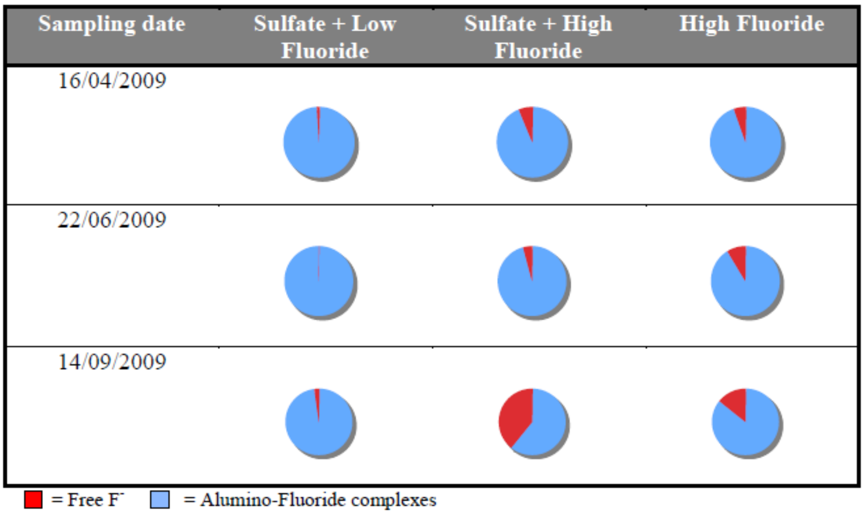
**Fig. 2.5** Mean F concentration in soil solution collected at 10 (top) and 30 (bottom) cm depth from control mesocosms compared to those treated with High Fluoride and Sulfate + High Fluoride. Points are an average of six replicates, bars represent standard deviation.

**Table 2.5** Spearman's rho correlations between chemical species in peat mesocosm soil solution

| | **Soil solution sampled at 10 cm depth** | | | | | **Soil solution sampled at 30 cm depth** | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | F | Acetate | $SO_4$ | Fe | Al | F | Acetate | $SO_4$ | Fe | Al |
| $SO_4$ | | - *** | | - *** | -*** | *** | * | | | |
| Na | *** | *** | | *** | *** | | | | *** | ** |
| Mg | | | | *** | *** | ** | *** | | *** | *** |
| P | | *** | -*** | *** | *** | | | -*** | *** | ** |
| S | | -** | *** | | | | | *** | *** | *** |
| Si | | ** | -*** | *** | *** | -* | -** | | * | *** |
| Ca | * | | -* | *** | *** | ** | *** | ** | *** | *** |
| K | | | -*** | *** | | | | -* | | |
| pH | *** | *** | -** | *** | *** | *** | *** | | *** | -*** |
| DOC | | *** | -*** | *** | *** | | * | | *** | *** |
| F | | *** | | *** | *** | | * | *** | | |
| Acetate | *** | | -*** | *** | *** | * | | * | *** | |
| Cl | | | | *** | *** | | | | *** | |
| Al | *** | *** | -*** | *** | | | | | *** | |
| Fe | *** | *** | -*** | | *** | | *** | | | *** |
| Mn | * | | -** | *** | *** | ** | *** | | *** | |
| Zn | | | -*** | *** | *** | | ** | | *** | *** |

* Correlation is significant at the 0.05 level, ** at the 0.01 level, ***at the 0.001 level. – indicates a negative relationship.

**Fig. 2.6** Speciation of F present in mesocosm soil solution sampled at 10 cm. Speciation modelled using CHEAQS PRO.



*Sulfate*

Concentrations of $SO_4$ in soil solution from mesocosms that were treated with $SO_4$ additions were not significantly different from those of control mesocosms at either depth (Table 2.6). The treatment load of $SO_4$ was greatest at the start of the experiment with 1770 µM solution being applied to each mesocosm in the first week. This decreased to much lower concentrations in subsequent weeks with 10 µM being applied in the third week of additions. However, the concentrations of $SO_4$ in the soil solutions of these mesocosms did not reflect this (Fig. 2.7). Sulfate concentrations remained at approximately 25 µmol $l^{-1}$ throughout the experiment until the end of August when a sharp increase in $SO_4$ concentration was observed for all treatments and the controls. This may be due to a lowering of the water table leading to oxidation of reduced S compounds and an increase in $SO_4$ concentrations in solution. Sulfate concentrations measured by the ECN network at the Moor House site also recorded low concentrations of 0.1 – 1.87 µmol $l^{-1}$ over the same time period as the mesocosm experiment.

Concentrations of $SO_4$ at 30 cm were 50% lower than $SO_4$ concentrations measured at 10 cm for all treatment groups apart from the High Fluoride mesocosms where a 4-fold increase in $SO_4$ concentration was seen with depth. Dissolved S as measured by ICP-OES also showed no significant treatment effect on S concentrations in solution at 10 or 30 cm (p= 0.17 and 0.26 respectively).

Sulfate concentrations in soil solution were negatively correlated with those of P, Si, Ca, K, DOC, acetate, Al, Fe, Mn and Zn and with pH at 10 cm (Table 2.5). The relationships between $SO_4$ and other chemical species were different at 30 cm depth. Sulfate had a negative relationship with P and K and positive correlations with Ca, F, acetate and $NH_3$.

Speciation modelling indicated that over 95% of $SO_4$ present in solution was as free $SO_4$ in all mesocosms at 10 and 30 cm. There were no differences between treatment groups and no changes in speciation over time.

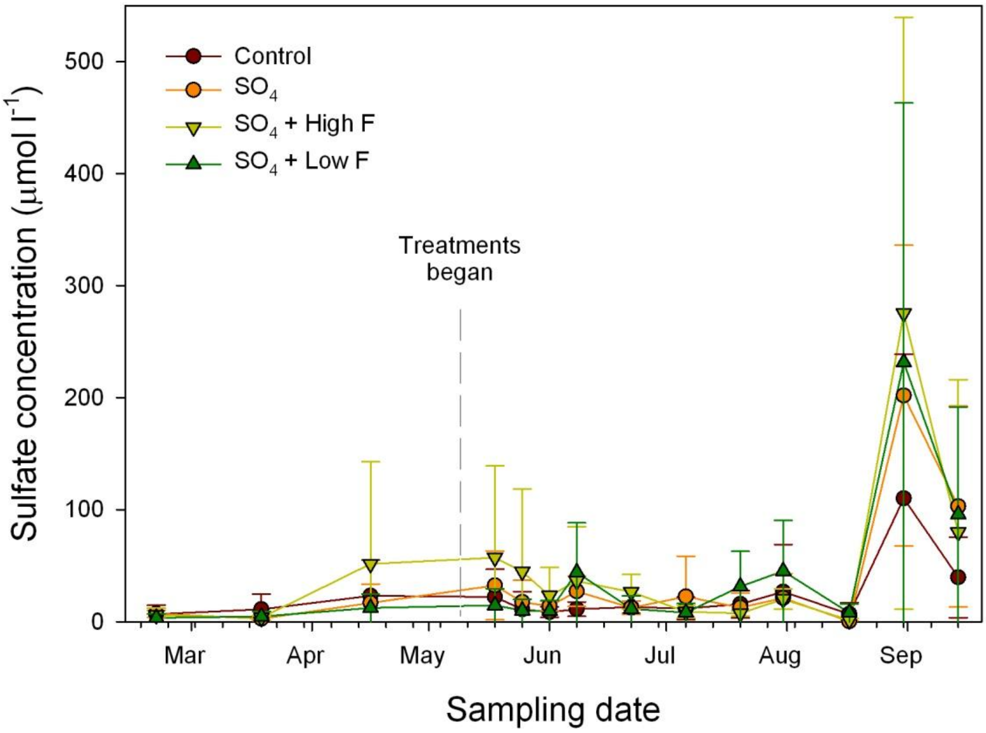


**Fig. 2.7** Mean $SO_4$ concentration in soil solution collected at 10 cm depth from control mesocosms compared to those treated with Sulfate, Sulfate + High Fluoride and Sulfate + Low Fluoride. Points are averages of six replicates, bars represent standard deviation.

**Table 2.6** Summary of post-treatment soil solution statistical analysis by RM-ANOVA

| Variable | Sampler position | Multivariate tests (Pillai's trace) | | | | Between subjects effects (Treatment) | | Post Hoc comparison (Dunnet (2 sided t-test) Control Vs. |
|---|---|---|---|---|---|---|---|---|
| | | Sampling date | | Sampling date * Treatment | | | | |
| | | F | *P* | F | *P* | F | *P* | |
| Sulfate | 10 cm | 22.01 | **0.00** | 1.09 | 0.37 | 0.71 | 0.59 | |
| | 30 cm | 30.08 | **0.00** | 1.09 | 0.37 | 0.95 | 0.45 | |
| pH | 10 cm | 37.08 | **0.00** | 1.12 | 0.32 | 3.08 | **0.03** | |
| | 30 cm | 44.28 | **0.00** | 1.24 | 0.21 | 1.58 | 0.21 | |
| Acetate | 10 cm | 25.27 | **0.00** | 1.92 | **0.007** | 9.59 | **0.000** | HF *P*= **0.017**<br>SO$_4$+HF *P*= **0.000** |
| | 30 cm | 14.08 | **0.00** | 1.37 | 0.12 | 2.05 | 0.12 | |
| DOC | 10 cm | 16.64 | **0.00** | 0.94 | 0.58 | 0.798 | 0.54 | |
| | 30 cm | 27.10 | **0.00** | 0.68 | 0.91 | 1.93 | 0.14 | |
| Aluminium | 10 cm | 23.63 | **0.00** | 2.34 | **0.001** | 10.13 | **0.000** | HF *P*= **0.001**<br>SO$_4$+HF *P*= **0.000** |
| | 30 cm | 24.94 | **0.00** | 1.12 | 0.33 | 1.34 | 0.28 | |
| Iron | 10 cm | 25.79 | **0.00** | 0.81 | 0.76 | 2.23 | 0.094 | HF *P*= 0.074<br>SO$_4$+HF *P*= 0.052 |
| | 30 cm | 12.37 | **0.00** | 0.99 | 0.50 | 3.76 | **0.016** | SO$_4$+HF *P*= **0.042** |
| Chloride | 10 cm | 5.45 | **0.001** | 1.22 | 0.224 | 0.98 | 0.44 | |
| | 30 cm | 14.82 | **0.00** | 1.54 | 0.06 | 1.55 | 0.22 | |
| Calcium | 10 cm | 19.30 | **0.00** | 1.21 | 0.24 | 1.17 | 0.35 | |
| | 30 cm | 3.05 | **0.023** | 0.96 | 0.55 | 5.31 | **0.003** | |
| Sodium | 10 cm | 36.76 | **0.00** | 2.24 | **0.001** | 3.83 | **0.015** | SO$_4$+LF *P*= 0.053<br>SO$_4$+HF *P*= **0.003** |
| | 30 cm | 22.29 | **0.00** | 1.10 | 0.36 | 5.61 | **0.002** | HF *P*= **0.013** |
| Sulfur | 10 cm | 15.09 | **0.00** | 1.27 | 0.185 | 1.77 | 0.17 | |
| | 30 cm | 13.93 | **0.00** | 0.82 | 0.75 | 1.42 | 0.26 | |
| Potassium | 10 cm | 49.21 | **0.00** | 1.47 | 0.083 | 0.25 | 0.91 | |
| | 30 cm | 36.7 | **0.00** | 1.59 | **0.046** | 0.21 | 0.93 | |
| Magnesium | 10 cm | 27.02 | **0.00** | 1.27 | 0.187 | 1.04 | 0.41 | |
| | 30 cm | 8.70 | **0.00** | 1.03 | 0.439 | 7.08 | **0.001** | HF *P*= **0.020** |

Values in bold indicate where $P<0.05$. Results for F are not included as these data were analysed non-parametrically using the Kruskal-Wallis test

*Acetate*

Concentrations of acetate in soil solution were significantly higher in mesocosms that received high concentrations of F than those for controls at 10 cm (Table 2.6). Acetate concentrations were highest in the Sulfate + High Fluoride mesocosms where mean concentrations exceeded 30 µmol l$^{-1}$ throughout July, August and September (Fig. 2.8). Average acetate concentrations in the control mesocosms during this period were below 5 µmol l$^{-}$

[1]. The mesocosms which received Sulfate + High Fluoride and High Fluoride treatments also had significantly greater acetate concentrations in solution than those treated with Sulfate + Low Fluoride and Sulfate alone. In samples taken at 30 cm depth there were no significant treatment effects on acetate concentration.

Acetate concentration is well correlated with F concentration in the Sulfate + High Fluoride and High Fluoride soil solutions (Fig. 2.9) and overall in all mesocosms (Table 2.5).

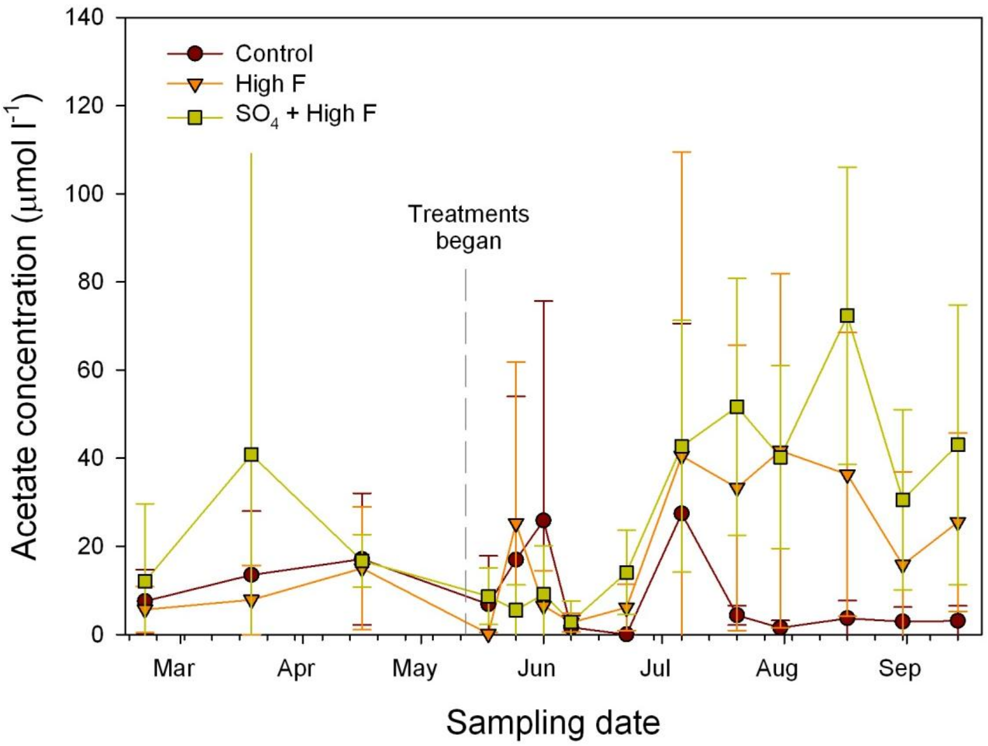


**Fig. 2.8** Mean acetate concentration in soil solution collected at 10 cm depth from control mesocosms compared to those treated with High Fluoride and Sulfate + High Fluoride. Points are averages of six replicates, bars represent standard deviation.

*Aluminium*

Soil solution Al concentrations were significantly higher in mesocosms which received the Sulfate + High Fluoride and High Fluoride treatments when compared to the control mesocosms and those which were treated with Sulfate alone (Fig. 2.10). Concentrations of Al began to increase in June and continued to increase throughout the treatment period. At the end of the experiment, average concentrations of Al in the soil solution of the Sulfate + High Fluoride mesocosms were five times greater than those in the control mesocosms; those for the High Fluoride mesocosms were over three times greater. However, this effect was only observed in samples taken at 10 cm depth and not further down the soil profile at 30 cm.

Concentrations of Al were in the range of 2 – 42 µmol $l^{-1}$in the Control mesocosms, which is comparatively higher than Al conentrations measured by the ECN at the Moor House site of 1.85 – 4.08 µmol $l^{-1}$. Ombrotrophic peats typically have insignificant Al contents, however the sampling site was located in a low bog area surrounded by gentle sloping hills which may have been a source of Al-enriched throughflow from surrounding mineral soils (Mulder et al. 1991).

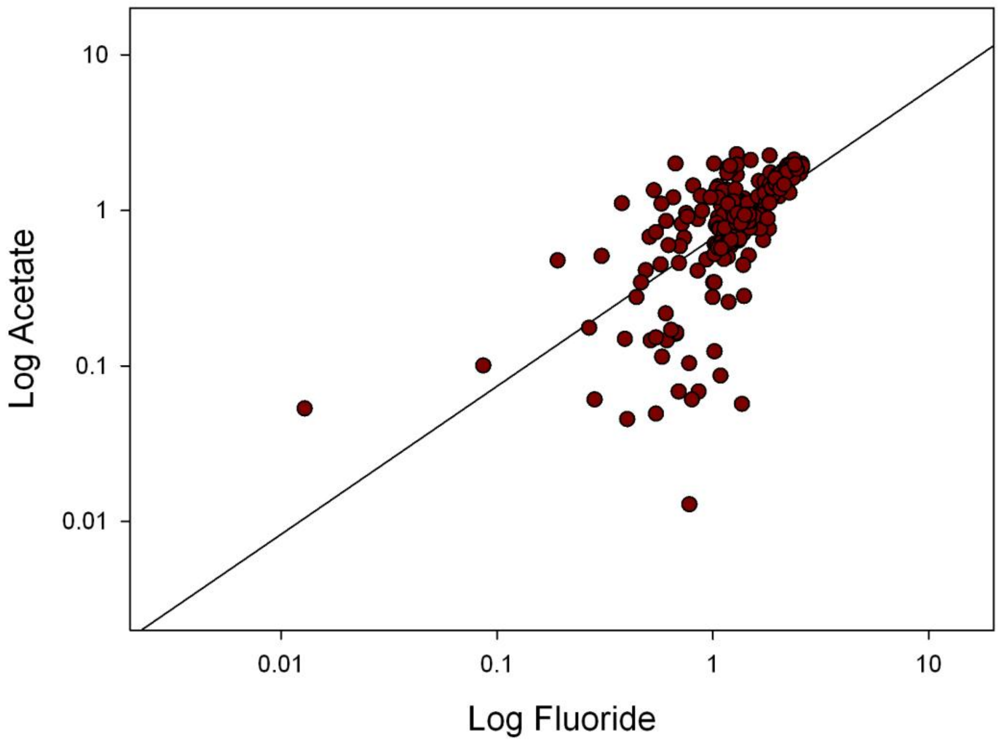


**Fig. 2.9** The relationship between F and acetate in soil solution collected at 10 cm from the High Fluoride and Sulfate + High Fluoride mesocosms.

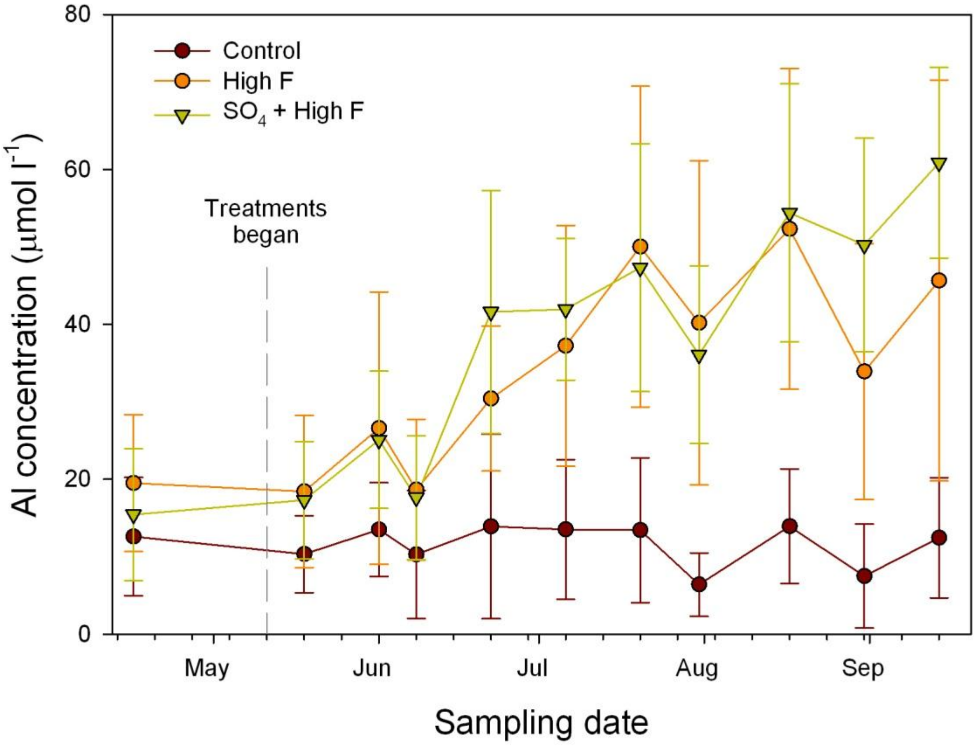
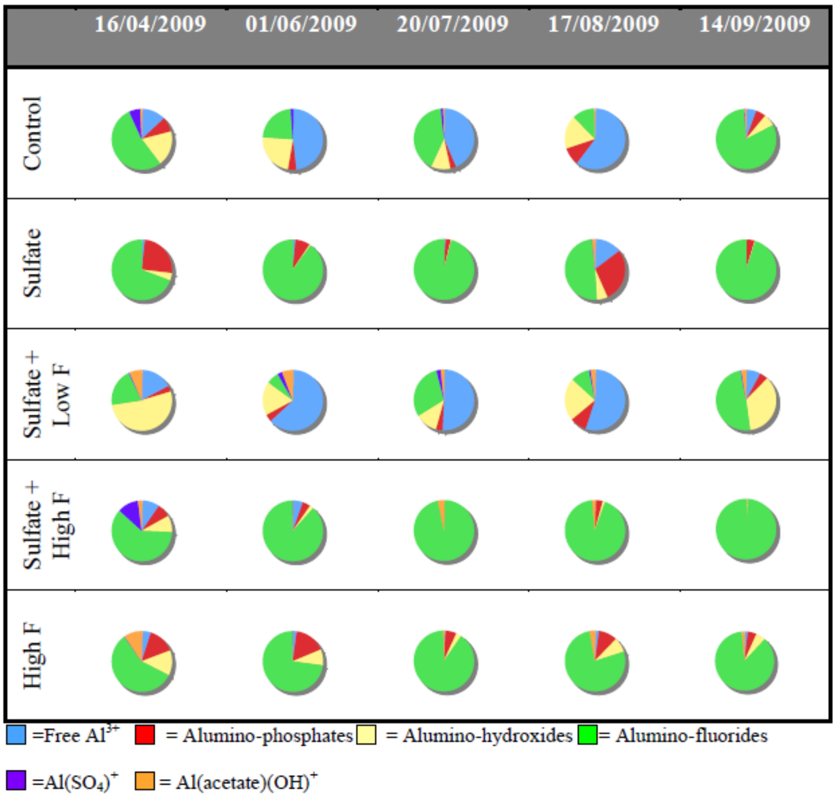


**Fig. 2.10** Mean aluminium concentration in soil solution collected at 10 cm depth from control mesocosms compared to those treated with High Fluoride and Sulfate + High Fluoride. Points are averages of six replicates, bars represent standard deviation.

Dissolved Al was mostly in the form of Al-F complexes (Fig. 2.11). At 10 cm, in mesocosms treated with Sulfate + High Fluoride and High Fluoride alone, the proportion of Al present as Al-F increased over time to ~97 and ~85%, respectively. The solution from the Sulfate + Low Fluoride did not show the same trend over time and had greater amounts of alumino-hydroxides than the other treatment groups. On the last sampling day, ~48% of Al was present as Al-F whereas ~36% was as Al-hydroxides. Speciation of Al in the Control and Sulfate mesocosms varied over time showing no trend. At 30 cm there was no clear pattern of speciation and the evolution over time was not clear. It should be noted that organic Al species were not included in the model as concentrations of humic and fulvic acids were not known.

**Fig. 2.11** Speciation of Al present in mesocosm soil solution sampled at 10 cm. Speciation modelled using CHEAQS PRO.



*Iron*

There were significant treatment effects on Fe concentration in solution at 30 cm (p=0.04) for mesocosms which were treated with Sulfate + High Fluoride. Average Fe concentrations over the treatment period from these mesocosms were ~70% greater than those for Control mesocosms (Fig. 2.12). In solutions collected at 10 cm, Fe concentration was three times greater for the Sulfate + High Fluoride and the High Fluoride mesocosms than for the Controls; however, this result was only of borderline significance (p=0.05 and 0.07 respectively). Iron concentrations were highly variable at 10 cm and standard deviations were large. At 10 cm, Fe was correlated with all of the chemical species tested apart from $SO_4$ (Table 2.5). A strong relationship was found between Fe and DOC at this depth (Fig. 2.13). At 30 cm, Fe was correlated with all species apart from $SO_4$, K and F.

### *Sodium*

Treatments of F and $SO_4$ were added to the mesocosms as salts and therefore, significant treatment effects on Na concentrations were observed. At 10 cm, all of the treatment mesocosms had higher concentrations of Na than controls but only the Sulfate + High Fluoride mesocosms had significantly higher values with almost four times the amount of Na than the controls ($p<0.01$). At 30 cm, the differences in Na concentration of soil solution between treatment groups and controls were much smaller. Only the High Fluoride treated mesocosms had significantly higher concentrations of Na than controls ($p<0.05$) and those receiving Sulfate + Low Fluoride treatments.

### *Magnesium*

At 10 cm, Mg concentrations in soil solution were unaffected by treatment but, at 30 cm, the pore water from mesocosms treated with High Fluoride had significantly more Mg than the control mesocosms ($p<0.05$). Mean concentrations of Mg in the High Fluoride mesocosms were approximately 30% greater than those in the Control mesocosms. The Sulfate + High Fluoride mesocosms had similarly high concentrations but the result was not significant as there was more variation between the six replicates.

### *Calcium*

Calcium concentrations in porewater sampled at 10 cm were not significantly affected by treatment, although concentrations in the High Fluoride and Sulfate+ High Fluoride mesocosms were over 100 µM greater than those for Control concentrations. At 30 cm there was a significant treatment effect ($p<0.01$). However, this effect was between treatment groups and not between treatment and Control mesocosms. The High Fluoride and the Sulfate + High Fluoride treated mesocosms had greater concentrations of Ca in solution than the mesocosms treated with Sulfate + Low Fluoride.

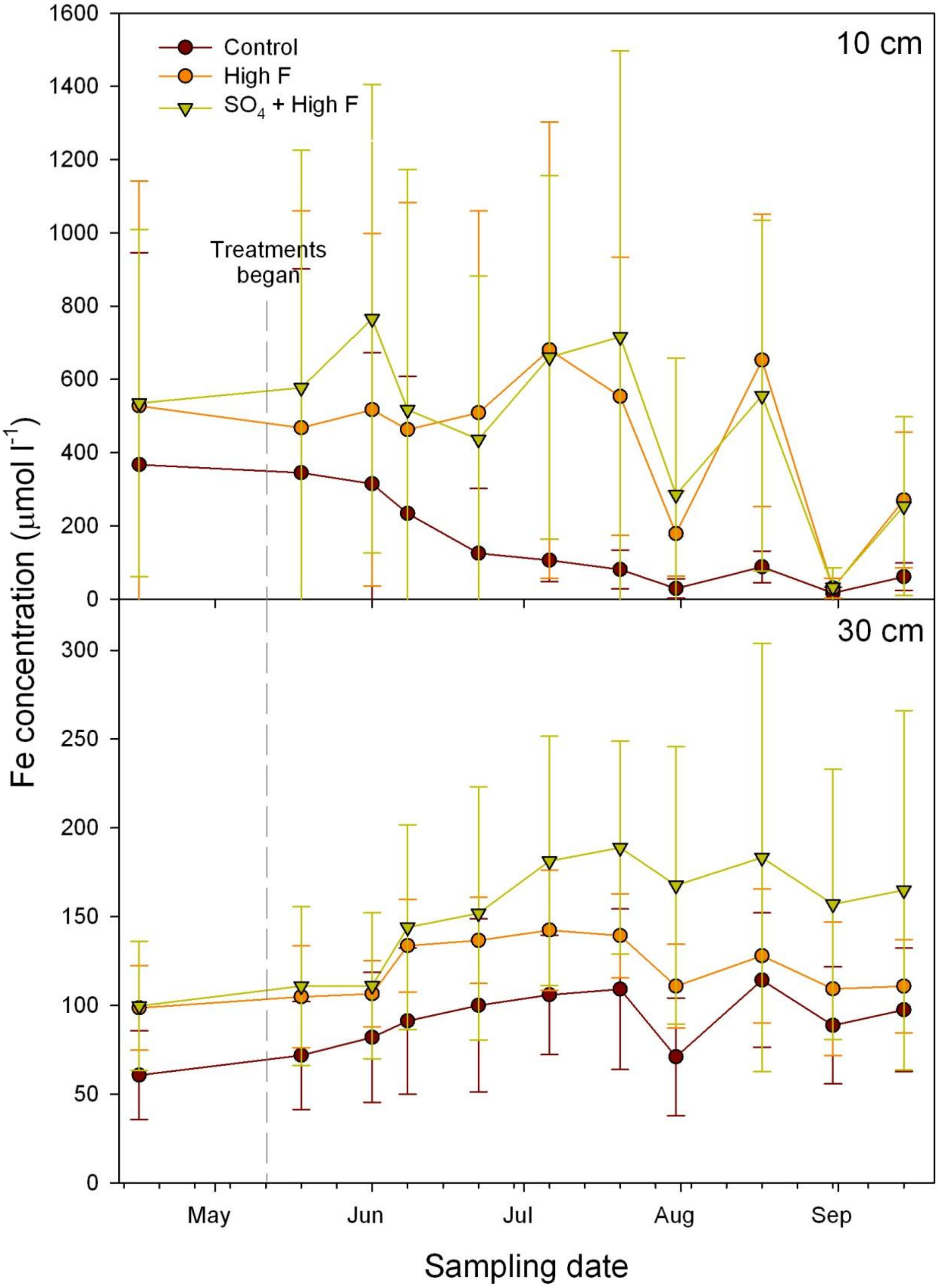


**Fig. 2.12** Mean Fe concentrations in soil solution collected at 10 cm depth from control mesocosms compared to those treated with High Fluoride and Sulfate + High Fluoride. Points are averages of six replicates, bars represent standard deviation. There was no pre-treatment data available for March and April as Fe concentration was only analysed for one pre-treatment sampling date.

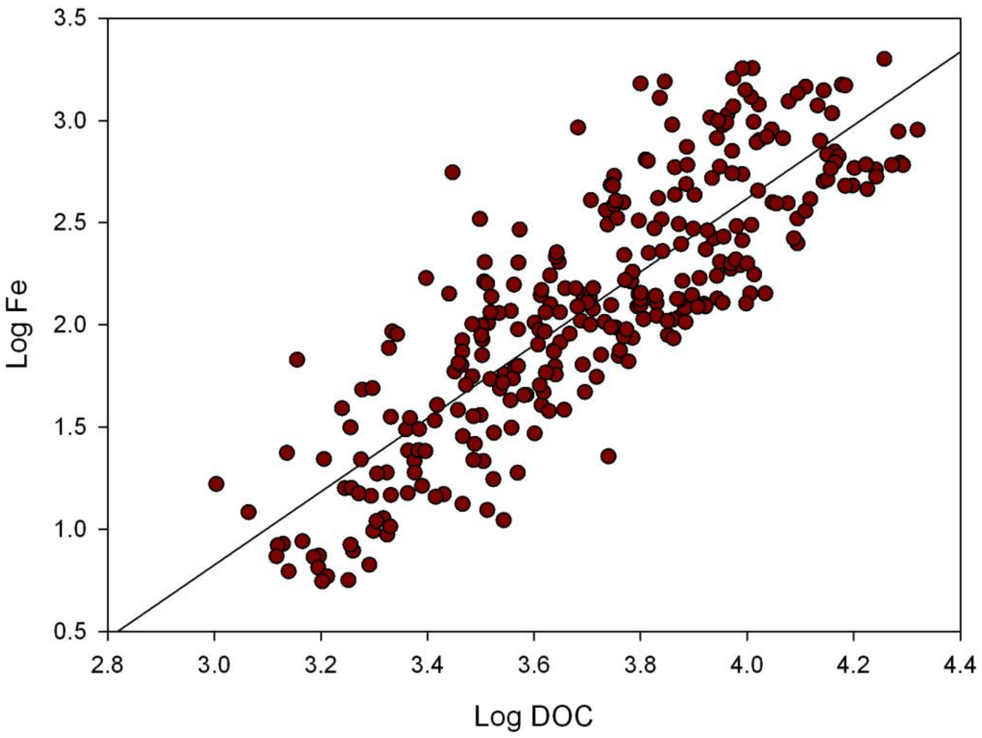


**Fig. 2.13** The relationship between Fe and DOC in soil solution collected at 10 cm from all mesocosms

*pH*

There were no significant differences between the pH of control mesocosm soil solutions and those of the mesocosms that had been treated (Fig. 2.14). However, there were significant differences in pH measured at 10 cm between two of the treatment groups. The solutions from High Fluoride treated mesocosms had a significantly higher pH than those from the mesocosms treated with Sulfate + Low Fluoride, with a mean pH of 5.15 compared to 4.40. The average pH of solution in the Control mesocosms was 4.60 over the treatment period, which is comparable to an average soil solution pH of 4.41 measured at the Moor House site over the same time period.

*Potassium, Dissolved organic carbon, Chloride, Manganese, Phosphorus, Silicon and Zinc*

No significant treatment effect was observed on these chemical species at any depth in the mesocosm profile.

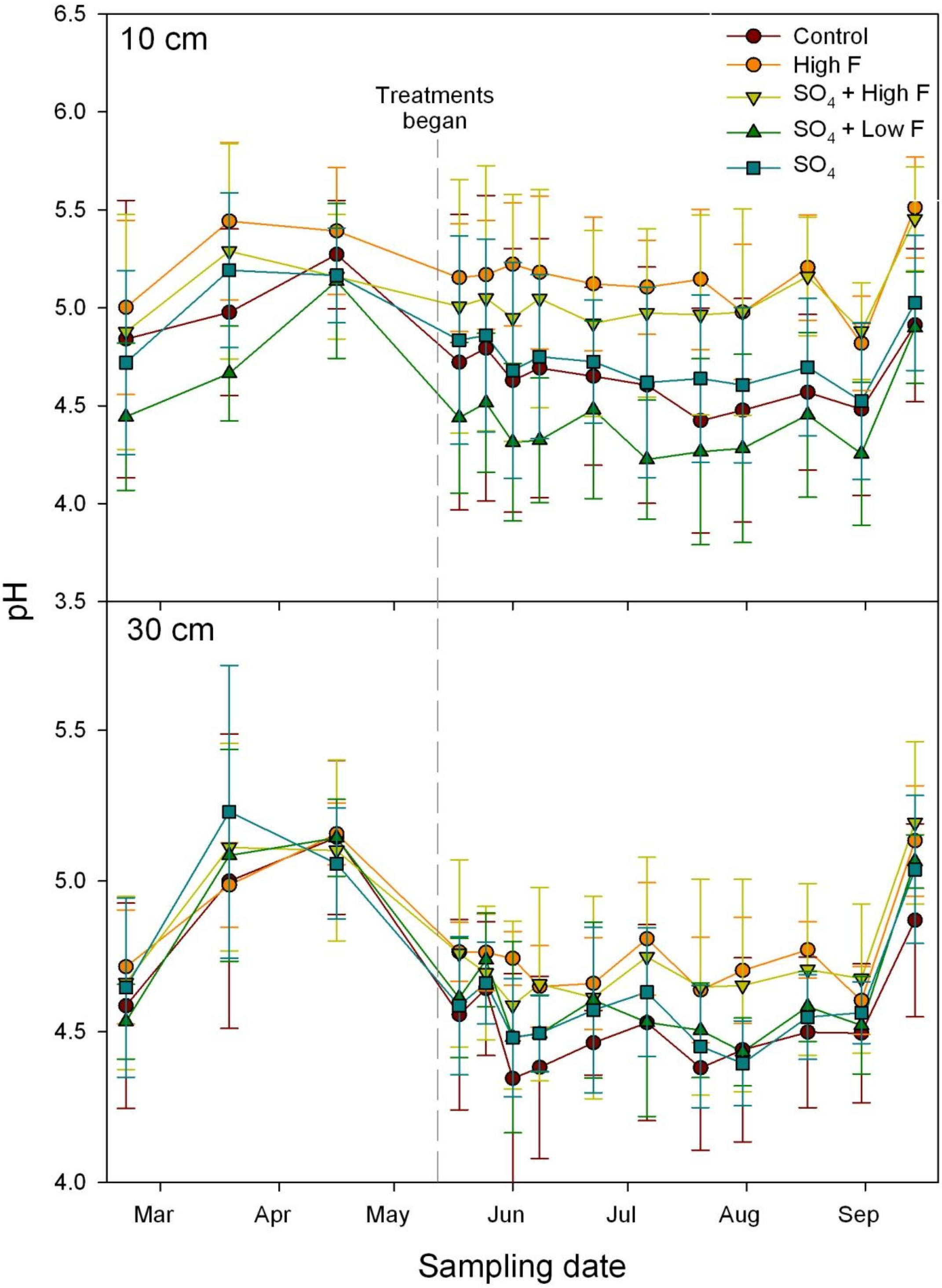


**Fig. 2.14** Mean pH in soil solutions collected at 10 cm and 30 cm depth from control mesocosms compared to treated mesocosms. Points are averages of six replicates, bars represent standard deviation.

### *Rainwater composition*

The chemical composition of rainwater collected from the experiment site is presented in Table 2.7. Fluoride was not present in rainwater, so the only additions of F came from the treatments. Concentrations of $SO_4$ in rainwater were in the range of 0-32 µmol $l^{-1}$, which corresponds to a bulk atmospheric S deposition of ~ 5.3 $kg^{-1}$ $ha^{-1}$ $y^{-1}$. Treatment $SO_4$ concentrations were 1770 µmol in week 1, 120 µmol in week 2 and 10 µmol from week 3 onwards added in 200 ml of solution. This means that rainwater concentrations of $SO_4$ were comparable to treatment additions from week 3 onwards, which increased concentrations of $SO_4$ added to the mesocosms each week. Concentrations of $SO_4$ in rainwater at the experiment site were higher than in rainwater from the mesocosm collection site where the monthly average (March – September 2009) $SO_4$ concentration was 7.66 µmol $l^{-1}$.

**Table 2.7** Chemical composition of rainwater sampled over the treatment period

| Date | mm of rain | Concentration (µmol $l^{-1}$) | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | DOC | $SO_4$ | $NO_3$ | Al | Ca | Fe | K | Mg | Na | P | S | Si | Zn |
| 19/05/09 | 30 | 351 | 17 | - | 0 | 27 | 0 | 1 | 7 | 18 | 1 | 21 | 5 | 0 |
| 23/05/09 | 12 | 412 | - | - | - | - | - | - | - | - | - | - | - | - |
| 29/05/09 | 10 | 241 | 18 | - | 1 | 66 | 0 | 7 | 12 | 36 | 0 | 21 | 8 | 0 |
| 09/06/09 | 25 | 397 | 27 | - | 1 | 57 | 0 | 4 | 15 | 79 | 1 | 31 | 6 | 1 |
| 16/06/09 | 15 | 389 | 32 | - | 1 | 44 | 0 | 5 | 11 | 51 | 0 | 32 | 7 | 3 |
| 23/06/09 | 12 | 351 | 10 | - | 1 | 59 | 1 | 3 | 10 | 42 | 1 | 15 | 8 | 0 |
| 30/06/09 | 0 | - | - | - | - | - | - | - | - | - | - | - | - | - |
| 07/07/09 | 22 | 305 | 0 | 12 | 1 | 52 | 0 | 9 | 9 | 31 | 1 | 24 | 5 | 1 |
| 14/07/09 | 14 | 278 | 13 | 14 | 1 | 38 | 1 | 2 | 6 | 28 | 1 | 10 | 9 | 0 |
| 21/07/09 | 52 | 212 | 11 | 21 | 0 | 24 | 0 | 5 | 4 | 26 | 0 | 10 | 3 | 0 |
| 28/07/09 | 6 | 366 | 10 | 20 | 3 | 58 | 0 | 5 | 12 | 33 | 1 | 21 | 12 | 0 |
| 04/08/09 | 29 | 157 | 14 | 20 | 0 | 41 | 1 | 4 | 7 | 23 | 0 | 23 | 0 | 0 |
| 11/08/09 | 17 | 343 | 15 | 17 | 1 | 39 | 3 | 7 | 7 | 17 | 1 | 21 | 2 | 1 |
| 18/08/09 | 1.5 | - | 12 | 16 | - | - | - | - | - | - | - | - | - | - |
| 25/08/09 | 3 | 542 | 17 | 19 | 1 | 99 | 1 | 17 | 14 | 41 | 2 | 50 | 6 | 0 |
| 01/09/09 | 16 | 247 | 29 | 25 | 1 | 36 | 0 | 3 | 7 | 25 | 2 | 12 | 0 | 0 |
| 08/09/09 | 22 | 230 | 11 | 19 | 1 | 27 | 4 | 6 | 6 | 27 | 2 | 9 | 0 | 0 |

### 2.3.2 Soil analysis

A summary of the means, standard deviations and significance levels for all the chemical parameters analysed is presented in Table 2.8.

*Fluoride*

Concentrations of F in the mesocosm soils were increased by the addition of the High Fluoride treatment at both depths ($p<0.05$) (Table 2.8). At 0-10 cm, the average concentration of F in these soils was almost four times greater than that of the Control soils, 22.3 µmol $g^{-1}$ compared to 5.9 µmol $g^{-1}$ (Fig. 2.15). At 10-20 cm, the increase was 2.5 times greater. Fluoride concentrations were also higher in the soils which received the Sulfate + High Fluoride treatment than in the Control soils, although this result was only significant at the 10-20 cm depth. There was no significant difference in soil F concentrations between the mesocosms that received a low F dose and the Controls.

*Sulfur*

At 0-10 cm there were no significant differences between the S content of the control soils and the treatment soils (Table 2.8). However, mesocosms which received the Sulfate + High Fluoride and High Fluoride treatments had approximately 30% lower concentrations of S in the soil than the controls (Fig. 2.15). This relationship was also seen at 10-20 cm, where mesocosms which received the Sulfate + High Fluoride and the High Fluoride treatments had significantly lower concentrations of S in the soil than the controls (91.4 and 108.6 compared to 169.7 µmol $g^{-1}$ respectively) (Table 2.8).

Mesocosm soils that were treated with $SO_4$ solutions did not have a significantly higher S content than the controls contrary to what might be expected. Mesocosms which received the Sulfate and Sulfate + Low Fluoride treatments did have slightly higher S concentrations than control mesocosms. At 10-20 cm, the mesocosms that received $SO_4$ amendments had approximately the same concentration of S in soil as the control mesocosms. Average S concentrations were higher at 10-20 cm than at 0-10 cm in the profile

**Table 2.8** Summary of chemical characteristics of the mesocosm soils

| | **Mean concentration in mesocosm soil (μmol g$^{-1}$ dw) (±Std dev)** | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | **0-10 cm** | | | | | **10-20 cm** | | | | |
| | **Control** | **SO$_4$** | **SO$_4$ + Low F** | **SO$_4$ + High F** | **High F** | **Control** | **SO$_4$** | **SO$_4$ + Low F** | **SO$_4$ + High F** | **High F** |
| **F** | **5.9 (5.5)** | **8.2 (1.0)** | **6.7 (0.8)** | **16.8 (13.0)** | **22.3 (5.6) *** | **8.6 (2.4)** | **5.8 (1.1)** | **6.8 (5.6)** | **22.8 (7.9) *** | **21.6 (8.9) *** |
| **Al** | **225.6 (228.4)** | **151.6 (37.1)** | **122.1 (4.9)** | **275.3 (170.1)** | **368.7 (132.1)** | **294.3 (108.9)** | **172.2 (16.3)** | **161.5 (29.6)** | **462.2 (156.4)** | **484.9 (69.6)** |
| **Ca** | **94.8 (19.3)** | **64.4 (13.0)** | **62.2 (18.1)** | **97.4 (24.4)** | **79.6 (32.5)** | **88.2 (26.6)** | **63.1 (4.5)** | **55.2 (7.9)** | **102.1 (21.1)** | **81.3 (32.6)** |
| **Fe** | **212.8 (100.1)** | **126.3 (45.2)** | **135.9 (114.8)** | **415.0 (146.4)** | **445.7 (132.7) *** | **84.9 (26.7)** | **93.0 (32.4)** | **79.4 (38.4)** | **191.4 (66.8) *** | **157.0 (48.8)** |
| **K** | **21.8 (16.6)** | **16.8 (3.0)** | **14.7 (1.5)** | **24.6 (11.6)** | **30.4 (8.1)** | **21.7 (6.7)** | **12.6 (3.0)** | **14.7 (1.1)** | **35.1 (10.7)** | **31.8 (8.2)** |
| **Mg** | **22.6 (8.3)** | **17.4 (1.7)** | **18.0 (0.7)** | **20.1 (4.5)** | **26.0 (5.6)** | **22.0 (5.7)** | **15.2 (1.2)** | **16.5 (0.9)** | **30.6 (9.9)** | **29.4 (4.9)** |
| **Mn** | **9.5 (14.4)** | **0.7 (0.1)** | **0.5 (0.1)** | **11.8 (9.9)** | **16.1 (6.7)** | **3.0 (4.0)** | **0.6 (0.0)** | **0.4 (0.1)** | **5.5 (4.4)** | **4.4 (1.1)** |
| **P** | **31.2 (4.6)** | **38.8 (3.0) *** | **40.6 (2.6) **** | **29.8 (2.7)** | **30.2 (2.0)** | **32.0 (4.5)** | **37.6 (6.8)** | **39.4 (6.2)** | **29.3 (8.6)** | **28.4 (7.2)** |
| **S** | **106.7 (35.1)** | **142.0 (20.4)** | **131.4 (35.2)** | **77.4 (9.6)** | **71.8 (6.0)** | **169.7 (9.5)** | **166.7 (16.5)** | **161.5 (32.2)** | **91.4 (21.1) **** | **108.6 (40.4) *** |
| **Si** | **35.2 (22.4)** | **30.0 (6.6)** | **29.9 (7.0)** | **40.2 (21.7)** | **47.9 (14.2)** | **38.7 (6.4)** | **26.9 (2.2) **** | **27.1 (0.4) **** | **53.1 (14.0)** | **40.0 (0.8)** |
| **Zn** | **11.2 (7.0)** | **7.1 (2.7)** | **5.1 (2.1)** | **15.2 (7.5)** | **12.5 (6.2)** | **27.8 (20.5)** | **11.0 (2.0)** | **6.6 (3.9)** | **15.6 (6.1)** | **23.0 (13.3)** |

Values are the mean of six (Control) or three (treatments) replicates. Starred values are results which are significantly different from the control values as calculated using Dunnett's 2-sided t-test or by the Mann-Whitney U test (S, K, Mn, Si and Zn). * indicates $p<0.05$, ** indicates $p<0.01$ and ***indicates $p<0.001$

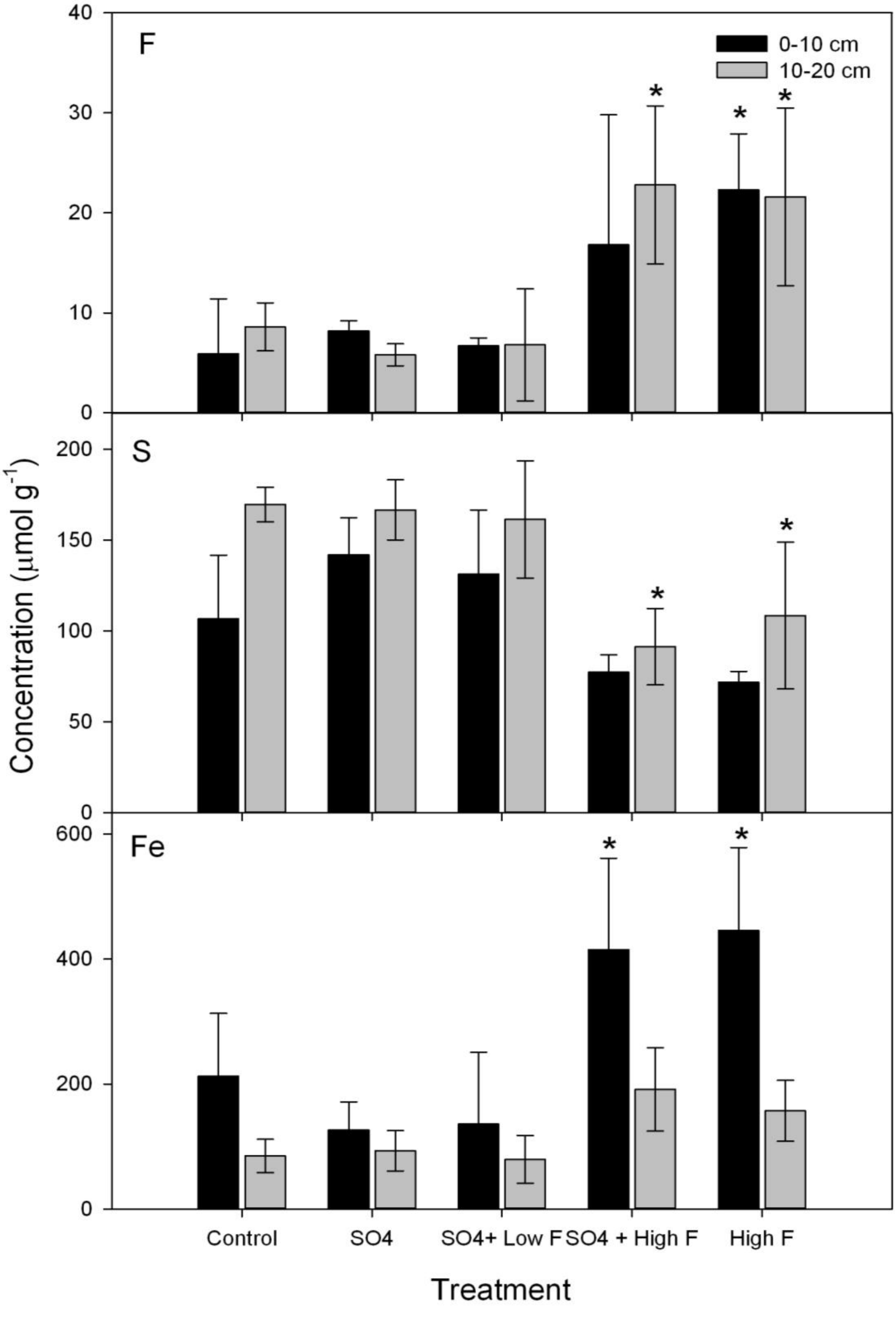


**Fig. 2.15** Concentrations of F, S and Fe in mesocosm soils at 0-10 and 10-20 cm. Bars represent averages of six replicates for Control mesocosms and three replicates for treatment mesocosms; error bars show standard deviation. * indicates significant difference from controls ($p< 0.05$).

### *Aluminium*

Concentrations of Al were greatest in soils at a depth of 10-20 cm (Table 2.8). At 0-10 cm there were no significant treatment effects on Al concentration. However, mean concentrations of Al in soils that received the High Fluoride treatment were approximately 60% greater than those for controls. The mean concentration of Al in the Sulfate + Low Fluoride mesocosms was approximately half that of the controls. These results are not significant due to the large standard deviation from the mean of the control soils (Table 2.8). At 10-20 cm there was a significant treatment effect on Al concentration ($p<0.01$). Post Hoc comparisons revealed that the soils treated with High Fluoride and Sulfate + High Fluoride had significantly higher concentrations of Al in the soil than the mesocosms treated with Sulfate and Sulfate + Low Fluoride. Al concentrations in the High Fluoride mesocosm soil were approximately 40% greater than those of control soils but the result was only of borderline significance ($p=0.052$). As at 0-10 cm, the addition of Sulfate and Sulfate + Low Fluoride reduced aluminium concentrations in the soil compared to the controls.

### *Iron*

Fe concentrations in mesocosm soils were affected significantly by treatment at both 0-10 and 10-20 cm ($p<0.01$ and $p<0.05$ respectively). At 0-10 cm, mean Fe concentration of the soils was approximately double that of the controls in the mesocosms treated with High Fluoride and Sulfate + High Fluoride (Fig. 2.15). The concentration of Fe in the High Fluoride mesocosm soils was significantly greater than concentrations in the control mesocosms and those which were treated with Sulfate and Sulfate + Low Fluoride ($p<0.05$ in all cases). At 10-20 cm, the Sulfate + High Fluoride treated soils had the highest mean Fe concentration of 191 µmol $g^{-1}$ making it significantly different from the control soils which on average contained 85 µmol $g^{-1}$ dw ($p<0.05$). The Fe concentrations in mesocosm soils which received this treatment were also significantly greater than the concentrations in soils which received the Sulfate + Low Fluoride treatment. It appears that the addition of treatments containing high concentrations of F to peat mesocosms increases the Fe content of the peat soil. This was seen at 0-10 cm in the High Fluoride mesocosms and at 10-20 cm in the Sulfate + High Fluoride mesocosms.

### *Phosphorus*

Concentrations of P in each mesocosm soil did not change with depth, a treatment effect was only observed at 0-10 cm due to larger standard deviations at 10-20 cm. At 0-10 cm, the soil from mesocosms treated with Sulfate + Low Fluoride and Sulfate alone had significantly higher soil P concentrations than the Control mesocosm soils ($p<0.01$ and $p< 0.05$ respectively). Mesocosms treated with Sulfate + High Fluoride and High Fluoride alone had approximately the same soil P content as controls. Soil in the Sulfate + Low Fluoride mesocosms therefore had significantly higher P concentrations than soil in the Sulfate + High Fluoride and the High Fluoride mesocosms.

### *Silicon*

Concentrations of Si were lower in the mesocosm soils treated with Sulfate + Low Fluoride and Sulfate alone at both depths although this result was only significant at 10-20 cm. This result suggests that the addition of $SO_4$ alone and in combination with low concentrations of F reduces the Si content of the peat at 10-20 cm. Concentrations of Si were greatest at both depths in mesocosms which received treatments of Sulfate + High Fluoride and High Fluoride although this result was not statistically significant.

### *Sodium*

Concentrations of Na were below detection limits in acid digest samples of all the mesocosm soils.

### *Calcium*

There were no significant treatment effects on soil Ca concentrations at 0-10 or 10-20 cm ($p= 0.15$ and 0.12 respectively).

### *Magnesium*

Soil Mg concentrations were not significantly affected by treatment at 0-10 cm but there was a treatment effect at 10-20 cm ($p<0.05$) where the Sulfate + High Fluoride mesocosm soils had significantly higher Mg concentrations than those mesocosms treated with Sulfate alone. There were no significant differences between soils from treatment groups and controls.

### *Potassium*

At 0-10 cm, K concentrations of soils from treated mesocosms were not significantly different from those of control soils. Soils which received the Sulfate + Low Fluoride and Sulfate treatments contained lower concentrations of K than the controls and those receiving the Sulfate + High Fluoride and High Fluoride treatments had higher concentrations of K. This same trend was observed at 10-20 cm, which produced a significant treatment effect ($p<0.01$). At this depth the Sulfate + High Fluoride mean K concentration was 35 µmol $g^{-1}$ dw which is higher than the mean control concentration of 22 µmol $g^{-1}$ dw, although this result is only of borderline significance ($p= 0.053$). The Sulfate + High Fluoride mesocosm soils did contain significantly higher concentrations of K than the mesocosms which were amended with the Sulfate + Low Fluoride and Sulfate treatments ($p<0.05$). The High Fluoride mesocosm soils also had significantly higher concentrations of K than the Sulfate mesocosm soils.

### *Manganese*

There were no significant treatment effects on Mn concentrations in mesocosm soils at 0-10 or 10-20 cm. Concentrations of Mn were considerably lower in the soils treated with Sulfate and Sulfate + Low Fluoride when compared to the controls but this result was not statistically significant (Table 2.8).

### 2.3.3 Vegetation analysis

There were no significant differences in the chemical parameters tested in the *Sphagnum* specimens between any of the treatments or controls (Table 2.9). In the *Eriophorum* samples, however, there were significant treatment effects on the concentrations of F, Al and P in the plant material ($p<0.5$, $p<0.001$ and $p<0.05$ respectively) (Fig. 2.16). *Eriophorum* shoots growing in mesocosms which received the Sulfate + High Fluoride and the High Fluoride alone treatments contained significantly higher concentrations of F and Al than those growing in the Control mesocosms and those which received the Sulfate + Low Fluoride and Sulfate alone treatments. Phosphorus concentrations in the *Eriophorum* shoots growing in the High Fluoride mesocosms were significantly lower than those grown in the Control mesocosms and mesocosms that received treatments of Sulfate + High Fluoride. These results suggest that the addition of solutions containing high concentrations of F causes increased uptake of F and Al by *Eriophorum vaginatum*. A decrease in P concentration in the shoots was also observed but only when F was added alone and not when it is added in combination with $SO_4$.

**Table 2.9** Summary of chemical characteristics of the mesocosm vegetation

| | Mean concentration in mesocosm vegetation (μmol g$^{-1}$ dw) (±Std dev) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Sedges (*Eriophorum vaginatum)* | | | | | Moss (*Sphagnum spp)* | | | | |
| | Control | SO$_4$ | SO$_4$ + Low F | SO$_4$ + High F | High F | Control | SO$_4$ | SO$_4$ + Low F | SO$_4$ + High F | High F |
| **F** | 0.2 (0.4) | 0.8 (0.2) | 0.9 (0.6) | 2.6 (0.6)<br>* | 2.4 (0.5)<br>* | 2.2 (1.2) | 2.4 (1.7) | 2.1 (0.4) | 7.2 | 12.1 (1.0) |
| **Al** | 0.9 (0.1) | 1.0 (0.1) | 0.9 (0.1) | 1.6 (0.2)<br>** | 1.5 (0.2)<br>** | 11.9 (2.4) | 9.6 (3.9) | 8.1 (1.6) | 17.5 | 23.8 (17.0) |
| **Ca** | 69.2 (16.5) | 54.7 (2.4) | 65.6 (6.9) | 59.6 (11.6) | 55.9 (16.0) | 87.2 (4.5) | 77.9 (34.1) | 75.1 (0.8) | 137.4 | 94.4 (13.9) |
| **Fe** | 1.9 (0.2) | 2.5 (0.6) | 1.8 (0.4) | 2.5 (0.1) | 2.5 (0.4) | 15.4 (5.2) | 12.9 (4.5) | 14.3 (7.5) | 22.5 | 33.5 (30.7) |
| **K** | 63.9 (15.0) | 71.8 (21.6) | 71.8 (21.6) | 98.1 (5.5) | 80.6 (15.7) | 61.2 (2.9) | 67.3 (4.3) | 60.9 (6.6) | 90.8 | 62.9 (3.6) |
| **Mg** | 56.8 (18.5) | 47.1 (7.1) | 74.7 (26.6) | 40.5 (11.6) | 34.7 (8.8) | 40.8 (2.6) | 44.0 (22.5) | 39.4 (4.7) | 58.6 | 58.0 (6.6) |
| **Mn** | 14.0 (13.8) | 4.0 (0.9) | 4.7 (1.0) | 13.0 (8.2) | 13.3 (4.4) | 5.4 (3.8) | 3.2 (1.9) | 3.2 (0.2) | 8.4 | 11.3 (9.7) |
| **P** | 18.4 (1.4) | 15.0 (2.9) | 17.2 (1.7) | 17.4 (1.8) | 11.9 (2.1)<br>** | 12.4 (0.7) | 12.9 (2.8) | 12.6 (2.8) | 22.0 | 17.9 (1.7) |
| **S** | 20.4 (1.6) | 21.5 (1.8) | 24.9 (2.3) | 24.0 (3.7) | 19.8 (0.3) | 20.4 (3.5) | 24.8 (0.4) | 20.7 (5.2) | 39.3 | 33.2 (10.3) |
| **Si** | 17.2 (4.2) | 16.9 (5.9) | 21.1 (8.3) | 20.4 (1.1) | 19.9 (3.8) | 14.9 (1.8) | 14.1 (9.0) | 12.5 (0.7) | 22.6 | 25.6 (14.5) |
| **Zn** | 2.7 (0.5) | 2.3 (0.6) | 2.9 (0.1) | 3.4 (1.3) | 3.1 (2.0) | 1.8 (1.0) | 1.8 (0.9) | 1.6 (0.7) | 5.1 | 3.0 (1.2) |

Values are the mean of three replicates for the sedges and two replicates for the moss samples apart from SO$_4$ + Low F which had 3 replicates and SO$_4$ + HF which only had one. Starred values are results which are significantly different from the control values as calculated using Dunnett's 2-sided t-test (sedges) or by the Mann-Whitney U test (mosses). * indicates $p<0.05$, ** indicates $p<0.01$ and ***indicates $p<0.001$

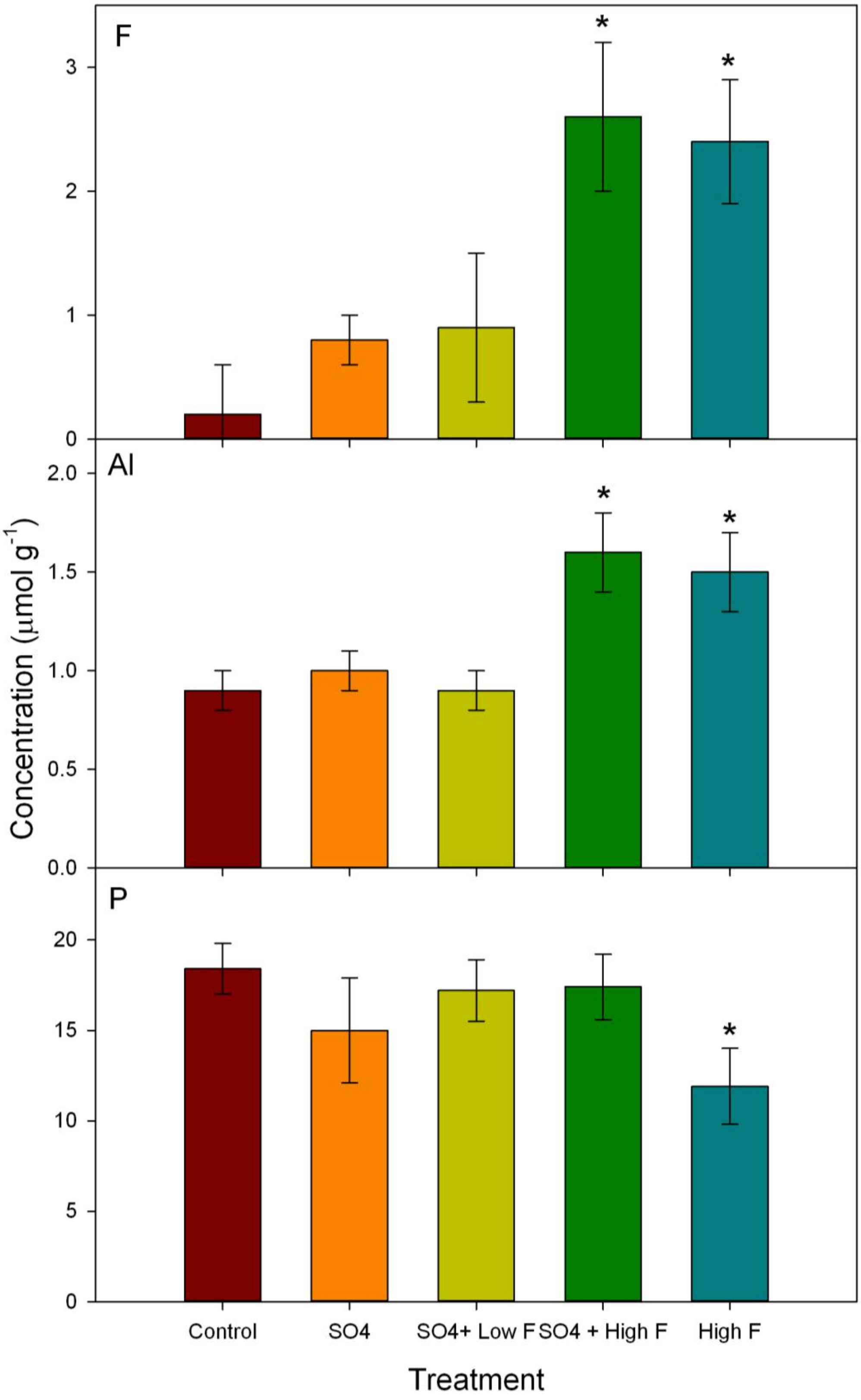


**Fig. 2.16** Mean concentrations of F, Al and P in *Eriophorum vaginatum* shoots. Bars represent averages of three replicates, error bars represent standard deviation. * indicates significant difference from controls ($p < 0.05$).

## 2.4 Discussion

The leaching of volcanic ash deposited on the surface of peatlands may have important implications for the whole peatland ecosystem. Soil chemistry plays an important role in regulating the composition of chemical species in the air, water and biomass compartments of the environment (Bohn et al. 2001). It can affect biochemical reactions carried out by soil micro-organisms, which play a major role in the cycling of elements such as C, S and N. It can affect the export of chemical species to surface waters often causing problems such as acidification and eutrophication. Changes in soil chemistry are also responsible for shifts in vegetation communities with more tolerant species replacing sensitive ones.

### 2.4.1 The effects of F addition on peat chemistry

In mesocosms which received the High Fluoride and Sulfate + High Fluoride treatments, concentrations of F were significantly higher in the soil, soil solution and sedge shoots. This probably indicates that a fraction of the added F was bound to the soil and the remaining soluble fraction was in a bio-available form that could be taken up by plants. The amount of F sorbed by soil is dependent upon soil type, pH and the concentration of F (Pickering 1985). The predominant retention mechanism of F in mineral soils is considered to be the replacement of $OH^-$ groups from poorly ordered materials such as gibbsite ($Al(OH)_3$) (Harrington et al. 2003; Pickering 1985) and from basic Al polymers adsorbed on mineral surfaces (Bower and Hatcher 1967).

As mentioned earlier, the Moor House soils are characterised by a low ash content (3.2% dry weight, (Gorham 1961)) and belong to the ombrotrophic peat group. (Shotyk 1988). These peats receive all nutrient inputs from precipitation and atmospheric deposition, so the only input of mineral material is from the deposition of soil dust from the surrounding environment on the surface of the bog (Charman 2002; Clymo 1983; Shotyk 1988). Therefore, sorption of F on mineral surfaces is expected to be minimal despite the existence in the peats of optimum pH conditions for F sorption (pH 5.5 and 6.5, (Omueti and Jones

1977)). The interaction of F with mineral soil colloids is normally associated with an increase in pH in the soil solution as dissolved F substitutes for $OH^-$ on exchange sites (Arnesen 1997; Elrashidi and Lindsay 1987; Omueti and Jones 1977; Romar et al. 2009; Wilke 1987). While the pH of mesocosms receiving High Fluoride treatments was slightly higher than the pH of Control mesocosms, this result was not statistically significant. If some F remains as a mobile anion in solution, this would tend to lower pH and this could offset the influence of the released $OH^-$, which may be why a significant increase in pH was not observed. This result further supports the idea that the increase in soil F must be attributed to another process than F reaction with mineral phases. The retention of F in the mesocosms may also be due to interactions with organic matter. The pools of organic matter in soils and transfer of organic material between these pools are illustrated in Fig. 2.17. The diagram indicates that soluble organic matter can adsorb to both inorganic minerals, including clays and to the solid organic matter fractions.

Qualls (2000) showed that soluble organic matter is involved in surface sorption/desorption reactions with solid organic matter. The mechanisms hypothesised are: (i) simple electrostatic attraction to cation or anion exchange sites; (ii) electrostatic cation bridging by divalent cations between adjacent carboxylic acid groups associated with solid organic material; (iii) ligand exchange on Fe or Al hydroxides precipitated on organic solid surfaces; (iv) Van der Waals forces and (v) hydrogen bonding. Peat has been reported to be effective at removing $PO_4$ from aqueous solutions via physical and chemical adsorption on Fe and Al oxides and hydroxides and by cation bridging onto organic functional group-metal or surface-metal complexes (Xiong and Mahmood 2010). If the organic matter solids are capable of adsorbing negatively charged $PO_4$ and dissolved organic matter, and exhibit similar surface chemical processes to mineral species it is likely that organic matter solids would be able to retain F, as well as via $–Al^+$- or $–Fe^+$- bridge bonding as discussed below.

Organic matter is a variable charge soil component containing exchange sites for both anionic and cationic species. As the pH increases above 3, the surface charge becomes increasingly negative due to the deprotonation or dissolution of $H^+$ from functional groups (Sparks 1995). The most chemically reactive components of organic matter are humic and fulvic acids, which are macromolecular species (Pickering 1985). The composition of these acids depends upon the nature of the original organic litter, which forms a variety of acidic functional groups (e.g. –COOH, -OH, $-NH_2$, -SH) (Pickering 1985). Fluoride can interact with counter ions associated with these humic acid functional groups (e.g. $Al^{3+}$, $Fe^{3+}$ and $Ca^{2+}$) (Farrah et al. 1985). This is known as electrostatic cation bridging as divalent cations form a bridge between adjacent carboxylic acid groups on humic acid providing an adsorption site for negatively charged F (Qualls 2000). The complex formed may look like:

peat—X—F where X is a divalent cation

The amount of F sorbed by organic samples increases as pH decreases (Farrah et al. 1985) because humic acids start to dissociate above pH 5 (Pickering 1985). Fluoride is also thought to form surface coatings on the peat solids as it binds to alkaline earth counter ions or compounds present in organic samples (Farrah et al. 1985).

Another mechanism of F retention in soils is by precipitation into solution and/or onto the soil colloid surfaces, which can occur at high concentrations of dissolved F (>7 mM) (Harrington et al. 2003). Concentrations of dissolved F in the mesocosms were not greater than 7 mM, and so the concentration of F in solution could be too low for precipitation to occur. Wilke (1987) found that a large portion of F was retained in a calcareous mull soil due to the formation of fluorite ($CaF_2$). Speciation modelling using CHEAQs of mesocosm porewater compositions indicated that $CaF_2$ was under-saturated (saturation index -1 to -5). Dissolved Ca concentrations in solution did not decrease significantly with the addition of F and soil Ca concentration did not increase, which may imply that retention of F by the precipitation of $CaF_2$ was not important in these soils. However if exchangeable Ca in the solid phase was redistributed to form $CaF_2$, this would also retain Ca in the soil solid phase.

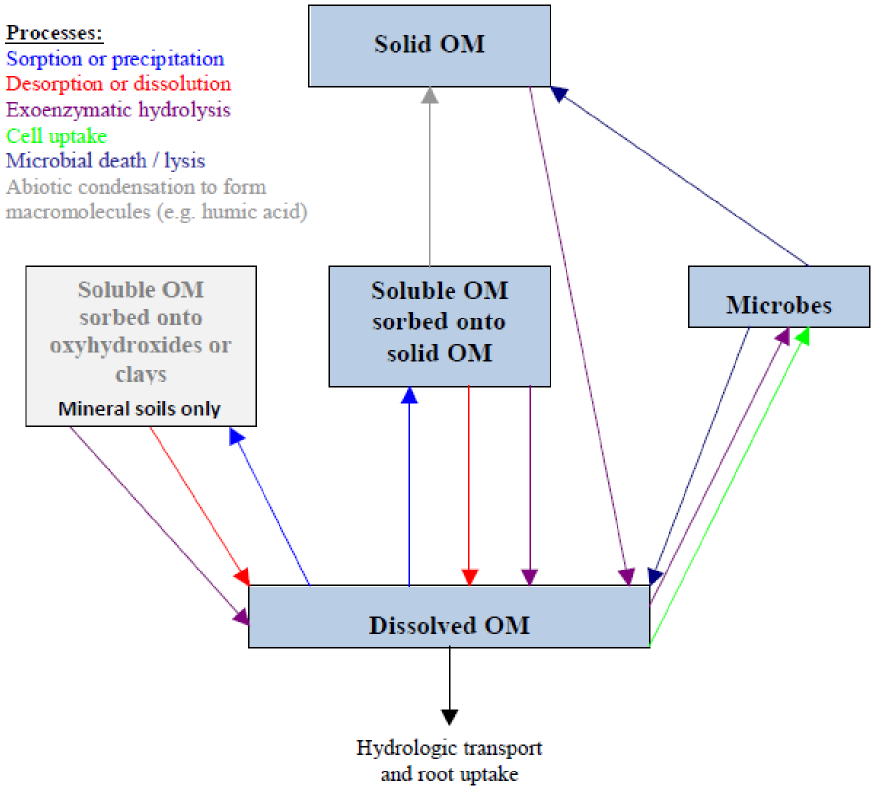


**Fig. 2.17** The pools of organic matter in soils and transfer processes between solid and dissolved states. Redrawn from Qualls (2000).

Interestingly, the increase in the soil F concentration in the mesocosms treated with High Fluoride and Sulfate + High Fluoride was systematically accompanied by a decrease (~40% when compared to controls) in the soil total S content. This result was not observed in the Sulfate + Low Fluoride or Sulfate alone mesocosms. In peat soils, most of the S is associated with organic matter (Brown 1985). Thus, the decrease in soil S concentrations in the High Fluoride and High Fluoride + Sulphate-treated mesocosms may be due to the dissolution or desorption of S-containing organic matter following addition of F. The dissolution of humic acids depends upon the pKa values of the dominant functional group, some disperse at pH >5, others at pH >9 (Pickering 1985). The addition of alkaline F solutions to the mesocosms may have resulted in the dissolution of organic matter complexes, if these complexes contained S species this would result in a decrease in soil S concentrations.

Fluoride is highly electronegative and is retained preferentially over other anions in mineral soils (Delmelle et al. 2003). It could potentially displace soluble organic matter containing S species on the organic matter solid surfaces, thus reducing the S concentration in the soil. An alternative explanation for the reduction in soil S concentrations may be that there was competition between F and $SO_4$ for exchange sites associated with organic matter colloids. It is well known that F readily replaces $SO_4$ on anion exchange sites in mineral soils (Rose 1998), thus reducing $SO_4$ retention in these soils (Chao 1964). However, very little is known about competitive anion sorption on organic matter but the sorption/desorption mechanisms may be operating in the same way. As the mesocosms were sealed, it is reasonable to assume that soil S concentration was increasing at depths below 20 cm.

The results of the statistical analyses showed that dissolved $SO_4$ in the soil solution did not increase following addition of F to the peat mesocosm. This observation seems to contradict the idea that F hampered S retention in the soil owing to the mechanisms hypothesised above. However it could be distributed between different S pools or mobilized as organic S species, which may be the reason why a significant increase in S in solution was not observed. If the S was released as sulfide ($S^{2-}$), some may have been lost by diffusion through the peat column, some may have been re-oxidised to $SO_4$ or a portion could have been lost through the precipitation of an iron sulfide (FeS) phase.

The possibility that F addition to the soil may have induced FeS precipitation deserves more attention as the soil Fe content in the Sulphate + High Fluoride and Fluoride-treated mesocosms was raised (Fig. 2.15). Further, thermodynamic modelling predicted saturation of a FeS phase (saturation index ~ 9.5) in the peat soil solution. It is also worth noting that no changes in the soil Fe concentrations were observed in the Sulfate or Low Fluoride + Sulfate mesocosms. If the addition of F caused an increase in $S^{2-}$ concentrations in solution (due to the breakdown of organic matter or via anion exchange as discussed above), this may have resulted in the precipitation of FeS out of solution thus increasing soil Fe concentrations. .

Soil solution F concentrations increased over time in mesocosms that received additions of Sulfate + High Fluoride and High Fluoride alone. There were no significant increases in F in mesocosms that were treated with Sulfate +

Low Fluoride. The observed increase in F in the High Fluoride mesocosms was also accompanied by an increase in Al, Fe and acetate in solution. This result is similar to previous experiments conducted on mineral soils, where the addition of F raised the concentrations of Al and Fe in solution (Arneson 1998; Braen and Weinstein 1985; Elrashidi and Lindsay 1987; Haidouti 1995; Hani 1978; Romar et al. 2009; Wilke 1987). Aluminium and Fe solubility in water is controlled by pH, but no changes in soil solution pH were observed over the duration of the experiment (Fig. 2.14). The increase in soluble Al and Fe may be the result of complexation with the F ion to form soluble Al-Fe and Al-F complexes. When F is added to solution it has a high affinity for Al and Fe (Moore and Ritchie 1988) and so forms complexes with the free Al and Fe ions present, which causes more Al and Fe to be released from the soil solid fraction to keep the system in equilibrium (Bower and Hatcher 1967). The solubilized Al and Fe are thought to originate from noncrystalline (organic and inorganic) compounds, which are the most labile forms of Al and Fe (Harrington et al. 2003; Romar et al. 2009). Romar et al. (2009) observed an increase in organic matter along with Al and Fe in solution due to the addition of F and reported that F could mobilize organic matter bound to Al or Fe on clay surfaces through the formation of mixed F—M—OM complexes (where M= Fe or Al). The reactions suggested were:

$$\text{Clay—M—OM} + \text{F} \rightarrow \text{Clay} + \text{F—M—OM}$$
$$\text{Clay—M—OM} + \text{F} \rightarrow \text{Clay—M—F} + \text{OM}$$

The increase in concentrations of dissolved organic matter has been reported in heavily polluted soils in the vicinity of Al smelters (Elrashidi and Lindsay 1987; Polomski et al. 1982; Rao and Pal 1978; Tscherko and Kandeler 1997). In an experiment where F was applied to a mor humus soil, significant dissolution of Al and Fe occurred along with large amounts of organic matter, which was seen as an increase in DOC concentrations in the leachate (Wilke 1987). The authors assumed that the leaching of Al and Fe was due to the breakdown of organo-metallic compounds. This mechanism was also suggested by Hani (1978) who determined that the increased Al present in solution after the addition of F was bound to the $COO^-$ groups of the low molecular weight fraction of organic matter. As soluble organic matter can adsorb to solid phase organic matter via ligand exchange (Qualls 2000), the addition of F to solution could result in the formation of mixed F—M—OM complexes as reported by Romar et al. (2009):

$$\text{OM—M—OM}_{\text{(soluble)}} + \text{F} \rightarrow \text{OM} + \text{F—M—OM}_{\text{(soluble)}} \text{ (where M=Fe or Al)}$$

Fluoride has a high affinity for ligand exchange sites (Greenland 1971); its addition to a forest soil facilitated the desorption of DOC from exchange sites and suppressed any further adsorption of DOC (Qualls 2000).

There was no significant increase in DOC in the soil solutions treated with high concentrations of F in the present experiment, only increases in acetate which is a product of microbial decomposition of organic matter. The reason why no significant increase in DOC was measured may be due to the large standard deviation in DOC measurements between mesocosms (over the treatment period standard deviation was ±50 %) possibly obscuring a trend. Analysis by IC also showed the presence of formate, another microbial decomposition product, in the High Fluoride and Sulfate + High Fluoride soil solutions towards the end of the treatment period, which may be another indication that F is breaking up Al-organic matter complexes causing increases in Al in soil solution and low molecular weight organic matter fractions. Speciation modelling of mesocosm solutions indicated that 65 - 75% of Al and Fe was present in solution as organic species. The measured increase in acetate concentration in soil solution with the addition of F has not been reported in any other study. It could reflect a change induced in the degredation of soil organic matter components.

An alternative explanation for the increase in acetate and formate in solution may be that F inhibits a microbial community that uses these species as substrates. Fluoride has been shown to inhibit the growth and reproduction of some microorganisms (Treshow 1965). Rao and Pal (1977) suggested that an increase in soil organic matter content near an Al smelter occurred because F present in plant litter and soils produced unfavourable conditions for the growth and activity of decomposers and other micro-organisms. In another heavily contaminated soil near to an Al smelter, which contained up to 189 mg F kg$^{-1}$, microbiological activities were decreased to 5-20% of those in the unpolluted soil (Tscherko and Kandeler 1997). The highest soil F concentration measured in the mesocosm experiment was 600 mg kg$^{-1}$, over three times the concentration measured by Tscherko and Kandler (1997), and so an effect on microorganisms may be expected. If F were to have a toxic effect on methanogens that use acetate as a substrate this would reduce $CH_4$ emissions. If F is toxic to a competitive species that normally utilise acetate, this could prove beneficial to methanogens and result in higher $CH_4$ emissions from the peat. This hypothesis will be investigated in Chapter 3.

Speciation modelling of the soil solution suggests that F is present mostly as Al-F complexes and free F ($F^-$). At the end of the experiment, Al-F complexes accounted for 85, 59 and 97% of F speciation according to the CHEAQs model in the High Fluoride, Sulfate + High Fluoride and Sulfate + Low Fluoride mesocosms respectively. The results for the Low F mesocosms are similar to those reported by Wilke (1987) who found that 95% of F was bound to Al in solution. However, in the mesocosms treated with high concentrations of F, the proportion of free $F^-$ increased over the treatment period indicating that the entire pool of Al had been complexed leaving an excess of F. This is confirmed by the Al speciation results for the Sulfate + High Fluoride mesocosms, which revealed that 97% of the Al present in solution was complexed with F. The observed increase in free $F^-$ could also be due to pH change. Below pH 6 Al-F complexes dominate in solution, above this value free $F^-$ predominates (Elrashidi and Lindsay 1986). In a grassland soil, where the pH was above 6, the predominant species in the equilibrium solution was free F. In the same study in a more acidic forest soil, the solution was dominated by Al-F complexes (Romar et al. 2009). The same result was also reported by Wilke (1987) who established that the F ion was the most abundant F species in mull leachates whereas the moder and mor leachates contained mainly Al-F complexes. The predominance of free F above pH 6 may be because at pH >5.5, $OH^-$ ions compete successfully with F to form Al-OH complexes (Alvarez et al. 2002; Monterroso et al. 1994; Romar et al. 2009). This would increase free F concentrations as Al complexes with OH instead of F. The pH of the Sulfate + High Fluoride and High Fluoride mesocosms was between 5.5- 6.0 on the last sampling day, which is higher compared to the pH of the Sulfate + Low Fluoride mesocosms (pH 4.5 - 5.0) which contained a higher percentage of Al-F complexes.

According to our measurements, the F and Al contents in the sedges from the peat mesocosms increased after treatment with High Fluoride and Sulfate + High Fluoride. This result suggests enhanced plant uptake of F and Al from the soil solution. Other authors have also reported an increase in F and Al in plant leaves in close proximity to Al smelters (Arneson 1998; Braen and Weinstein 1985; Hani 1978). The absorption of F by plants varies between species and is also controlled by solution F activity, pH and F speciation (Mackowiak et al. 2003). Plants uptake F from solution through the roots and the F is subsequently translocated to the shoots. Root concentrations of F are affected by the pH of the plant tissues, which determines whether F is present as $F^-$ or HF, and the charge density on the cell walls. Root cell walls have fixed negative charges, which can promote anion exclusion. The negative charge on plant roots may therefore make the uptake of F difficult in its anionic form. It has been suggested that the complexation of F with Al may increase plant uptake of both species because of the more favourable charge on the Al-F complexes (Takmaz-Nisancioglu and Davison 1988). Alumino-fluoro complexes are neutral ($AlF_3$) or display a positive electrical charge (e.g., $AlF^{2+}$, $AlF_2^+$) and are therefore are able to permeate cell membranes more readily than free F (Takmaz-Nisancioglu and Davison 1988). In an experiment to test this hypothesis, Takmaz-Nisancioglu and Davison (1988) found that F concentration in the roots of beans exposed to NaF were 47 times greater than those of controls, but when the same concentration of F was given in the form of $AlF_3$, root concentrations were 83 times greater than those of controls. Support for this idea was also reported by Stevens et al. (1997) who found that positively charged Al-F species enhanced F uptake by oat and tomato plants.

Despite the increase in both F and Al in plant material there were no physical signs of toxicity and no difference in sedge densities when compared to the control mesocosms. Levels of F in both sedge (1.8 - 3 $\mu g\ g^{-1}$) and moss (2 – 3.3 $\mu g\ g^{-1}$) shoots were above 0.53 $\mu g\ g^{-1}$, which is the level considered as the ‘background concentration’ of F in plant material (Weinstein 1977). Measured concentrations were also greater than the maximum recommended limit for hay and pasture grass of 1.58 µg $g^{-1}$ (Arnesen 1997). Accumulation of F in the plant roots is also likely; this is based on previous observations where root concentrations of F were greater than leaf concentrations (Cooke et al. 1978; Keller 1980; Takmaz-Nisancioglu and Davison 1988). Ryegrass growth was significantly inhibited by F in peaty soils due to the synergistic effect of low pH (pH< 5.6) and F addition (Horner and Bell 1995). However, Braen and Weinstein (1985) concluded that the uptake of F from soil is not an important source of toxic levels of F to most plants. On the last sampling date (14/09/2009), mean concentrations of Al in solution collected at 10 cm were 60 and 45 µmol $l^{-1}$ from those treated with Sulfate + High Fluoride and High Fluoride alone, respectively. Aluminium in soil solution can inhibit the growth of sensitive plants at levels as low as 37 µmol $l^{-1}$ (Foy et al. 1978).

Even though concentrations of F and Al measured in solution are deemed to be at potentially toxic levels for some species, there was no effect on the mesocosm vegetation. It has been suggested that Al-F complexes are less toxic than the effect of the Al and F species alone (Arnesen 1997; MacLean et al. 1992; Romar et al. 2009; Takmaz-Nisancioglu and Davison 1988) so this may be the reason why no signs of damage were observed. Under acid conditions, the most common form of Al is $Al^{3+}$ (Monterroso et al. 1994; Wagatsuma and Ezoe 1985), which is considered to be the most toxic of Al species (Stevens et al. 1997). The addition of F reduces the toxicity of $Al^{3+}$ by complexation (MacLean et al. 1992). Stevens (1997) added various combinations of Al and F to oat and tomato plants and reported that the most toxic species were $Al^{3+}$, $AlOH^{2+}$ and $Al(OH)_2^{+}$. $AlF^{2+}$ and $AlF_2^{+}$ were toxic to a lesser extent and $AlF_3$, $AlF_4^{-}$ and $F^{-}$ were least toxic. Davison (1983; 1985) found high concentrations of F and Al in *Theaceae* species and suggest mutual detoxification in these plants as they accumulate high concentrations of both species but do not show and adverse effects.

Measured P concentrations in the sedges from mesocosms that received the High Fluoride treatment were significantly lower than concentrations of P in Control sedges. This may be due to F occupying exchange sites on the sedge roots where $PO_4$ is normally positioned.  Van Wensem (1991) added F to poplar litter for 9 weeks and found that concentrations of $PO_4$, $NH_3$ and $NO_3$ were decreased in the litter over time indicating that N and P mineralization are sensitive to F.  There was no significant effect of F treatments on the concentrations of dissolved $NH_3$ or $NO_3$ (unpublished data).  Phosphorus is a macronutrient, which is vital for the growth and health of plants.  If the sedges developed a P-deficiency over time due to F addition it would be expected that sedge growth would become stunted and leaves discoloured.  There were no signs of these symptoms in the mesocosms.

### 2.4.2 The effects of $SO_4$ addition on peat chemistry

In mesocosms that received additions of $SO_4$ (Sulfate + Low Fluoride, Sulfate + High Fluoride and Sulfate alone) there were no significant increases in $SO_4$ concentrations in the soil, soil solution or vegetation.  The highest $SO_4$ doses were added at the beginning of the experiment but were not reflected in the soil solution concentrations.  Average $SO_4$ concentrations over the treatment period were twice the concentration of the controls in the Sulfate + High Fluoride mesocosms at 10 cm but this result was not statistically significant.  Mean concentrations in solution were also higher than those for Controls in the Sulfate + Low Fluoride and Sulfate alone mesocosms but again not significantly.  Soil solution was sampled 3 days after treatment addition, which may have been sufficient time for some of the $SO_4$ to be reduced by Sulfate Reducing Bacteria (SRB).  This increase in $SO_4$ in the mesocosms may be sufficient to suppress the emission of methane ($CH_4$) from the peat through a shift in microbial communities as SRB out-compete methanogens for substrates (Dise and Verry 2001; Fowler et al. 1995; Gauci and Dise 2002; Gauci et al. 2004a; Granberg et al. 2001; Watson and Nedwell 1998).  This hypothesis will be investigated in Chapter 3.

Concentrations of $SO_4$ in pore water at the Moor House site, where the mesocosms were collected, showed no change between 1993 and 2008 unlike two ECN sites in Scotland, Sourhope and Glensaugh (both peaty podzols), which show a decrease in $SO_4$ concentration between these years (DEFRA 2010; Morecroft et al. 2009).  At the site, $SO_4$ and $NO_3$ were mostly below detection limits in the Moor house soil solution samples like the mesocosm soils in this experiment, which had low concentrations of $SO_4$ that did not increase when treatments incorporating $SO_4$ were added. In a study by Gauci et al. (2004a), $SO_4$ additions to peat monoliths over 6 months actually caused a 50% reduction in the concentrations of $SO_4$ in solution when compared to the controls. The authors postulate that the addition of $SO_4$ stimulated SRB populations so that they were better able to scavenge available $SO_4$. High rates of $SO_4$ reduction can be maintained even if concentrations of $SO_4$ in solution are low (Wieder and Lang 1988). This is because the turnover and cycling of inorganic S between oxidised and reduced pools occurs rapidly and can ensure a continuous supply of $SO_4$ for SRB (Blodau 2002; Blodau et al. 2007; Gauci et al. 2004a; Wieder and Lang 1988).

The addition of $Na_2SO_4$ to peat soils can cause acidification as Na replaces H on exchange sites thus increasing $H^+$ concentrations in solution (Wiklander 1975). However, there was no observed decrease in pH over the treatment period in mesocosms, which received $SO_4$ containing treatments. This maybe due to an increase in $SO_4$ reduction rates which consumes $H^+$ ions and increases alkalinity (Abd-el-Malek and Rizk 1963). This initial short-term acidification due to $Na_2SO_4$ addition followed by rapid rates of $SO_4$ reduction enhancing pH would result in no overall change in pH.

The reduction of $SO_4$ in soil solution produces sulfide ($S^{2-}$), which is known to interfere with iron-phosphorus cycling in the soil. Sulfide reacts with Fe in iron-phosphate complexes to form iron sulfides such as FeS and $FeS_2$, which results in the release of $PO_4$ into solution (Boström et al. 1988; Caraco et al. 1989; Lamers et al. 2001; Roelofs 1991; Smolders and Roelofs 1993). Lamers et al. (1998) reported a significant increase in $PO_4$ concentrations 27 weeks after $SO_4$ was applied to wetland soil mesocosms. There were no significant increases of $PO_4$ in the solution of mesocosms receiving $SO_4$ additions in this experiment but there was a significant increase in the concentration of P in the soil of mesocosms treated with Sulfate + Low Fluoride and Sulfate alone. This increase in P was accompanied by a simultaneous decrease in soil Si concentrations. When solution concentrations of $PO_4$ are high, anaerobic soils can adsorb more

$PO_4$ than aerobic soils (Patrick and Khalid 1974). Mishra and Khanna (Mishra and Khanna 1979), investigated the effect of $PO_4$-containing fertilizers on an acid brown earth soil and reported leaching of high concentrations of Si. The authors argued that silicate ions were displaced from the soil by phosphate ions (mainly $H_2PO_4^-$) in accordance with previous studies (Obihara and Russell 1972). In lake sediments, $PO_4$ and $SiO_4$ compete with each other for sorption sites (Hartikainen et al. 1996). It is possible that a sequence of events occurred in the Sulfate + Low Fluoride and Sulfate alone mesocosms where the addition of $SO_4$ caused the mobilization of $PO_4$ which built up in solution and then displaced Si on exchange sites. This resulted in an increase in soil P concentrations and a decrease in soil Si concentrations, which may have important implications for P and Si cycling within the peat.

## 2.5 Conclusions and environmental implications

The results of the mesocosm experiment indicate that the deposition and subsequent leaching of F-containing tephra on distal peatlands may cause disruption to ecosystem functioning. Addition of treatments containing high concentrations of F to peat mesocosms had significant effects upon concentrations of some chemical species present in the soil, vegetation and soil solution. If it is assumed that the sealed mesocosms conserve elements, this implies that treatments must be causing redistribution within the plant/ soil system, unless the differences are due to the amounts removed in water samples or involve conversions to gaseous compounds. In the soil, complicated exchange processes between the soil solution and the solid phase organic matter components led to increased concentrations of F and Fe and decreases in S over the treatment period. These findings are interesting, as they have not been reported elsewhere. The mechanisms for these changes remain unclear and should be investigated with further work closely following redox potentials and the speciation of Fe and S after the addition of F. The addition of F to peat soils could have important impacts upon the biogeochemical cycling of S and Fe.

In the soil solution, F addition increased the solubility of Al, Fe and acetate resulting in increased concentrations of these species in solution near the peat surface. This build up of acetate, Al and Fe over the treatment period suggests that F breaks down organo-metallic compounds causing leaching of organic matter along with metal ions. This may have important implications for microbial communities within the peat that are associated with decomposition of organic matter and carbon cycling. Processes such as methanogenesis can be inhibited by the presence of alternative electron acceptors such as $Fe^{3+}$ (Zinder 1993). But methanogens use acetate as a substrate so methanogenesis could be boosted by the increase in acetate concentrations in solution. The effects of F treatments on C gas fluxes will be considered in Chapter 3. There was no significant increase in pH with the addition of F, unlike what has been reported previously in mineral soils which suggests that F substitution for OH on mineral surfaces is not the dominant sorption mechanism in the peat soils tested or a compensatory mobile anion effect on pH. Further work should be carried out to investigate anion adsorption and competition for exchange sites on organic matter solids to increase understanding of the behaviour of anions in peat soils.

Changes in soil solution composition can affect the chemistry of surface waters fed by these soils. Inputs of Al into surface waters could increase acidification and have potentially toxic effects on aquatic organisms. The potential increase in organic matter concentrations in solution could impact upon the concentration of humic substances exported to surface waters. This has local effects on water quality and may impact upon water treatment operations with extra costs incurred to remove coloured humic substances from drinking water. If the export of DOC from peatlands is increased, this also impacts upon the size of the peatland C store as $CO_2$ is released back into the atmosphere.

Soil solution chemistry can also have a major effect on vegetation communities. In the mesocosms treated with high F, concentrations of F and Al were significantly increased in *Eriophorum* shoots, indicating that those species were bio-available in solution. However, there were no signs of toxicity that are sometimes observed due to the presence of F and Al and no change in sedge density, which provides further evidence to support the argument that Al-F complexes are less toxic than F and Al separately. Fluoride damage to vegetation is usually caused by gaseous F compounds with leaf injury in the form of necrosis and chlorosis described for a number of species in relation to emissions from point sources such as Al smelters (Vike 1999). Distal volcanic effects on peatland vegetation are most likely to occur due to uptake of ash leachates in the soil solution rather than via gaseous pollutants. There was no effect of F treatments on mesocosm vegetation in the present study but perhaps F and Al uptake over a longer time period may cause damage. There may also be further effects when the F and Al containing plant litter is incorporated into the peat. The incorporation of more F into the soil may have further effects on the biogeochemical cycling of C, S and Fe and may have detrimental effects on decomposers and other micro-organisms within the peat.

### 2.5.1 Summary of findings

- The addition of F resulted in an increase in F concentrations in soil, soil solution and plant material.

- Fluoride behaved in a similar manner as reported in mineral soils i.e. addition of F increased the solubility of Al and Fe resulting in elevated concentrations of these metals in the soil solution. DOC concentrations were not increased as has been reported recently but interestingly, acetate concentrations did increase over the treatment period. There was no change in soil solution pH as has been reported in mineral soils. In the soil, concentrations of F and Fe were increased and concentrations of S were decreased. In the *Eriophorum* shoots, concentrations of F and Al were increased.

- The addition of $SO_4$ resulted in no change in $SO_4$ or S concentrations in soil, soil solution and plant material. There was also no effect of treatment on soil solution pH. The only significant changes to peat mesocosms which received the $SO_4$ and $SO_4$ + Low F treatments were an increased in soil P concentrations and a decrease in soil Si concentrations.

# Chapter 3: The effects of volcanic deposition on peatland carbon gas fluxes

## 3.1 Introduction

Northern peatlands play a major role in the global C cycle. Although they cover only 2-3% of the world's total land surface (Rydin and Jeglum 2006), they store approximately one-third of the global soil C (455 Pg C) (Gorham 1991). Consequently, it is important to quantify processes that might influence exchanges of carbon, in its various forms, between peatlands and the atmosphere. One such gas, $CH_4$, is 25 times more powerful than $CO_2$ as a greenhouse gas (IPCC 2007) and contributes 22% of the total climate forcing of all long-lived greenhouse gases (IPCC 2007). Biogenic sources account for more than 70% of the global total $CH_4$ emission (Denman et al. 2007) with wetland soils being the main natural source producing an estimated 100-200 Tg year$^{-1}$ (Le Mer and Roger 2001). Peatland $CH_4$ emissions are regulated by temperature, peat composition, water table, pH and vegetation type (Lai 2009). Further, emissions may also be influenced by a change in the composition and flux of atmospheric deposition namely anthropogenic $SO_4$ and $NO_3$ (Blodau 2002). Recent studies indicate that acid rain $SO_4$ deposition decreases $CH_4$ emission in peatlands in the northern hemisphere due to a shift in microbial communities as $SO_4$ reducing bacteria out-compete methanogens for substrates (Dise and Verry 2001; Fowler et al. 1995; Gauci and Dise 2002; Gauci et al. 2004b; Granberg et al. 2001; Watson and Nedwell 1998).

Recently, *Gauci et al* (2008) investigated the potential link between volcanic activity and the release of $CH_4$ by peatlands. In this work, the impact of the Icelandic eruption of Lakagigar in 1783 on the Northern wetland $CH_4$ source was modeled based on responses observed in pristine (i.e. unpolluted) peats to simulated $SO_4$ deposition that was of a similar magnitude to volcanogenic $SO_4$ inputs from the Lakagigar eruption (Gauci et al. 2008; Gauci et al. 2004b). The results showed that the combined effect of cooling from volcanic aerosols with deposition of S on wetlands was sufficient to suppress $CH_4$ emissions by 14 % (from 160 to 137 Tg year$^{-1}$). Based on previous results (Gauci et al. 2005), the same authors argued that the volcanogenic $SO_4$ deposition on $CH_4$ fluxes may only decrease over decade-long timescales due to re-oxidation of reduced S-compounds in the peat soil. While these findings provide important insights into the environmental effects of volcanogenic emissions, the potential impact of F must also be assessed, in particular when considering the long-range transport of soluble $SO_4$ and F-bearing tephra.

Several authors have discussed the distal environmental effects of volcanic emissions on peatlands. The focus has been on vegetation change, porewater chemistry, humification and effects on testate amoebae communities with suggestions for further research on a number of variables including C gas fluxes (Blackford et al. 1992; Hotes et al. 2006; Hotes et al. 2004; Payne and Blackford 2005; Payne and Blackford 2008). A greater understanding of the effects of volcanic deposition on C fluxes in peatlands has important implications for better evaluating the connection between volcanism and environmental changes. The results from Chapter 2 indicate a significant change in peat soil solution chemistry with the addition of F. These changes may impact upon the microbial communities within the peat. The objective of this chapter is to assess the effect of volcanic $SO_4$ and F addition, both alone and in combination, on $CH_4$ and $CO_2$ gas emissions from peat mesocosms. The following hypotheses will be tested:

*The effects of treatments on peat soil $CH_4$ emissions*

- The addition of $SO_4$ will stimulate a population of $SO_4$ reducing bacteria to outcompete methanogens for substrates thus reducing $CH_4$ emissions.

- Increased F in soil solution will become toxic to methanogens thereby reducing $CH_4$ emissions. It will also be toxic to methanotrophs, reducing $CH_4$ oxidation rates and therefore increasing $CH_4$ flux. If F reduces both

$CH_4$ production and oxidation there may be no overall effect on measured $CH_4$ emissions.

- Alternatively, the increased concentrations of acetate in solution as reported in Chapter 2 will provide more substrates in solution thus stimulating the emission of $CH_4$.
- Co-addition of F and $SO_4$ will lead to a reduction in $CH_4$ production rates.

*The effects of treatments on peat soil $CO_2$ fluxes*

- An increase in soil solution F will decrease ecosystem respiration due to toxicity. Increased plant uptake of F will cause plant damage and reduce photosynthesis rates therefore reducing $CO_2$ uptake. A decrease in ecosystem respiration and photosynthesis would result in no overall effect on net ecosystem exchange during the daytime when both processes occur. There would be an overall decrease in $CO_2$ release to the atmosphere at night due to reduced respiration rates.
- The addition of $SO_4$ would have no effect on respiration or photosynthesis rates and therefore there would be no overall effect on net ecosystem exchange.
- The co-addition of $SO_4$ and F would have the same effect as if F was added alone.

## 3.2 Methodology

The peat mesocosms described in Chapter 2 were used to assess the effect of F and $SO_4$ on peatland $CH_4$ and $CO_2$ fluxes. Peat cores were sampled from the northern Pennine uplands and taken to the University of York where they were dosed with small weekly additions of F and $SO_4$ for twenty weeks and carbon gas fluxes were monitored. For a detailed description of the sampling site, experimental design and treatment regime see Section 2.2.

### 3.2.1 Methane measurements

*Pre-treatment $CH_4$ emissions*

To arrange the mesocosms into treatment groups, background $CH_4$ emissions from the mesocosms were measured every month from September 2008 until April 2009 (method described in post-treatment $CH_4$ flux section). The mesocosms were then grouped into five groups of six according to their $CH_4$ fluxes with each group having approximately the same average rates of $CH_4$ emission. Selecting groups of equal emissions provides a good base to add treatments to as effects can be seen more clearly.

*Post-treatment $CH_4$ emissions*

Methane emission from mesocosms was measured twice weekly for the first 4 weeks of treatment additions and then once a fortnight for the remainder of the 20 weeks. For the measurements, a sealed headspace above the core was created using a cuvette (height: 24 cm, diameter: 20 cm). The cuvette was made using PVC tubing identical to that of the mesocosms. One end was sealed using a PVC cap and silicon sealant. A hole was drilled through the cap and a rubber suba seal inserted. A hole was pierced through the seal and the end of a 1.5 m length of Tygon tubing (inner diameter: 1.6 mm, outer diameter: 3.2 mm) inserted. The tubing allows sampling to be carried out with minimal disturbance to the mesocosm and cuvette to prevent $CH_4$ ebullition from the soil. It also prevents pressure building up in the cuvette in between sampling. The cuvette was then wrapped in aluminium foil to reflect solar radiation, and reduce the temperature increase inside the cuvette which could affect the rate of $CH_4$ emission. Lastly a section of rubber tyre inner tube (approximately 10 cm) was stretched around the open end of the cuvette, which was used to seal the cuvette and mesocosm together and create an air-tight headspace.

**Fig. 3.1** Photograph of a cuvette on top of a peat soil mesocosm ready for $CH_4$ sampling.

To sample, a cuvette was placed on top of the mesocosm for 2 hours and sealed using the rubber band taking care not to knock the mesocosm in the process (Fig. 3.1). The end of the tygon tubing was clamped using a bulldog clip. The needle of a 20 ml syringe was inserted into the tubing and the syringe was filled and emptied 3 times to mix the headspace gas. The syringe was filled once more and 20 ml of headspace gas was removed from the tube and injected into a 12 ml pre-evacuated septum-capped glass vial (Exetainer, Labco Ltd). Samples were collected this way at times 0, 30, 60, 90 and 120 minutes and the exact sampling time was recorded. Headspace samples were analysed on a Perkin Elmer-Arnel gas chromatograph (AutoSystem XL, Perkin Elmer Instruments, Shelton, CT, USA) equipped with a flame ionisation detector and a 3.7 m Porapak Q 60/80 mesh column ($N_2$ carrier gas flow of 30 ml $min^{-1}$; and injector, column and detector temperatures of 120, 40 and 350 ºC, respectively).

On the day of $CH_4$ sampling the height of vegetation cover at the soil surface in each mesocosm was estimated so that the volume of the headspace could be calculated. To do this, the vegetation height above the rim of the PVC core was measured at 3 points and an average taken. Soil temperature was also measured in each mesocosm after $CH_4$ sampling had finished at 2 cm and 18 cm using a temperature probe. Air temperature was also recorded and photographs taken of each mesocosm to see if there was any visible change or damage to plant species with time.

As vascular plants act as a major transportation route for $CH_4$ from the soil to the atmosphere (Schimel 1995), the density of the dominant species (*Eriophorum vaginatum*) was calculated by counting the number of live shoots in each mesocosm every four weeks.

Methane fluxes were calculated using simple linear regressions of headspace $CH_4$ concentrations versus sampling time to give a rate of $CH_4$ emission for each mesocosm expressed as mg $CH_4$ $m^{-2}$ $h^{-1}$. Mesocosms which had a $r^2 < 0.9$ were rejected and the rate of $CH_4$ emission was assumed to be zero when there was no change or negligible change in $CH_4$ concentration over the 2 hour period, otherwise the measurement was discarded (Toet et al, 2011). Only 0.3% of measurements were disregarded.

### 3.2.2 Carbon dioxide measurements

Carbon dioxide flux was measured in light and dark conditions using a portable Infra Red Gas Analyser (IRGA) (LICOR LI-8100). In light, processes of respiration and photosynthesis are occurring and so the resulting $CO_2$ concentration in the chamber is the Net Ecosystem Exchange (NEE), which in this case is always negative as there is more photosynthesis than respiration. In dark conditions there is no photosynthesis and so $CO_2$ concentrations in the chamber start to increase due to Ecosystem Respiration (ER) after closure.

The IRGA was connected to a transparent custom made vented chamber (20 cm diameter, 24 cm height) (Fig. 3.2). The chamber is vented to reduce changes in chamber pressure, which could affect $CO_2$ diffusion rates from the soil. This is important as $CO_2$ movement from the soil is driven by diffusion. The chamber is placed on top of the mesocosm and sealed with a rubber band to make it air tight, the initial $CO_2$ concentration in the chamber is ambient. Each $CO_2$ measurement took 3 minutes. The first minute was an equilibration period, which allowed the air to mix in the chamber. This is important as the IRGA only uses a small volume of air to measure the $CO_2$ concentration and so it needs to be well mixed. During the following two minutes $CO_2$ concentration in the chamber was measured once every second.  The chamber was removed from the mesocosm for 2 minutes between sampling to allow ambient $CO_2$ concentrations to return. Each mesocosm was first sampled in light and then dark conditions.  To create dark conditions, the same transparent chamber is used but it is covered with a cloche.  Light and dark measurements were made one after the other as changes in air and soil temperatures could affect $CO_2$ flux from the soil.

During light measurements, the amount of Photosynthetically Active Radiation (PAR) was measured at 0, 0.5, 1, 2 and 3 minutes.  Flux measurements were only carried out if the PAR was greater than 200 $\mu$mol/m$^2$/s.  Measurements of soil temperature at 2 and 18 cm and air temperature were made immediately before flux measurements.  Vegetation height above the rim of the PVC core was also measured so that chamber volumes could be corrected.  Sampling was carried out twice a month in May and June and then once a month in July and August. The $CO_2$ flux was calculated by linear regression of the $CO_2$ concentrations measured over time.  Gross Photosynthesis (GP) can be calculated by subtracting ER from NEE.

**Fig. 3.2** A transparent chamber attached to the IRGA to measure mesocosm $CO_2$ flux in light.

### 3.2.2 Statistical Analysis

To compare the effects of treatments on $CH_4$ emissions, the $CH_4$ flux data were split into two categories prior to statistical analysis. These were pre-treatment $CH_4$ fluxes (08/09/2008 to 12/05/2009) and post-treatment $CH_4$ fluxes (13/05/2009 to 25/09/2009). Carbon dioxide fluxes were not measured before treatments began and so the $CO_2$ flux data were analysed as one dataset. Both the $CH_4$ and $CO_2$ data were first tested for normality using the Kolmogorov-Smirnov tests of normality ($p > 0.05$) and for homogeneity of variances with Levene's test of equality of error variances ($p > 0.05$). The $CO_2$ flux data did meet the requirements of these tests but the $CH_4$ flux data did not and so were log transformed which considerably improved the normality and homogeneity of variances. Repeated-measures multivariate analysis of variance (RM-MANOVA) (Pillai's trace) were used to analyse the effects of the treatments on the log transformed $CH_4$ fluxes and the untransformed $CO_2$ fluxes, with sampling date as the within-subject factor and treatment as the between-subjects factor. A number of covariates were tested in the model to explain within-treatment variability but were only included if $p < 0.1$. For the $CH_4$ flux data, the covariates tested were sedge density and soil temperature at 2 and 18 cm depth. For $CO_2$ fluxes, PAR, sedge density and temperature at 2 and 18 cm were tested as covariates. RM-MANOVA also allowed examination of within treatment variability (time effect and interactions between time and treatment (time times treatment)). Post Hoc comparisons were included if treatment was a significant factor (Tukey HSD) or to test if the fluxes from the treated mesocosms were significantly different to those of the control mesocosms (Dunnett t-tests).

To assess whether any of the treatments affected the total quantity of $CH_4$ emitted from the soils over the 20-week period, the cumulative $CH_4$ emission over the post-treatment period was calculated. For each mesocosm data were interpolated to provide values of $CH_4$ emission for each day since the beginning of treatments. The values for each mesocosm were summed and results expressed as g $CH_4$ $m^{-2}$ for the post-treatment period. The mean total for each treatment group was calculated. These data were not normally distributed and the homogeneity of variances were not equal and so the data were ranked and tested non-parametrically using the Kruskal Wallis test to assess whether any of the treatments were significantly different to the controls. All analyses were performed with SPSS Statistics 17.0.

## 3.3 Results

### 3.3.1 Methane emissions

*Pre-treatment*

Over the pre-treatment period (08/09/2008 to 12/05/2009) there were no significant differences among treatments (F= 0.21, *p*= 0.93) (Fig. 3.3, Table 3.1 & Table 3.2). Of the covariates tested, only sedge density was of borderline significance (F= 3.08, *p*= 0.09) but it did not alter the significance of the treatment effect and so was not used. Soil temperature at 2 and 18 cm showed no correlation to $CH_4$ flux (F= 0.99, *p*=0.33 and F= 0.16, *p*= 0.69 respectively). There was also no significant difference in cumulative $CH_4$ emissions over the pre-treatment period between any of the treatment groups (H= 0.602, *p*= 0.96).

*Post-treatment*

There were no significant differences between $CH_4$ emissions from treated mesocosms and the control mesocosms, which only received deionised water over the post-treatment period (13/05/2009-25/09/2009) (Fig. 3.3, Table 3.1 & Table 3.2). The results of a RM-MANOVA verified that there were no significant differences in $CH_4$ emission from the different treatment groups (F= 1.16, *p*= 0.35). Soil temperature at depths 2 and 18 cm were tested as covariates but showed no correlation to $CH_4$ flux (*p*= 0.84 and 0.36 respectively. Post-treatment $CH_4$ fluxes had no relationship to average sedge density (F=0.07, *p*= 0.80) and therefore log $CH_4$ fluxes were analysed with no covariates. Sedge density did not change over the treatment period (Fig. 3.5) and was not affected by treatment (F= 0.511, *p*= 0.729).

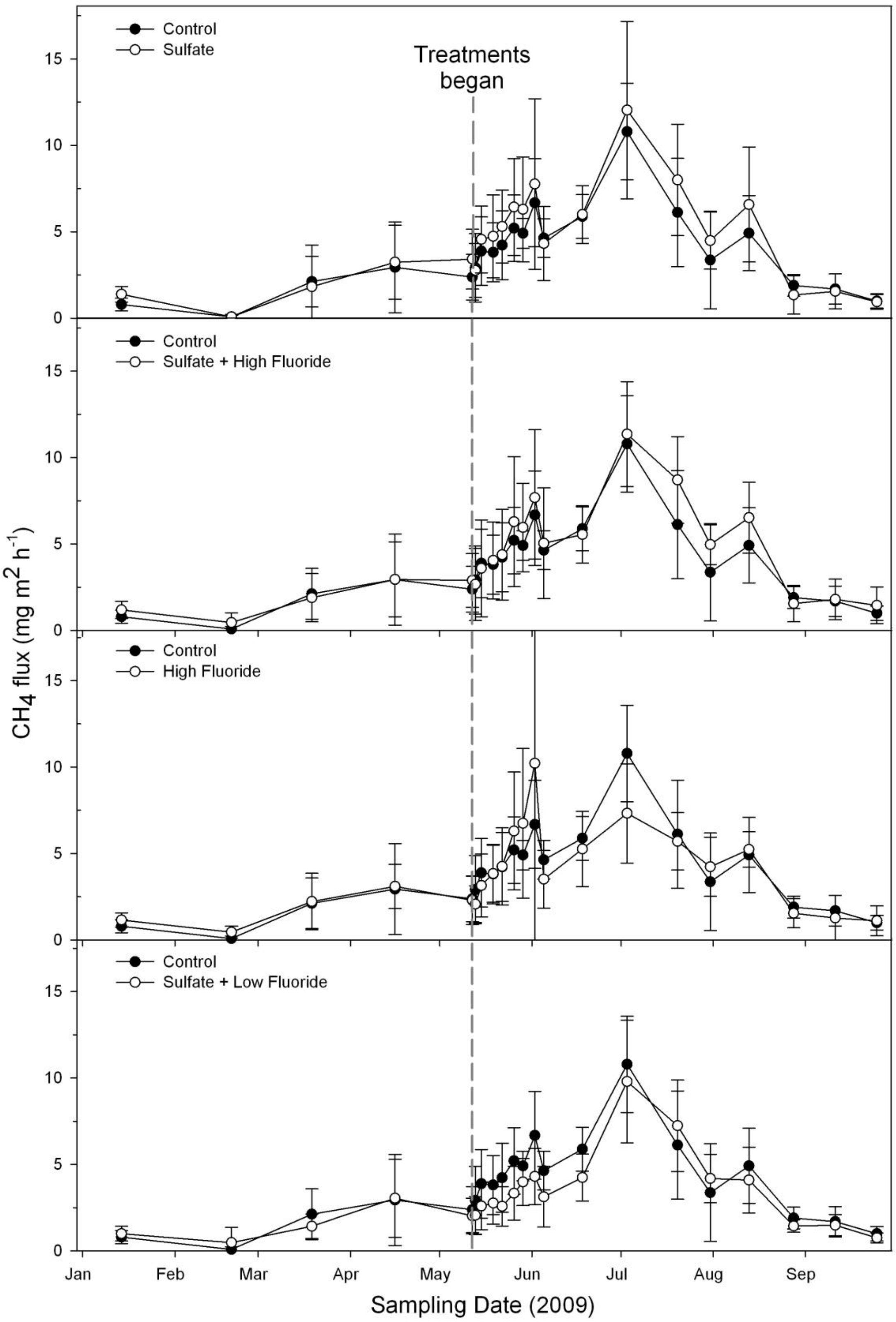


**Fig. 3.3** Methane emission from treated mesocosms against emissions from control mesocosms, which only received deionised water. Each point represents the mean flux from 6 replicates. Error bars represent standard deviation.

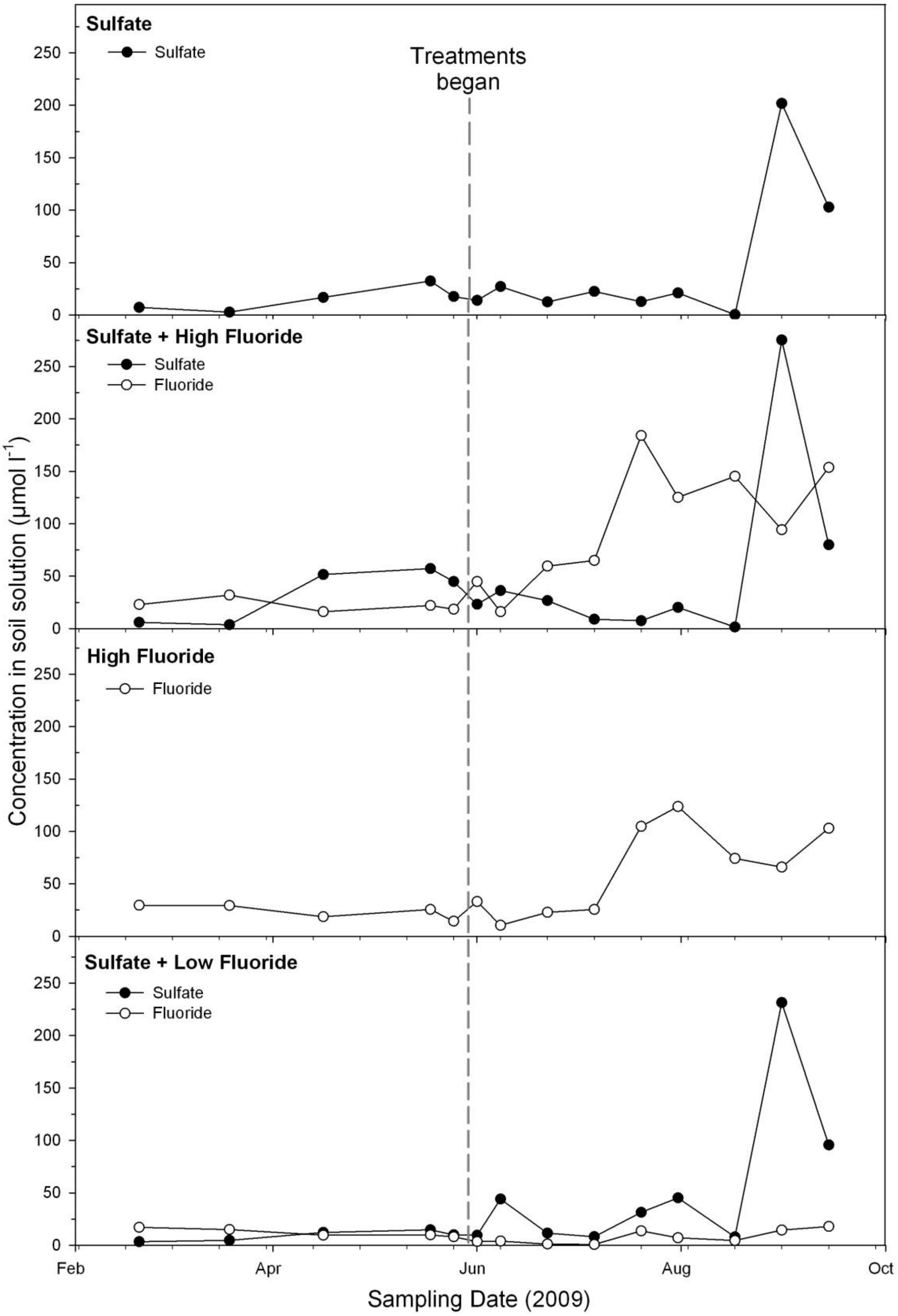


**Fig. 3.4** Average $SO_4$ and F concentrations in the mesocosm soil solution over time. Each point represents the mean from 6 replicates.

Table 3.1 shows that there were no significant statistical differences between any of the treatments and the controls.

**Table 3.1** Summary of average $CH_4$ emissions [a]

| | Pre-treatment [b] | | Post-treatment [c] | |
|---|---|---|---|---|
| Treatment group | Mean $CH_4$ flux (mg $m^{-2}h^{-1}$) (± Std Dev) | p value Control versus treatment | Mean $CH_4$ flux (mg $m^{-2}h^{-1}$) (± Std Dev) | p value Control versus treatment |
| Control | 4.03 (4.54) | n/a | 4.49 (2.88) | n/a |
| Sulfate | 4.42 (4.14) | 0.91 | 5.19 (3.60) | 0.93 |
| Sulfate + High Fluoride | 4.09 (4.16) | 1.00 | 5.09 (3.48) | 0.97 |
| High Fluoride | 3.89 (4.42) | 1.00 | 4.48 (3.72) | 0.99 |
| Sulfate + Low Fluoride | 3.59 (4.48) | 1.00 | 3.62 (4.03) | 0.51 |

[a] p values indicate the significance of treatment effects on mean $CH_4$ flux when compared to the control fluxes. Values were generated using repeated measures MANOVA (Dunnett 2 sided t test).

[b] 8th September 2008 to 12th May 2009; n= 42.

[c] 13th May 2009 to 25th September 2009; n= 96.

Cumulative $CH_4$ emissions over the 20 week treatment period were not significantly influenced by treatment (H= 4.043, *p*= 0.40). Mesocosms which received the Sulfate and the Sulfate + High Fluoride treatments emitted in total 14% more $CH_4$ than mesocosms which received only deionised water, 17.81 and 17.84 g $m^{-2}$ respectively compared to 15.56 g $m^{-2}$ (Fig. 3.6). Cumulative emissions from the mesocosms treated with High Fluoride and Sulfate + Low Fluoride were 14.25 and 13.62 g $m^{-2}$ respectively which were 8% and 12% lower respectively, than emissions from the control mesocosms.

**Table 3.2** Summary of repeated measures ANOVA results for pre-treatment and post-treatment $CH_4$ emissions

| | **Source** | **Type III Sum of Squares** | **df** | **Mean Square** | **F** | **Sig.** |
|---|---|---|---|---|---|---|
| Pre-treatment | Intercept | 10.703 | 1 | 10.703 | 553.754 | **0.000** |
| | Treatment | 0.016 | 4 | 0.004 | 0.210 | 0.930 |
| | Error | 0.483 | 25 | 0.019 | | |
| Post-treatment | Intercept | 13.610 | 1 | 13.610 | 1325.553 | **0.000** |
| | Treatment | 0.048 | 4 | 0.012 | 1.164 | 0.351 |
| | Error | 0.257 | 25 | 0.010 | | |

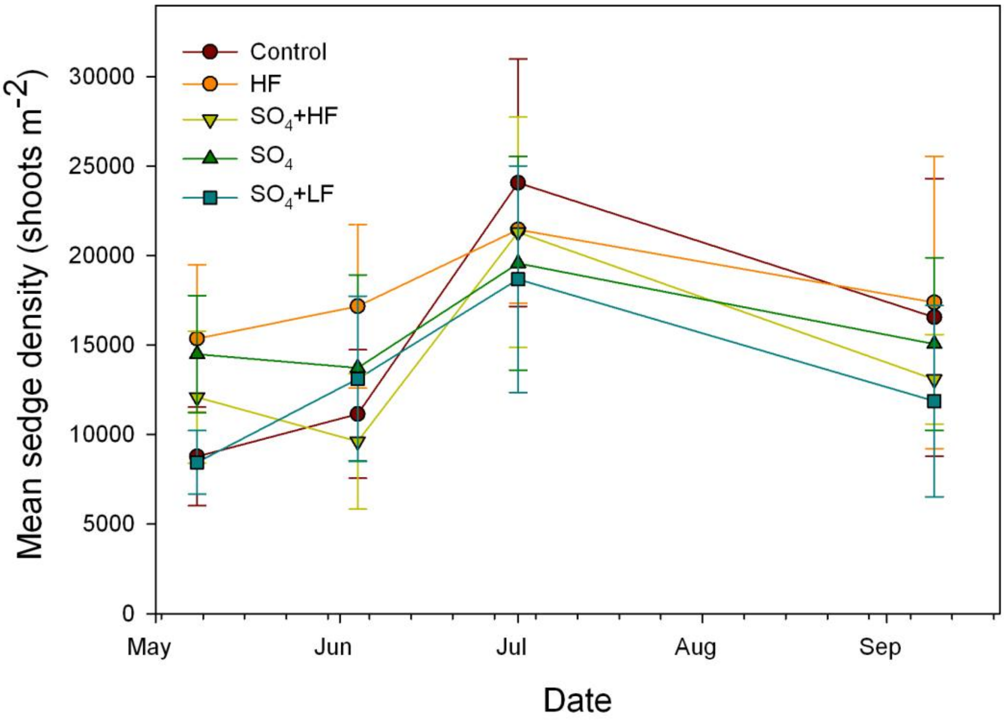


**Fig. 3.5** Average density of live shoots per mesocosm over time. Points represent the average of 6 replicates. Error bars represent standard deviation.

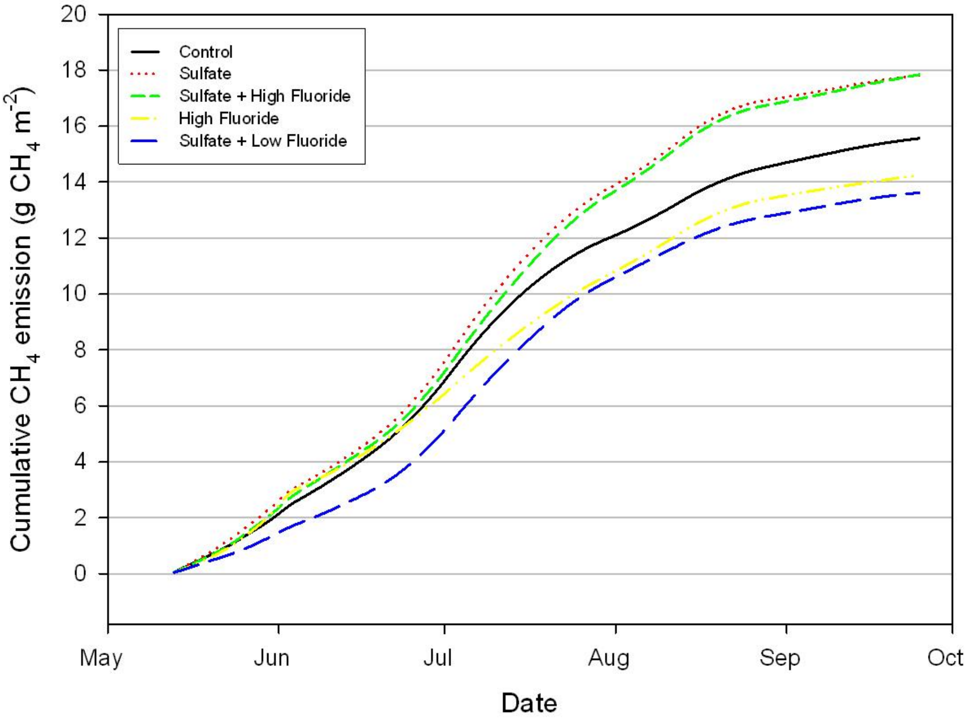


**Fig. 3.6** Cumulative daily $CH_4$ flux after treatment. Lines represent the mean methane flux from 6 replicates.

### 3.3.1.3 Seasonal effect on $CH_4$ emissions

Mesocosm $CH_4$ emissions have a distinct seasonal pattern (Fig. 3.3) with lowest emissions during the winter months following a cold period of snow and frost and highest emissions in July when mean monthly rainfall peaked at 90 mm and air temperatures were above 20°C (Fig. 3.7). Analysis of $CH_4$ flux data by RM-MANOVA found a within subjects time effect on $CH_4$ values which can be explained by this seasonality. There were no interactions between treatment and time (time x treatment) for any of the mesocosms.

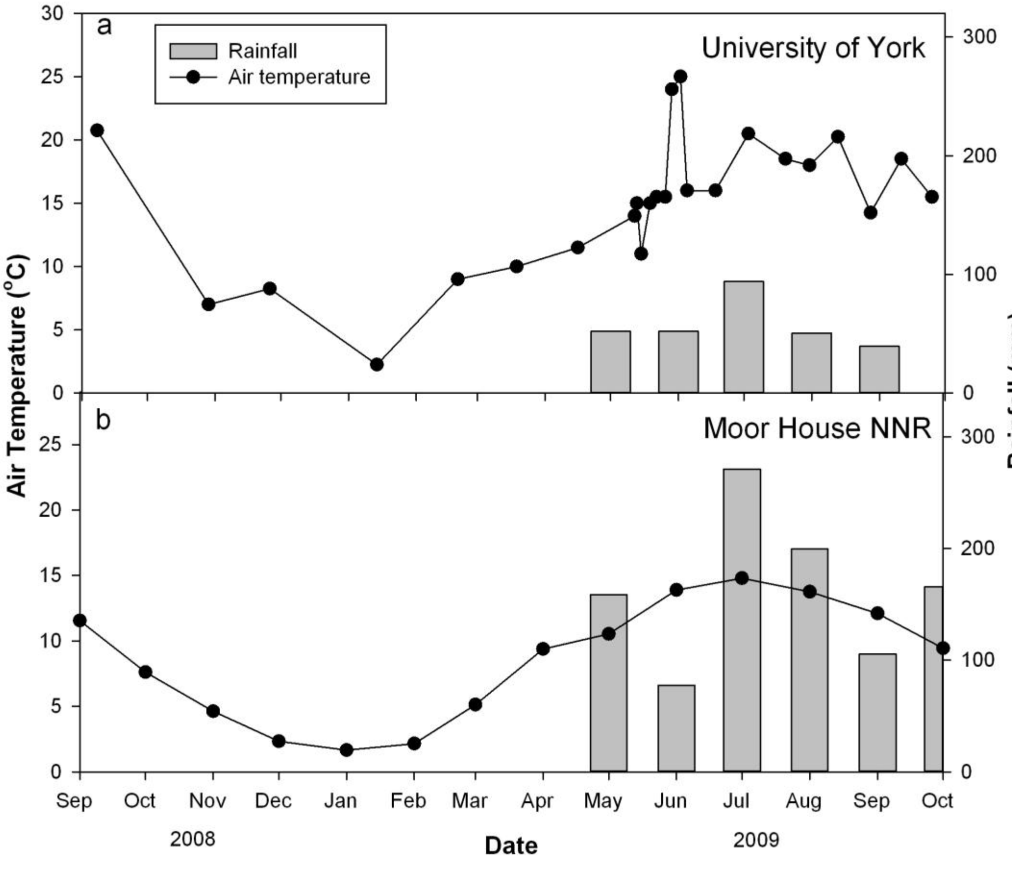


**Fig. 3.7** Total monthly rainfall and air temperature on each sampling date a.) in the walled garden at the University of York where the mesocosm experiment was based and b.) measurements from the Moor House NNR sampling site over the same time period (values calculated from summary data on http://www.ecn.ac.uk/Database/index.html).

Average temperatures at the mesocosm collection site were lower than those in York where the experiment was based (Fig. 3.7). Temperatures peaked at 15 °C in July 2009 when temperatures in York were approximately 5 °C higher.

The sampling site also received greater average rainfall compared to at the University of York, which received approximately 100 mm rain compared to 270 mm at Moor House.

### 3.3.2 Carbon dioxide emissions

There were no treatment effects on NEE (RM-MANOVA F= 0.45, *p* = 0.77) (Fig. 3.8). None of the treatments were significantly different from one another or from the controls (Table 3.3). There was also no treatment effect on ER (F= 2.09, *p* = 0.11) (Fig. 3.9) or on GP (F= 0.49, *p*= 0.74) (Fig. 3.10). Sedge density and soil temperature were not used in the analysis as there was no covariate effect (*p*>0.3) for any of the measurements. When PAR was tested as a covariate for GP it was of borderline significance (*p*= 0.07) but it was not used in the model as it did not affect the significance of the treatment. PAR also had no effect as a covariate on NEE (p>0.6). There was a significant time effect but no interactive effect between time and treatment (time x treatment). The NEE was always negative as photosynthesis was the dominant process using more $CO_2$ than was being produced by respiration..

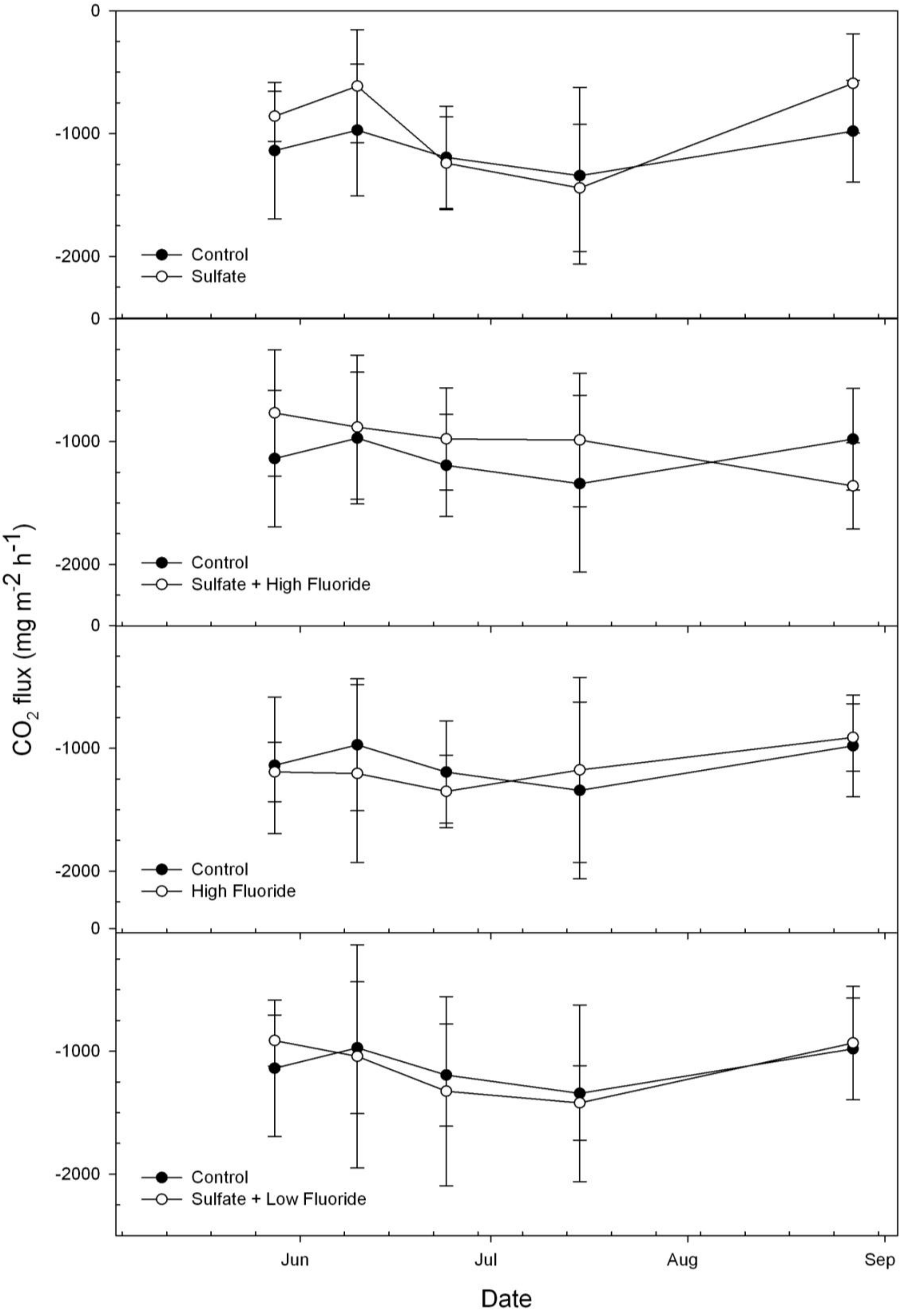


**Fig. 3.8** Net Ecosystem Exchange from treated mesocosms against emissions from the control mesocosms which only received deionised water. Each point represents the mean flux from 6 replicates. Error bars represent standard deviation.

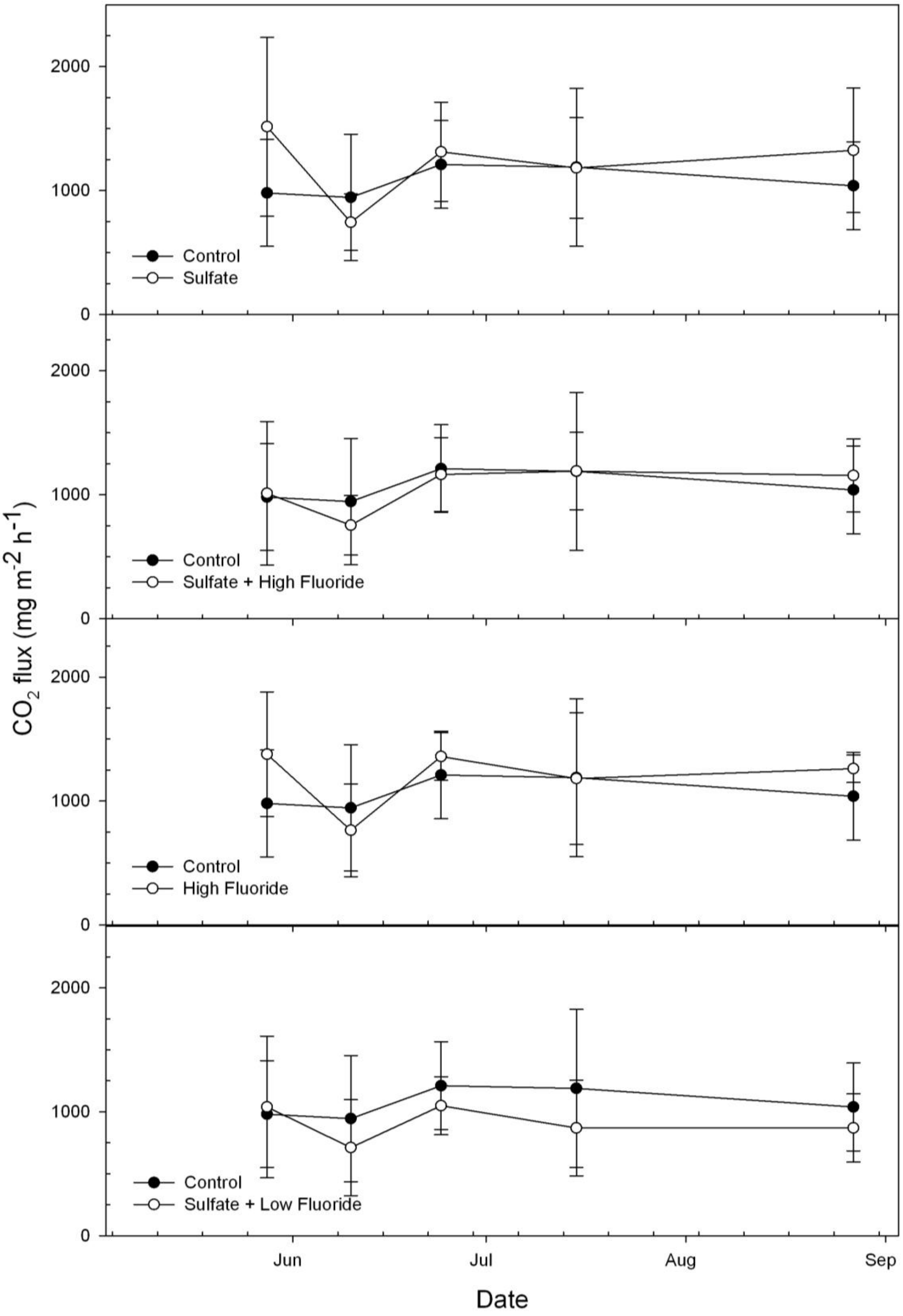


**Fig. 3.9** Ecosystem Respiration from treated mesocosms against emissions from the control mesocosms, which only received deionised water. Each point represents the mean flux from 6 replicates. Error bars represent standard deviation.

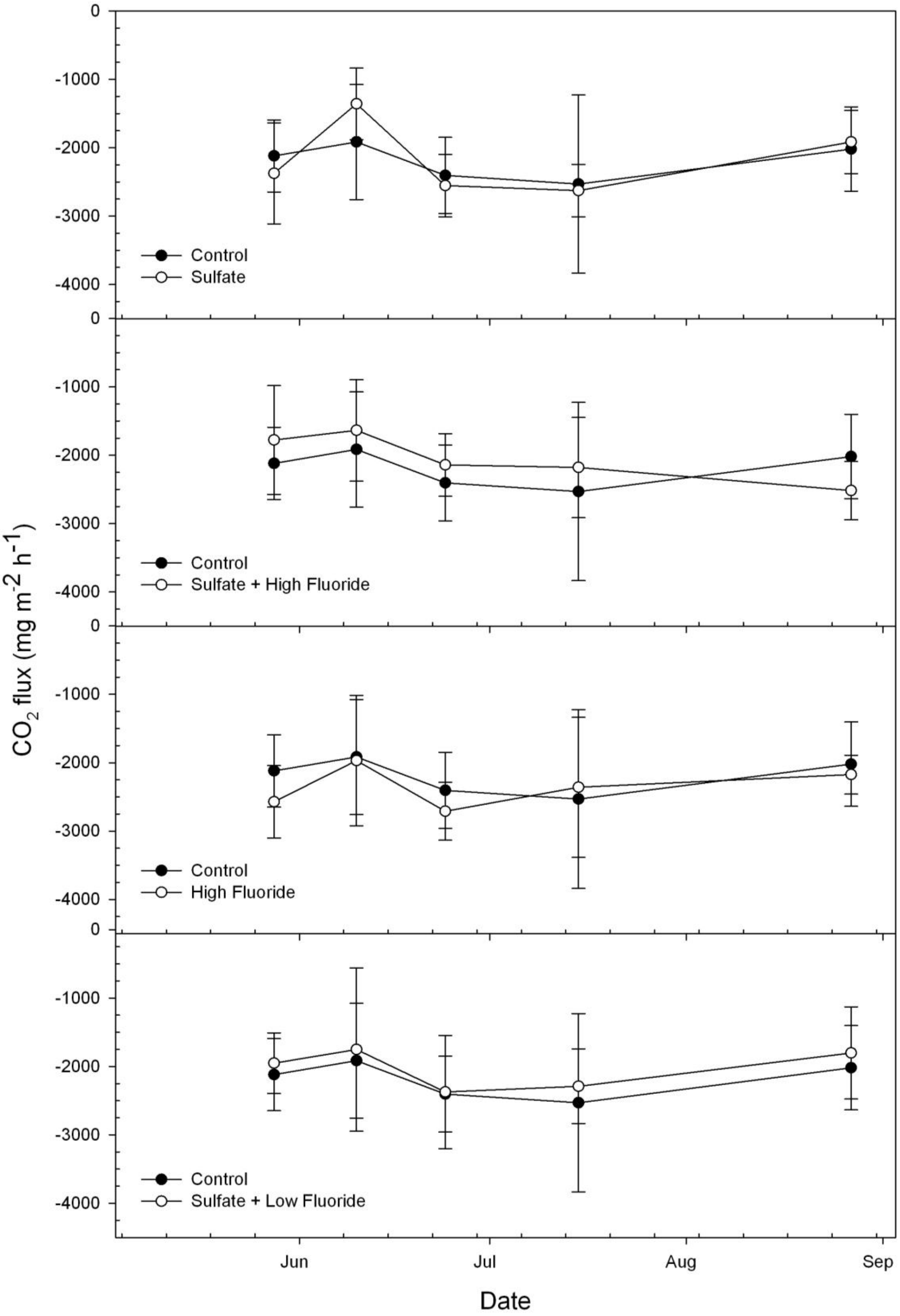


**Fig. 3.10** Gross photosynthesis from treated mesocosms against emissions from the control mesocosms, which only received deionised water. Each point represents the mean flux from 6 replicates. Error bars represent standard deviation.

**Table 3.3** Summary of average $CO_2$ emissions

| | Treatment | Mean $CO_2$ flux ($mg\ m^{-2}\ h^{-1}$) (± Std Dev) | Between subjects effects (treatment) | p value[a] Control Versus treatment |
|---|---|---|---|---|
| Net Ecosystem Exchange | Control | -1125 (520) | F= 0.45<br>*P*= 0.77 | n/a |
| | Sulfate | -949 (511) | | 0.79 |
| | Sulfate + High Fluoride | -995 (497) | | 0.91 |
| | High Fluoride | -1167 (496) | | 1.00 |
| | Sulfate + Low Fluoride | -1126 (590) | | 1.00 |
| Ecosystem Respiration | Control | 1072 (449) | F= 2.09<br>*P*= 0.11 | n/a |
| | Sulfate | 1215 (517) | | 0.58 |
| | Sulfate + High Fluoride | 1055 (377) | | 1.00 |
| | High Fluoride | 1188 (420) | | 0.74 |
| | Sulfate + Low Fluoride | 907 (383) | | 0.46 |
| Gross Photosynthesis | Control | -2198 (798) | F= 0.49<br>*P*= 0.74 | n/a |
| | Sulfate | -2165 (686) | | 1.00 |
| | Sulfate + High Fluoride | -2050 (681) | | 0.95 |
| | High Fluoride | -2356 (709) | | 0.93 |
| | Sulfate + Low Fluoride | -2034 (769) | | 0.92 |

[a] *p* values indicate the significance of treatment effects on mean $CO_2$ flux when compared to the control fluxes. Values were generated using repeated measures MANOVA (Dunnett 2 sided t test).

## 3.4 Discussion

### 3.4.1 Methane emissions

*Effects of Sulfate additions on methane flux*

The results of this experiment indicate no suppression of $CH_4$ emission from peat soils with the addition of $SO_4$ at concentrations that could be leached from volcanic ash deposited on the surface of a peat bog after a volcanic eruption. This result is in contrast to other research by authors in Table 3.4 (Dise and Verry 2001; Fowler et al. 1995; Gauci and Dise 2002; Gauci et al. 2004a; Granberg et al. 2001). In this study mesocosms were treated with $Na_2SO_4$ at a deposition rate of 24.5 kg S $ha^{-1}$ (over 20 weeks). This is comparable to low acid rain scenarios investigated by Gauci et al. (2002) who added 25 kg S $ha^{-1}$ $y^{-1}$ for

18 months and saw a 36% average reduction in $CH_4$ emission in the last 12 months of the experiment. Dise and Very (2001) added 24 kg S $ha^{-1}$ $y^{-1}$ over 9 weeks and saw a 32% average suppression of $CH_4$ over the growing season. Granberg et al. (2001) added 20 kg S $ha^{-1}$ $y^{-1}$ for 3 years and saw an average suppression of 6% over the course of the treatment. No $CH_4$ suppression occurred in this study; in fact cumulative emissions from the sulfate mesocosms were greater than the controls, although this result was not statistically significant (Fig. 3.6).

The addition of $SO_4$ to the peat soil did not cause a suppression of $CH_4$ emission. The possible hypotheses for this result will be discussed below.

**a.** Peat soil composition, microbiology and history was different to soils used in other experiments

**b.** Seasonal temperature variation reduced the suppressive effect of $SO_4$ (Gauci and Dise 2002; Granberg et al. 2001)

**c.** The water table position controlled $CH_4$ flux overriding the effect of $SO_4$ addition (Gauci and Dise 2002)

**d.** Vegetation type and density enhanced $CH_4$ production and transport reducing the competition with sulfate reducing bacteria

**e.** The concentration and frequency of $SO_4$ applications was insufficient to cause an effect on $CH_4$ flux

**f.** The use of peat mesocosms as a proxy for larger scale peatland processes was inappropriate

**g.** Inadequate sampling methods prevented the measurement of accurate $CH_4$ fluxes

**Table 3.4** Summary of previous peatland sulfate addition experiments

| Study | Experiment type | Peat type | $CH_4$ sampling method | Sulfate addition | % Suppression | Notes |
|---|---|---|---|---|---|---|
| Gauci and Dise (2002) | Field measurements from June 1997 – December 1998. 5 replicates of 2 m$^2$ plots per treatment.<br>Ambient temperatures, natural water table. | Pristine raised mire. Moidach More, Northeast Scotland | Static chamber method. Sampling at 0 + 20 minutes weekly or monthly | 25 kg S ha$^{-1}$ y$^{-1}$ | 36% (1998) | Over the 18 months, treatment plots emitted 22-32 % less $CH_4$ than controls. Two years after the end of treatments, plots emitted 30-40 % less $CH_4$ than controls. Five years after the end of treatments there was no significant difference between treatments and controls. |
| | | | | 50 kg S ha$^{-1}$ y$^{-1}$ | 21% (1998) | |
| | | | | 100 kg S ha$^{-1}$ y$^{-1}$ | 42% (1998) | |
| | | | | Treatments added as $Na_2SO_4$ on a weekly basis (monthly in winter) in 1L deionised water for 18 months | | |
| Granberg, Sundh et al. (2001) | Field measurements. 2 plots per treatment containing 5 sampling collars (20 x 8 cm). Experiments carried out at ambient temperatures and at raised temperatures (+3.6 °C). Natural water table. | Boreal mixed mire. Degerö Stormyr, Västerbotten Sweeden. | Static chamber method. Sampling at 0, 5, 10 + 15 minutes fortnightly may-September 1995-1996 | 20 kg S ha$^{-1}$ y$^{-1}$ for 3 years | 6% | Suppression seen at ambient temperatures but there was no effect at raised temperatures.<br>After the first two years of sulphate additions, S concentrations in the soil increased by 70-80 % in the uppermost 0-0.05 m peat. |
| | | | | Treatments applied as $Na_2SO_4$ dissolved in 10 L of surface mire water. One third of the treatment applied directly after the snow melt, then one sixth doses once a month from June – September | | |
| Gauci et al. (2004a) | Peat monoliths (30 cm x 40 cm), 4 replicates per treatment manipulated in controlled environment cabinets (Temp: 10 °C, relative humidity: 80%, controlled light). Water table at peat surface. | Blanket bog. Loch More, Northern Scotland | Static chamber method. Sampling at 0, 20 + 40 minutes four times per week. | 50 kg S ha$^{-1}$ y$^{-1}$ (single dose) | 31% | No increased suppression at larger deposition rates than 15 kg S ha$^{-1}$ y$^{-1}$.<br>At lower temperatures there was a greater proportional suppression than at higher temperatures.<br>A significant proportion of the treatment $SO_4$ was taken up by vascular plants. |
| | | | | 15 kg S ha$^{-1}$ y$^{-1}$ | 28% | |
| | | | | 50 kg S ha$^{-1}$ y$^{-1}$ | 31% | |
| | | | | 100 kg S ha$^{-1}$ y$^{-1}$ | 29% | |
| | | | | Treatments added as $Na_2SO_4$ on a weekly basis in 350 ml deionised water for 3 months | | |

| Study | Experiment type | Peat type | $CH_4$ sampling method | Sulfate addition | % Suppression | Notes |
|---|---|---|---|---|---|---|
| Dise and Very (2001) | Field measurements from June – September. 4 replicate plots (62.5 $cm^2$ x 45 cm deep) per treatment. Ambient temperatures and natural water table. | Nutrient poor fen. Bog Lake peatland, Minnesota, USA. | Static chamber method. Sampling at 0, 4, 8, 12, 16 + 20 minutes weekly | 24 Kg S $ha^{-1}$ over 9 weeks | 37% average each day<br>32% over the growing season | Net primary productivity may be stimulated by the addition of $NH_4$, which could enhance $CH_4$ flux to the atmosphere. Therefore methane emission may have been suppressed even further than the 30 – 40 % shown. |
| | | | | Treatments applied as $(NH_4)SO_4$ dissolved in 500 ml distilled water applied weekly for 9 weeks. | | |
| Fowler, MacDonald et al. (1995) | Peat monoliths (30 cm x 40 cm). | Blanket bog. Sutherland, Scotland. | Static chamber method in controlled environment cabinets and a dynamic $CH_4$ flux measuring system in open top chambers | 100 kg S $ha^{-1}$ applied as one large dose as $(NH_4)SO_4$ and $Na_2SO_4$ | 50% in 2 weeks | |

The pollution history of Moor House is likely to be an important factor in determining the outcome of this experiment as the previous acid rain $SO_4$ studies presented in Table 3.4 were all carried out on pristine peat soils with no history of large $SO_4$ inputs, volcanogenic or otherwise. The Pennine uplands were once a heavily polluted area of the UK due to the expansion of the industrial cities of Manchester, Sheffield and Leeds during the industrial revolution (Ferguson and Lee 1983). During the period of 1986–1988, total annual S deposition in the area was 20–40 kg $ha^{-1}$ (RGAR 1990), these values are within the range known to suppress $CH_4$ emissions by ~40% (Gauci et al. 2004b). Deposition rates may have been even higher before this period as it was only in the 1950's that there had been substantial reductions in $SO_2$ deposition following the implementation of the Clean Air Act (1956) and the UNECE Convention on Long-Range Transboundary Pollution (1979). Current deposition estimates of 8-10 kg S $ha^{-1}$ $y^{-1}$ (CEH pollutant deposition data for 2006 from http://www.uk-pollutantdeposition.ceh.ac.uk/data) are still capable of affecting emissions (Gauci et al. 2004b). Sulphur is known to be recycled within peat soils between different organic and inorganic pools through biologically mediated reduction and oxidation (Blodau et al. 2007; Wieder and Lang 1988) such that sulfate reduction rates can be sustained at a far higher level that would be suggested by ambient $SO_4$ concentrations.

There is evidence that S can persist in soils despite a decrease in atmospheric S deposition; Vanguelova et al. (2010) monitored forest soils between 1995 and 2006 and recorded no change in soil solution $SO_4$ concentrations in soils with a high organic content over that period. It is therefore possible that the soils may still have high S concentrations now, which may have had an effect on the microbial communities. If S is already present in the soil and additions of $SO_4$ have no effect i.e. they don't cause a shift in microbial communities as has been documented before; then the methanogens may have evolved so that they use a different substrate than the SRB and they can share the same space without competition. Blodau and Moore (2003) speculated that methanogenic and sulfidogenic communities can adapt to coexist in different zones within surface layers of peatlands due to $SO_4$ pulses from the remineralization of organic S (the dominant form of S in most peat) and reoxidation of iron sulfides. It is possible that $SO_4$ addition did not affect $CH_4$ emission in this experiment because the methanogenic communities have adapted to a high S environment either through zonation or the utilisation of alternative substrates to SRB. One way to test this would be to measure $CH_4$ production rates over small depth increments. A suppression of $CH_4$ emission may have been observed at some depths and not at others as suggested in other studies (Blodau and Moore 2003; Eriksson et al. 2010; Yavitt et al. 1987).

It was reported in Chapter 2 that concentrations of $SO_4$ in the soil solution were low and did not increase in the mesocosms that received $SO_4$ additions (Fig. 2.7). The concentration of $SO_4$ measured in solution is a balance between the rate of $SO_4$ addition Vs the rate of reduction. As the initial high treatment addition of $SO_4$ was not represented in the soil solution it can be assumed that $SO_4$ reduction rates in this peat were high. At the Moor House site, where the mesocosms were collected from, concentrations of $SO_4$ in pore water were mostly below detection limits and showed no change between 1993 and 2008 unlike sites in Scotland, which show a decrease in $SO_4$ concentration between these years (DEFRA 2010; Morecroft et al. 2009). The total S content of soil from Control mesocosms was 106 µmol $g^{-1}$ at 0-10 cm and 169 µmol $g^{-1}$ at 10-20 cm (Table 2.8). Gauci et al. (2004a) reported an average S content of 73 µmol $g^{-1}$ in peat used in their $SO_4$ addition experiments where $CH_4$ suppression was observed. The S content of our soils is almost 2.5 times greater than the values reported by Gauci (Gauci et al. 2004a) but is still within the range of 31–365 µmol $g^{-1}$ reported for freshwater peat soils (Wieder and Lang (1988) and references therein), therefore the values measured in our experiment are not exceptionally high. Total S content is not a good indicator of the amount of S microbial communities are exposed to. A more important factor is the pools of bio-available S and the recycling of S species, which are converted to bio-available forms. One way to assess the past pollution at the Moor House site would be to use stable isotopes to determine the origin of the S (Bottrell and Novak 1997). Natural sources of deposited S have different isotopic ratios of S ($^{34}S/^{32}S$) to pollutant sources and so a distinction can be made between the two (Coulson et al. 2005).

The suppressive effect of $SO_4$ may have been reduced by the temperature-stimulated increase of $CH_4$ emission over the summer months. If the experiment had been extended over the winter period when temperature induced methanogenesis had ceased, a suppression of $CH_4$ may have been seen. Methane fluxes exhibited a seasonal variation with lowest fluxes in February (0.08 – 0.47 mg $m^{-2}$ $h^{-1}$) and highest fluxes in July (7.33 – 12.04 mg $m^{-2}$ $h^{-1}$) (Fig. 3.3). This seasonal variation is due to temperature, which has a major influence on $CH_4$ dynamics in northern peatlands (Lai 2009) and has been reported in other studies (Dise et al. 1993; Shannon and White 1994; Ward et al. 2007). The growth of methanogens is temperature dependant with higher temperatures encouraging growth (Zinder 1993). Methanogens are stimulated in summer months to a greater extent than SRB with a temperature characteristic of 208 kJ $K^{-1}$ $mol^{-1}$ (Nedwell and Watson, 1995) compared to 60 kJ $K^{-1}$ $mol^{-1}$ for $SO_4$ reduction (Abdollahi and Nedwell 1979) thus favouring $CH_4$ production over $SO_4$ reduction. Temperature also affects the growth cycle of plants, which in turn can affect $CH_4$ emission. Towards the end of the growing season when plants go into senescence they produce labile organic matter inputs to the soil via root degradation and root exudates. This provides an excess of substrate for microbial use and therefore reduces substrate competition thus increasing methanogenesis (Gauci et al. 2004). This was observed in studies by Gauci et al. (2002) and Granberg et al. (2001), where higher summer temperatures decreased the suppressive impact of $SO_4$ additions and $CH_4$ fluxes began to recover to the same levels as control fluxes. This experiment was carried out over the warm summer months when daytime temperatures often exceeded 20 ºC. It is a possibility that these high temperatures masked the suppressive effect of $SO_4$ by reducing the competition between methanogens and SRB by increasing plant organic matter inputs. If the experiment had lasted longer $SO_4$ suppression of $CH_4$ may have been seen. However, it must be noted that firstly $CH_4$ fluxes from peatlands are much lower in winter anyway so the suppressive effect of $SO_4$ may not be as significant on a global scale. Secondly, $SO_4$ additions began in May 2009 when daytime temperatures were a maximum of 15 ºC, the vegetation was not in senescence and $SO_4$ additions were highest and still no suppression was seen.

Temperatures at the mesocosm experiment site in York were approximately 5 - 10 °C higher than temperatures at the Moor House sampling site (Fig. 3.7). As $SO_4$ reduction rates are temperature dependant with greatest rates at higher temperatures (Nedwell and Abram 1979) it can be assumed that $SO_4$ reduction rates would have been higher in the mesocosms than if the experiment had been carried out in situ. These higher $SO_4$ reduction rates would have resulted in all of the $SO_4$ been used up quickly and so competitive effects between methanogens and $SO_4$ reducing bacteria were not seen. If the experiment had been carried out in situ at Moor House where temperatures were lower, $SO_4$ reduction rates may have been lower resulting in more $SO_4$ in solution and so a suppression of $CH_4$ emission may have been seen.

Temperature in combination with rainfall can affect water table levels in peatlands, which is another important factor that regulates $CH_4$ emission (Kettunen et al. 1999). The height of the water table dictates the depth of the aerobic and anaerobic layers in the peat and therefore the space available for methanogens and methanotrophs. Also, the availability of suitable organic substrates for methanogenesis is reduced at depth and so water table position is a major controlling factor affecting $CH_4$ emission. Here the water table was fixed at the surface so that the peat column was waterlogged and anaerobic to limit the oxidation of $CH_4$ by methanotrophs. In the field based simulated acid rain studies, the water table was not controlled and so was dependent upon natural rainfall and temperature. In the first year of $SO_4$ additions, Gauci et al. (2002) found water table depth to be the most important factor regulating $CH_4$ flux, as there was no significant difference in $CH_4$ flux between treated plots and control plots. The field site received 26 % less rainfall in 1997 than 1998, which led to a low water table. This not only reduced the volume of anaerobic peat and therefore the potential for $CH_4$ production but it increased the aerobic layer of peat which allowed a greater proportion of $CH_4$ to be oxidised before it could be released to the atmosphere. This led to $CH_4$ emissions being 51 % lower in 1997 than over the same period in 1998. Water table depth and temperature explained 64 % of the variability in $CH_4$ flux in 1997. In this situation water table depth was a more important factor than $SO_4$ addition as $CH_4$ emission was reduced from both treatment plots and control plots and there wasn’t any greater suppression from the plots that received $SO_4$. After a field study, Freeman et al. (1994) correlated peatland methane emission after a time of drought with $SO_4$ concentration. They found that lower water table levels promote higher $SO_4$ concentrations as sulphide in the soil is re-oxidised to $SO_4$. The higher $SO_4$ concentration in the soils causes $CH_4$ emissions to be suppressed even after the drought has ended.

Vegetation type and density enhanced $CH_4$ production by reducing the need for substrate competition with sulfate reducing bacteria and enabling high rates of plant-mediated transport of $CH_4$ to the atmosphere. In this study, sedge density was high for all mesocosms with average values of approximately 14,000 shoots / $m^2$. This indicates a generous supply of root exudates for methanogens, which could mean that there were enough substrates present in the soil to reduce competition between sulfate reducing bacteria and methanogens and so $CH_4$ production was not suppressed. Vegetation type can affect the composition of the peat, which can also affect rates of $CH_4$ production. Watson and Nedwell (1998) found no simple relationship between $SO_4$ load and $CH_4$ emission at two UK peatland sites because of the different types of plant material contributing to the peat at each site. Peat from Great Dunn Fell (Cumbria, England) exhibited slower rates of $CH_4$ production and $SO_4$ reduction than the Ellergower site (Dumfriesshire, Scotland) due to the lower decomposability of the peat organic matter, which limited the amount of available organic substrates.

Sulfate treatments were applied as irregular pulses over a short timescale (20 weeks) providing a supply of $SO_4$ to the soil with variable concentrations, which may have prevented the shift in microbial communities that was seen in other experiments and therefore $CH_4$ emission was not suppressed. Approximately 85% of the total $SO_4$ addition was added in the first pulse followed by 5% in the second pulse and 0.5% in the subsequent 18 pulses (Section 2.2.3). Treatments were added in this way to represent the results of the preliminary ash leaching experiment (Fig. 2.4) designed to quantify the concentrations of $SO_4$ that would be leached under natural conditions from a layer of volcanic ash deposited on a peat soil. The experiment showed that $SO_4$ in volcanic ash is highly soluble and is easily leached from the ash surface. This means that during a volcanic eruption, when ash is deposited on the surface of the peat soil, the majority of the $SO_4$ should leach into the soil in the first pulse of rain rather than the same concentration being leached with each rainfall event, which is the case for F. The addition of $SO_4$ in this way is different from simulated acid rain additions, which are applied either as one high dose pulse or as small regular pulses of the same concentration. Gauci et al. (2004) compared these two application methods and found no statistical difference between the single dose application and the small weekly pulses. This indicates that the method of $SO_4$ application is not an important factor and so the addition of irregular sized pulses in this experiment should not have had an effect on the suppression of $CH_4$.

Sulfate was added to the mesocosms for 20 weeks. If additions had been extended for a longer time period then possibly suppression of $CH_4$ would be observed. In studies by Gauci et al. (2002) and Granberg (2001), $SO_4$ was added for 18 and 36 months respectively and suppression was only seen in the second year of additions due to other factors regulating $CH_4$ emission. However, this may not be representative of distal volcanic tephra deposition. For example, the Laki eruption in Iceland in 1783 was the largest recent Icelandic eruption and it only lasted 8 months with tephra being emitted only in the initial stages (Thordarson et al. 1996). Therefore it seems unlikely in a volcanic context that inputs of $SO_4$ into peatlands would last longer than a few months. However, flood basalt eruptions should not be forgotten as they can last for decades, maintaining a source of volcanic pollutants to the atmosphere for considerable time periods. The 934 AD Eldjá basaltic flood lava eruption in southern Iceland is thought to have lasted 3 – 8 years featuring at least 8 distinct episodes (Thordarson et al. 2001).

The manipulation of peat mesocosms may not be representative of the processes and fluxes that occur at a larger scale in natural peat bogs and therefore a suppression of $CH_4$ may have been seen if the experiments had been carried out in situ. The simulated acid rain experiments (Dise and Verry 2001; Granberg, Sundh et al. 2001; Gauci and Dise 2002) were all field-based studies where plots were sectioned off in situ and treatments applied. These studies were subject to natural variations in temperature, light, precipitation and water table levels. In this experiment, the decision was taken to use large intact peat mesocosms so that the water table level could be controlled to focus on the effects of additions on $CH_4$ production alone. The mesocosms received natural light, rainfall and ambient temperatures as they were placed outside and so are still comparable to the field-based studies. Care was taken during sampling to prevent compaction of the soil and damage to the vegetation, which could have affected $CH_4$ emission. Peat mesocosms were sampled randomly over a large area, which encompassed a variety of soils and so the results should be applicable to the whole bog. Rates of $CH_4$ emission from the control mesocosms (0-13 mg $CH_4$ $m^{-2}h^{-1}$) are higher than field measurements taken from the Moor House site in the summer of 2005 (0-3 mg $CH_4$ $m^{-2}h^{-1}$) (McNamara et al. 2008). This is understandable as water table levels were raised, saturating the peat and causing anoxic conditions. Other authors have also used peat mesocosms to study the effect of $SO_4$ addition on $CH_4$ flux (Fowler et al. 1995; Gauci et al. 2004a) but they have done so in controlled environment cabinets so that temperature, light and humidity could also be manipulated. These mesocosm studies did also see a suppression of $CH_4$ with the addition of $SO_4$. Gauci et al. (2004) saw a 28% suppression of $CH_4$ in mesocosms treated with 15 kg S $ha^{-1}$ $y^{-1}$, they treated other mesocosms with 50 and 100 kg S $ha^{-1}$ $y^{-1}$ and saw similar rates of $CH_4$ suppression. It can therefore be concluded that it is acceptable to use peat mesocosms to study the effects of $SO_4$ addition on $CH_4$ flux and that this is not a valid explanation of why $SO_4$ did not suppress $CH_4$ emission.

Another possible reason why suppression of $CH_4$ emission by $SO_4$ addition was not observed is that inadequate sampling methods were used. Methane was measured using a static chamber method where the headspace was sampled using a syringe and samples were analysed by GC-FID. All of the simulated acid rain studies in Table 3.4 also used this method although sampling frequencies differ in each study. Six replicate mesocosms were used for each treatment to produce accurate and reliable average treatment results. All mesocosms were handled in the same way and $CH_4$ sampling was carried out in a random order each time to reduce temporal effects of sampling in the same order each day. There was a large variation between $CH_4$ fluxes of the 6 replicates because soils are dynamic natural systems and are heterogeneous by nature. They have different microbial communities and therefore different decomposition rates and substrates for methanogenesis all of which are factors that affect the emission of $CH_4$ from peatlands. This experiment was carried out using standard methods, which have been used in acid rain studies where a suppression of $CH_4$ was seen, therefore the contrasting results in this experiment are not due to the sampling methods used or the experimental design.

Considering all of the issues discussed above, $SO_4$ deposition is just one factor of many that regulates the emission of $CH_4$ from peat soils. The conclusion of other authors working in this field that $SO_4$ from volcanic depositions can suppress the emission of $CH_4$ from peatlands is perhaps too simplistic, as it does not take into account any of the other regulating factors. Peat soils are dynamic and heterogeneous by nature especially in regards to $CH_4$ emissions. It is therefore questionable whether data collected from a select number of pristine peatlands should be extrapolated out over the northern hemisphere without taking into account the background history, the peat type, vegetation type and density or water table levels of the peat soils. It can be seen from this experiment that the Moor House site does not behave as expected by the Michaelis-Menton model developed by Gauci et al. (2004b) (Fig. 3.10) which would have predicted a $CH_4$ suppression of 25-30% at the S deposition rate used. The suppression of $CH_4$ emission by $SO_4$ deposition has been modelled using results from field and lab experiments from four different peat bogs, two from the UK, one from Sweden and one in the USA (Gauci et al. 2004b). Using this model, Gauci et al. (2008) concluded that the emission, $SO_4$ aerosol cooling and subsequent deposition of $SO_4$ produced by the 8-month long Icelandic fissure eruption of Lakagigar in 1783 was sufficient to suppress $CH_4$ emissions by 14% (from 160 to 137 Tg year$^{-1}$). The majority of the total suppression occurred in latitudes north of 30°N where wetland $CH_4$ emissions were halved from ~42 Tg to ~22 Tg, of which 20% was the likely result of competitive exclusion of methanogenesis. However, all of the sites used to create the model are classed as pristine and so maybe the modelled relationship between S deposition and $CH_4$ flux only holds true for soils that have not been exposed to pollution sources previously.

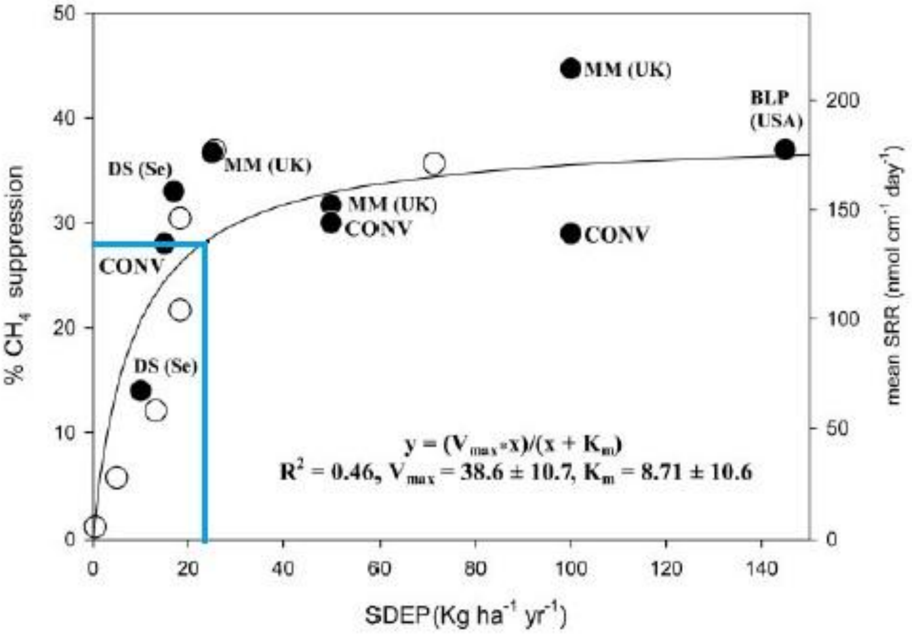


**Fig. 3.11** Modelled relationship between S deposition rate and % $CH_4$ suppression taken from Gauci et al. (2004b). The blue line indicates the S deposition rate used in the mesocosm study and the % $CH_4$ suppression that would be predicted by this model.

An alternative hypothesis for the lack of $SO_4$ response in $CH_4$ emissions is that the peat at Moor House has not fully recovered from the heavy S loadings it received in the past due to prolonged S deposition from anthropogenic acid rain. Recycling of this S within steep rhizosphere redox gradients is likely to have sustained higher rates of $SO_4$ reduction than would be suggested from current S deposition rates alone. In other words the emission of $CH_4$ is still suppressed as predicted by the Gauci model (Gauci et al. 2008), several decades after the rate of S deposition had decreased. Gauci *et al.* (2005) reported that it would take 5-10 years for $CH_4$ emissions to recover from a discrete short-term pollution event such as the Lakakigar eruption. However, the Pennines have received S inputs since the onset of the industrial revolution over 150 years ago and therefore, it is plausible that the $CH_4$ emission recovery period for these soils would be far longer than for such a short-term deposition event. This raises the intriguing possibility that for periods of very large and prolonged continental scale volcanism, recovery in wetland $CH_4$ emissions may take place only after several decades have past or possibly even centuries.

*Effects of Fluoride additions on $CH_4$ flux*

The effect of F on peatland gas fluxes has never before been assessed. The results of this experiment suggest that the deposition of F has no effect on $CH_4$ fluxes at concentrations that could possibly be leached from volcanic ash deposited on the surface of a peat bog. Fluoride has a number of characteristics that enable it to cause an impact on the natural environment. Fluorine is the most reactive and electronegative of all elements meaning that it has a powerful attraction to electrons and can attack other elements (Weinstein and Davison 2004). It has a small charge to radius ratio and so ranks highly in the selectivity series of anions for mineral surfaces meaning it could easily replace other anions on the exchange sites of soil minerals or organic matter (Sumner 1999). The behaviour of F in anion exchange reactions affects the biochemistry of soils, altering the pH and the bioavailability of other nutrients (Romar et al. 2009). Fluoride forms complexes with dissolved aluminium and ferric iron, which increases its mobility and thus its bioavailability potentially causing problems of toxicity to plants and micro-organisms (Elrashidi and Lindsay 1987). There are a number of ways in which F could potentially disrupt peatland processes and impact $CH_4$ fluxes these will be discussed below.

The toxicity of F to soil micro-organisms and microbial processes has been studied by many workers investigating the effects of Al smelters on surrounding soils (Nowak et al. 2005; Rao and Pal 1978; Tscherko and Kandeler 1997; Van Wensem and Adema 1991; Wilke 1987). In soils with highest concentrations of F, closest to the smelter, microbiological activities decreased to 5-20 % of those in the unpolluted soil (Tscherko and Kandeler 1997). An accumulation of organic matter has been reported in soils receiving high levels of F pollution due to the inhibition of microbial activities and a slowing down of decomposition processes (Rao and Pal 1978; Tscherko and Kandeler 1997; Wilke 1987). This could reduce substrate inputs to methanogens if they are not affected by direct toxicity of F. Fluoride has also been found to inhibit the growth and reproduction of micro-organisms (Treshow 1965) meaning that population numbers may not be sustained after the addition of F. The effect of F on biological wastewater treatment systems has recently been studied by Ochoa-Herrera et al. (2009). They found that addition of F to digested sewage sludge inhibited $CH_4$ production from mesophilic and thermophilic acetoclastic methanogens. Hydrogen utilising methanogens however tolerated F at very high concentrations (500 mg $l^{-1}$). These results suggest that F could have an effect on $CH_4$ fluxes from peat soils either through direct toxicity to acetoclastic methanogens, reducing $CH_4$ production and $CH_4$ flux or to methanotrophs thereby reducing $CH_4$ oxidation and increasing $CH_4$ flux to the atmosphere. Methyl fluoride ($CH_3F$) is commonly used as an inhibitor of $CH_4$ oxidation in lab experiments and has been found to inhibit acetoclastic methanogenesis (Frenzel and Bosse 1996; Janssen and Frenzel 1997). However, naturally occurring organofluorine compounds are rare and so it is unlikely that $CH_3F$ could be formed naturally in a peat bog due to volcanic deposition. Only 12 naturally occurring organofluorine compounds have been identified in a small number of tropical and sub-tropical plants although the origin remains unclear (Harper and O'Hagan 1994). Methyl fluoride has not been discovered in nature. Fluoride had no effect on $CH_4$ flux in this experiment, which suggests that the methanogens and methanotrophs were tolerant of F at the concentrations applied. It may also suggest that the main substrate for methanogenesis is $H_2$ rather than acetate as $H_2$ utilising methanogens are more tolerant to F than acetoclastic methanogens (Ochoa-Herrera et al. 2009). This is further supported by the fact that the increase in acetate concentration observed in the soil solution of the mesocosms that received high doses of F (Fig. 2.8) did not increase $CH_4$ emission rates (Fig. 3.3). During the period of July - September 2009, mean acetate concentrations at 0-10 cm in the mesocosms that were treated with Sulfate + High Fluoride exceeded 30 µmol $l^{-1}$. This is comparatively higher than concentrations of below 5 µmol $l^{-1}$ that were measured in the Control mesocosms over the same period. Although acetate concentrations in the Sulfate + High Fluoride mesocosms were over 6 times greater than in Control mesocosms there was no related $CH_4$ flux increase that would be expected if acetoclastic methanogenesis were taking place.

Fluoride can be toxic to plants depending upon the species, the concentration of F and the exposure duration. It may cause injury to susceptible plant species at atmospheric concentrations 10 to 1000 times lower than other pollutants (<1 ppb) (Garrec et al. 1984). Vegetation damage is mainly caused by exposure to gaseous F compounds but F can also be taken up through the roots from the soil or if F is dissolved in water on leaf surfaces it may be adsorbed by diffusion through the cuticle (Vike 1999). Visible injury symptoms such as necrosis and chlorosis have been reported in plants around industrial sources (Divan Junior et al. 2008; Klumpp et al. 1996; Vike 1999) and those exposed to volcanic emissions (Bellomo et al. 2007; Bellomo et al. 2003; Fridriksson 1983; Grattan and Pyatt 1994). In peatland ecosystems, plants are major transport pathways of $CH_4$ to the atmosphere. Up to 90% of $CH_4$ emissions may be via root transport where sedges are the dominating plant species (Schimel 1995). If vegetation is damaged by the addition of F, a greater proportion of the $CH_4$ produced in the catotelm will diffuse through the acrotelm where it can be oxidised to $CO_2$ therefore reducing $CH_4$ flux to the atmosphere. The oxidation of $CH_4$ to $CO_2$ in the acrotelm can reduce $CH_4$ flux to the atmosphere by up to 90% (Dedysh et al. 1998). If the vegetation is damaged it could also affect the supply of oxygen to the rhizosphere therefore reducing suitable supply of oxygen to methanotrophs. At the end of the experiment, sedge shoots did contain significantly higher concentrations of F and Al when compared to Control sedges (Table 2.9). However, photographs taken of the mesocosms over the duration of the experiment show no signs of visible injury to the vegetation species present, sedge density did not change (Fig. 3.5) and there was no significant effect on $CH_4$ flux. This may be due to the uptake of Al-F complexes, which are reported to be less toxic than F and Al species separately (Arnesen 1997; MacLean et al. 1992; Romar et al. 2009; Takmaz-Nisancioglu and Davison 1988).

The results of Chapter 2 showed that volcanic inputs containing $SO_4$ and F could affect the biogeochemical processes that occur in peatlands. The addition of F to peat soils resulted in a significant increase in concentrations of Al, Fe and acetate in solution, which suggests that F breaks down organo-metallic compounds causing leaching of organic matter along with metal ions. This may have important implications for microbial communities within the peat that are associated with decomposition of organic matter and carbon cycling. Iron is required by methanogens for growth and so an increase in solubility may have a positive effect on methanogens but, Ferric iron reducers may also be stimulated and compete with methanogens for substrates (Zinder 1993). A number of studies have reported that F addition to soils leads to an increase in solution pH as F replaces hydroxyl ions on minerals (Elrashidi and Lindsay 1987; Nowak et al. 2005; Romar et al. 2009; Wilke 1987). The pH did not change in the mesocosm study but this may be an important factor if F was applied to another soil as methanogens are very sensitive to changes in pH (Zinder 1993). The optimum pH for methanogenic activity is neutral to slightly alkaline (Williams and Crawford 1984). Methanotrophs are more tolerant to pH variations than methanogens (Zinder 1993). Fluoride is highly electronegative and so can easily displace other anions on exchange sites (Weinstein and Davison 2004). There is evidence that F replaced $SO_4$ on exchange sites in the soil. At the end of the experiment, concentrations of soil S were significantly lower in mesocosms receiving F when compared to Controls and concentrations of F were higher. The displacement of $SO_4$ from the soil would increase the $SO_4$ concentration of the soil solution, but this was not measured. If $SO_4$ reduction rates were high, this $SO_4$ would be quickly used up and therefore an increase in soil solution $SO_4$ concentrations would not be seen.

There was no effect on $CH_4$ flux with the addition of F to peat mesocosms. This could be due to the dilution of F in the waterlogged peat so that the F in solution was not at toxic levels to plants or microorganisms. The deposition rate of F used in the high F treatment was obtained from the leaching of volcanic ash from the 1970 eruption of Hekla, Iceland. The concentration of F used is greater than values reported from other volcanic ash leaching experiments (Bellomo et al. 2007; Cronin et al. 2003; de Hoog et al. 2001; Hinkley and Smith 1982; Nogami et al. 2001; Varekamp et al. 1984) but these studies use water-soluble F values for ash leachate composition. However, organic acids in the peat could cause greater leaching of ash particles than water as the insoluble F forms on the ash surface may be leached and so higher concentrations of F may be released. The low F treatment is a good proxy for anthropogenic emissions (Franzaring et al. 2006) as well as a wide range of volcanic eruptions (Armienta et al. 2002; Bellomo et al. 2007; Jones and Gislason 2008; Oskarsson 1980). This experiment has shown that $CH_4$ fluxes from the Moor House site would not be affected by the deposition of volcanic ash containing F. As discussed with $SO_4$, peat soils are different around the world and so the effects of F on other peat soils should be tested.

### 3.4.2 Carbon dioxide fluxes

The NEE was always negative as photosynthesis was the dominant process using more $CO_2$ than was being produced by respiration. The overall $CO_2$ balance for Moor House was estimated from mean NEE and ER values from the control mesocosms based on 12 hour daytime using NEE values and 12 hour night time using ER values. The calculation resulted in a value of 63 g C $m^{-2}$ $y^{-1}$, which means that Moor House is acting as a C sink. This is in accordance to Worrell et al (2003) who used modelled data to calculate an overall C budget for Moor House of 26.7 g C $m^{-2}$ $y^{-1}$ using a net $CO_2$ exchange of 55 g C $m^{-2}$ $y^{-1}$. It is also in accordance with a study by Lloyd (2010) who measured fluxes of $CO_2$ at Bog End, a site within the Moor House NNR (54° 41’ 27” N, 02° 21’ 50” W; 564m elevation). This site was an overall $CO_2$ sink of 173 g C $m^{-2}$ $y^{-1}$, which was a balance of an annual $CO_2$ uptake of 891 g C $m^{-2}$ as GPP and an annual $CO_2$ loss of 718 g C $m^{-2}$ as ER. There was no seasonal effect on NEE, GP or ER.

*Effects of Sulfate additions on $CO_2$ fluxes*

There was no effect of $SO_4$ addition to peat mesocosms on NEE, ER or GP. Dissimilatory $SO_4$ reduction is an anaerobic process coupled to the oxidation of organic C, which can lead to increased $CO_2$ emission as C from acetate and other organics is oxidised and released to the atmosphere. For every mole of $SO_4$ reduced, 2 moles of $CO_2$ are produced (Conrad, 1989). Vile et al (2003) tested this theory and found that increased $SO_4$ reduction did not lead to increased $CO_2$ production. Whereas, Yavitt (1987) found that $CO_2$ production was stimulated by the addition of $SO_4$ but there was not a proportional increase in $CO_2$ production to exactly compensate for the decrease in $CH_4$ production. It is not surprising that $SO_4$ did not affect $CO_2$ fluxes as there was no change in $CH_4$ fluxes indicating that the balance between methanogenesis and $SO_4$ reduction was unchanged.

*Effects of Fluoride additions on $CO_2$ fluxes*

Addition of F to the peat mesocosms had no effect on $CO_2$ fluxes. Other experimental work has been carried out to investigate the effects of F on respiration and photosynthesis, but there have been mixed results. Wilke (1987) found no effect of F additions of up to 3700 mg $kg^{-1}$ to mull, moder and mor soils on respiration or $CO_2$ production. This is in contrast to findings by Van Wensem and Adema (1991) who found an increase in respiration rate and total $CO_2$ production with the addition of 170 µmol $g^{-1}$ F to poplar litter. Fluoride has also been shown to either stimulate or inhibit respiration in plants depending on a number of factors such as plant species, F concentration, exposure duration, age of tissues and interactions between F and mineral elements (Weinstein and Davison 2004). It is thought that F changes the glucose catabolism via the respiratory pathways which results in changes in oxygen consumption and $CO_2$ evolution (Miller 1993). There have been many studies on the effect of F on photosynthesis; some show an inhibition others show no effect. F can combine with the $Mg^{2+}$ of chlorophyll to inhibit photosynthesis in mosses and lichen (LeBlanc et al. 1971). Photosynthesis was inhibited in pine and hardwood trees after foliage uptake of NaF (McLaughlin and Barnes 1975). There is evidence that the effects of photosynthesis are linked to visible injury symptoms from F exposure (Weinstein and Davison 2004). There was no visible damage to mesocosm vegetation after the addition of F, which may be a reason why no effect on photosynthesis was seen.

## 3.5 Conclusion

Application of $SO_4$ and F to the Moor House peat soils had no effect upon $CH_4$ and $CO_2$ gas fluxes. There was no evidence of $CH_4$ emission suppression with the addition of $SO_4$ at a rate of 73.7 Kg $ha^{-1}$ over 20 weeks. There are two possible reasons for this; firstly, it may be due to peat soil heterogeneity with local conditions, i.e., microbial communities and peat composition etc. playing a more important role in regulating $CH_4$ fluxes than S inputs. An alternative explanation may be that past anthropogenic S pollution at the sampling site may mean that the suppressive effect of sulfate on methane emission was already at its limit, i.e., $SO_4$ availability within the peat was such as to render $CH_4$ emissions insensitive to additional experimental $SO_4$ inputs. These findings highlight the complexity of the relationship between S deposition and $CH_4$ suppression and point to a very long period of $CH_4$ emission recovery in peats subjected to past high S deposition events.

This study found no effect of F addition of 13.5 and 135 kg $ha^{-1}$ on C gas fluxes from the mesocosm peat soils, despite the potentially toxic and reactive nature of F.  There was evidence of F uptake by *Eriophorum* shoots, but there were no signs of visible injury.  Plant damage through F toxicity is species dependent therefore other peatland species may be more sensitive which would have implications for $CH_4$ transport to the atmosphere.  Although there was no effect of F on $CH_4$ emissions from Moor House peat soils, further studies should investigate the effect of F in combination with $SO_4$ on fens and other peat types as F may have an effect on different pathways of $CH_4$ production, e.g., acetoclastic methanogenesis.  This information may be important to improve our understanding of the effects of volcanic deposition on terrestrial ecosystems.

# Chapter 4: The use of incubation experiments to assess the effects of volcanic deposition on potential methane production and oxidation

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## 4.1 Introduction

The results presented in Chapter 3 illustrated that the addition of $SO_4$ and F at realistic concentrations that could be leached from distal volcanic ash deposition, had no effect on the emissions of $CH_4$ or $CO_2$ from peat mesocosms. In the mesocosm experiment, water table levels were fixed at the surface to reduce $CH_4$ oxidation and focus on the effects of $CH_4$ production alone, therefore there may have been effects at the process level that were not seen due to the preference for $CH_4$ production over $CH_4$ oxidation. An alternative hypothesis as to why no suppression of $CH_4$ was observed is that if $CH_4$ production was reduced but $CH_4$ oxidation was also reduced there would be no overall effect on emissions due to the levelling out of the two $CH_4$ processes. Therefore by looking at these two processes separately any effects of $SO_4$ or F addition on $CH_4$ fluxes may be seen.

In Chapter 2, the addition of High Fluoride treatments to the mesocosms caused increased uptake of F, probably in the forms of Al-F complexes, in *Eriophorum vaginatum* shoots (Fig. 2.16). This sedge species acts as a major transport route for $CH_4$ to the atmosphere as the gas travels through the aerenchyma therefore bypassing the oxidation zone in the peat (Schimel 1995; Whiting and Chanton 1992). Although there were no visible signs of damage to the sedges, the Al-F complexes may have caused damage internally to the sedges, which may reduce $CH_4$ transport from the soil. Therefore if $CH_4$

production rates were increased but transport through sedges was reduced, there would be no increase in overall $CH_4$ emissions. It is therefore important to assess the effect of the treatments without the presence of vegetation as this may mask any microbiological effects within the soil.

One way to measure the $CH_4$ production and oxidation rates of the soil is to incubate small samples of the peat in bottles under anaerobic or aerobic conditions respectively and measure headspace concentrations of $CH_4$ over time. There have been a number of peat incubation experiments focussing on the effects of $SO_4$ addition on $CH_4$ production rates alone (Blodau and Moore 2003; Eriksson et al. 2010; Gauci and Chapman 2006; Nedwell and Watson 1995; Vile et al. 2003; Watson and Nedwell 1998; Yavitt et al. 1987). These lab-based experiments have been carried out by incubating peat samples from experimental treatment plots or mesocosms under controlled conditions of temperature and light, to estimate potential $CH_4$ production and oxidation rates. A number of these investigations have found no effect or variable effects of $SO_4$ addition on $CH_4$ production rates dependant upon the location of the peat in the soil profile (Table 4.1).

The objective of this chapter was to use lab incubations to investigate:

1. If the F and $SO_4$ treatments, at the end of the treatment period of 20 weeks, applied as part of the Moor House mesocosm experiment had any effect upon the individual processes of $CH_4$ production or $CH_4$ oxidation without the presence of vegetation.

2. If the F and $SO_4$ treatments applied throughout the experiment had an effect upon microbial biomass.

3. If similar F and $SO_4$ treatments were applied to peat sampled from a pristine peat bog in Scotland would the short-term results be the same as for the mesocosm peats.

To meet these objectives, peat samples from the Moor House mesocosms (a the end of the 20-week treatment period) and collected from a pristine Scottish peat bog (Moidach) were incubated in the laboratory and rates of $CH_4$

production and oxidation measured. The laboratory experiments were designed to investigate the following research hypotheses:

### *Moorhouse mesocosms at end of 20-week treatment period*

*The effects of $SO_4$ and F treatments on peat soil $CH_4$ production and $CH_4$ oxidation potentials*

- Fluoride addition decreases both $CH_4$ production and $CH_4$ oxidation potentials.
- Sulfate addition would have no effect on $CH_4$ production or $CH_4$ oxidation potentials.
- The co-addition of $SO_4$ and F would have the same effect as if F was added alone.

*The effects of F and $SO_4$ treatments on aerobic and anaerobic peat soil respiration*

- Addition of F will decrease soil respiration.
- The addition of $SO_4$ would have no effect on soil respiration.
- The co-addition of $SO_4$ and F would have the same effect as if F was added alone.

*The effects of F and $SO_4$ treatments on microbial biomass*

- Mesocosms that received F treatments would have a lower microbial biomass due to the toxicity of F.
- The addition of $SO_4$ would have no effect on microbial biomass.
- The co-addition of $SO_4$ and F would have the same effect as if F was added alone.

***Pristine peat bog (Moidach)***

*The effects of F and $SO_4$ treatments on pristine peat soil $CH_4$ production and $CH_4$ oxidation potentials*

- Increased $SO_4$ in soil solution will stimulate a population of $SO_4$ reducing bacteria to outcompete methanogens for substrates thus reducing $CH_4$ production potentialFluoride addition decreases both $CH_4$ production and $CH_4$ oxidation potentials. The co-addition of $SO_4$ and F decreases both $CH_4$ production and $CH_4$ oxidation potentials.

**Table 4.1** Summary of previous peat incubation experiments investigating the effects of $SO_4$ on methane production rates

| Study | Peat type | Sulfate addition | Suppression observed |
|---|---|---|---|
| Eriksson et al. (2010) | Oligotrophic mire. Degerö stormyr, Sweden | Used peat that had been treated with 20 kg S $ha^{-1}$ $y^{-1}$ for 12 years | No effect at the depth of maximum $CH_4$ production, but 8 cm above this depth, $CH_4$ production rates were significantly reduced by 45% when compared to controls. |
| Gauci and Chapman (2006) | Pristine raised mire. Moidach More, Northeast Scotland | Used peat that had been treated with 50 kg S $ha^{-1}$ $y^{-1}$ previously | Found no significant difference between the methane oxidation potential of treatments and controls. |
| Blodau and Moore (2003) | Oligotrophic peatland.<br>Mer Bleue site, Ontario, Canada | 500 µM $Na_2SO_4$ | $CH_4$ production significantly increased by ~50% in the surface layers and significantly reduced by ~40 % in deeper peat layers. |
| Vile et al. (2003) | Ombrotrophic bog. Bleak lake bog, Alberta, Canada | Used peat treated with 80.5 mmol $m^{-2}y^{-1}$ previously | No significant treatment effect on $CH_4$ production rates |
| Watson and Nedwell (1998) | Ombrotrophic bog. Ellergower Moss, Southwest Scotland and Great Dun Fell, Cumbria, England | Ellergower: 50, 100, 250, 500 and 1000 µM<br>Great Dunn Fell: 250, 500, 1000 and 5000 µM<br>Sulfate added as $Na_2SO_4$ | Ellergower: addition of 500 and 1000 µM significantly reduced methane production. 50 and 100 µM had no significant effect.<br>Great Dunn Fell: Production was more than halved by addition of 250 µM, additions above this caused further suppression. |
| Nedwell and Watson (1995) | Ombrotrophic bog. Ellergower Moss, Southwest Scotland | 50, 100, 250, 500, 1000 and 5000 µM $SO_4$ | Addition of 5000 µM inhibited methane production by 49 %. Concentrations above 500 µM significantly decreased the rate of methane production. |
| Yavitt et al. (1987) | Sphagnum-dominated peat. Big run bog, West Virginia | Final $SO_4$ concentration of 0.1, 1 and 5 mM $l^{-1}$ | $CH_4$ production decreased with increasing rates of $SO_4$ at 0-25 cm. At 30-45 cm, there was a 4-fold increase in $CH_4$ production in the 0.1 mmol $l^{-1}$ treatment and rates higher than controls in the other treatments. |

## 4.2 Methodology

### 4.2.1 Moor House mesocosm soils

*Mesocosm experiment*

Peat mesocosms were collected from the Moor House NNR in the northern Pennine uplands of the UK. Full details of the site description and sampling methods can be found in section 2.2. The mesocosms received additions of $SO_4$ and F on a weekly basis for 20 weeks and the effects of these additions on $CH_4$ flux (Chapter 3) and soil solution chemistry (Chapter 2) were assessed. Five different treatments were applied to the mesocosms, these were: Control, Sulfate, Sulfate + High Fluoride, High Fluoride and Sulfate + Low Fluoride. Each treatment had six replicates. The total amount of $SO_4$ and F that the mesocosms received over the 20-week treatment period can be found in Table 4.2. The soils from these mesocosms were then used to assess whether the treatments received had any effect upon the potential $CH_4$ production or oxidation rates of the soil.

**Table 4.2** Amounts of $SO_4$ and F applied to peat mesocosms over the 20-week treatment period

| Treatment | Amount (μM) | |
|---|---|---|
| | F | $SO_4$ |
| Control | Deionised water | |
| Sulfate | - | 2109 |
| Sulfate + High Fluoride | 19582 | 2109 |
| High Fluoride | 19582 | - |
| Sulfate + Low Fluoride | 1953 | 2109 |

### *Soil sampling*

At the end of the mesocosm experiment described in Chapters 2 and 3, the vegetation layer was removed from each mesocosm and samples of peat soil were collected from 0-10 cm and 10-20 cm. The samples were placed in bags and returned to the laboratory. Here the soil was sorted inside a glove box containing oxygen-free nitrogen (OFN) to remove large roots and plant parts and then homogenised. A 10 g sub-sample of each soil was weighed and then dried in the oven at 70 °C for 24 hours to determine the water content of the soil. Peat samples were stored in the fridge until they were ready to be analysed.

### *Potential $CH_4$ production measurement*

For each sample, 15 g of peat was added to a 100 ml Wheaton bottle along with 10 ml of deionised water, the resulting slurry was mixed well. The pH of the soil slurry was measured using a glass/calomel electrode and pre-calibrated Thermo Orion pH meter (model 420 A+). The headspace of the bottle was then flushed with OFN for two minutes to create anoxic conditions. The flask was then sealed with a rubber septa and an aluminium crimp cap to ensure the bottle was airtight. It was of the greatest importance to reduce oxygen concentrations in the bottles as much as possible to prevent toxicity to the methanogens.

The headspace of the bottle was sampled immediately after it was sealed (t=0) by adding 6 ml of OFN using a 10 ml syringe. The syringe was left in the stopper for one minute and then it was used to mix the headspace gas before the sample was taken. Mixing was carried out by filling and emptying the syringe three times and was important to ensure even distribution of headspace gases.

Finally, a 6 ml sample of the headspace was removed and injected into a 3 ml pre-evacuated septum-capped glass vial (Exetainer, Labco ltd). The 6 ml of OFN was added at the beginning to replace the sample that would be removed so that the change in headspace volume did not affect the gas pressure within the headspace. The exact time of gas sampling was noted and the bottles were incubated in the dark at 20°C until the next sample was taken. Sampling was carried out at t= 0, 1, 2, 4, 8, 24, 48 and 72 hours. Gas samples were analysed for $CH_4$ and $CO_2$ concentrations using a Perkin Elmer-Arnel gas chromatograph (AutoSystem XL, Perkin Elmer Instruments, Shelton, CT, USA) equipped with a flame ionisation detector and a 3.7 m Porapak Q 60/80 mesh column ($N_2$ carrier gas flow of 30 ml $min^{-1}$; and injector, column and detector temperatures of 120, 40 and 350 ºC, respectively).

After the last headspace samples had been taken, the caps were removed from the bottles and the pH of the soil slurries was measured again. The volume of the headspace of each bottle was then determined by weighing the bottle, filling it with water and then weighing it again. The difference in weight (g) is the same as the headspace volume in ml.

### *Potential $CH_4$ oxidation measurement*

To measure the potential $CH_4$ oxidation rates of the peat, the soil was first aerated, as this is an aerobic process, which is restricted by oxygen supply. For each soil sample, 15 g of peat was weighed into a Wheaton bottle. The top of each bottle was covered with parafilm, which was punctured with a needle. The bottles were stored in the dark at 20°C for 24 hours to aerate the soils. When the bottles had been aerated, 2 ml of deionised water was added to each to create a slurry. The bottles were then taken outside for thirty minutes to stabilise $CO_2$ concentrations, which would have built up in the headspace. The pH of the soil slurries was measured as above and the bottles were sealed with a rubber septa and an aluminium crimp cap. The bottles were then returned immediately to the laboratory for sampling.

To each bottle, 5 ml of 2000 ppm $CH_4$ and 1 ml of air was added at t=0 to give an initial concentration of approximately 100 ppm in the bottle. The headspace was then sampled by inserting a 10 ml syringe into the septa and mixing the headspace gas as above, before removing a 6 ml sample. Gas samples were injected into 3 ml Exetainers and stored until analysis by gas chromatography. Bottles were incubated in the dark at approximately 20°C on a shaker in between sampling times. The headspace of the bottles was sampled at t= 0, 1, 2, 4, 8 and 24 hours. For sampling points after t= 0, 6 ml of air was added to the bottles before the sample was taken to prevent changes in gas pressure within the bottles that could affect emissions of $CH_4$ or $CO_2$ from the soil.

At the end of the sampling period, the pH of the soil slurries was measured and the volume of the headspace of each of the bottles calculated as with the potential $CH_4$ production bottles.

*Calculations*

The headspace concentrations of $CH_4$ and $CO_2$ measured by GC were corrected for the removal of 6 ml of headspace gas during sampling and the dilution of the headspace when 6 ml of $N_2$ or air was added at each sampling time. The corrected concentrations were then converted from ppm to µg g $soil^{-1}$ on a dry weight basis. The concentration of $CH_4$ and $CO_2$ dissolved in soil water was then calculated using Henry's law adjusted for the appropriate temperature and pH (Stumm and Morgan 1981). For $CO_2$, the fraction of total inorganic C ($HCO_3^-$ form) dissolved in the soil water was also calculated. Headspace concentrations and soil water concentrations were summed to give total $CH_4$ and $CO_2$ concentrations at each sampling time. Methane and $CO_2$ fluxes were calculated using simple linear regressions of headspace concentrations versus sampling time to give a rate of $CH_4$ and $CO_2$ emission for each bottle expressed as µg $m^{-2}$ $h^{-1}$. Bottles which had a $r^2 < 0.9$ were rejected and the rate of $CH_4$ /$CO_2$ emission was assumed to be zero when there was no change or negligible change in concentration over the sampling period, otherwise the measurement was discarded.

*Microbial biomass*

Microbial biomass C and N were measured using a method adapted from Voroney et al. (2003) to assess if there was any significant difference between treatments.  For each mesocosm at each depth, three 20 g samples were weighed out.  One was oven dried at 105 ºC for 24 hours to determine the water content of the soil.  One of the samples was used as a control and was immediately extracted using a $K_2SO_4$ solution.  The other sub-sample was put into a 100 ml glass beaker to be fumigated with chloroform before the extraction procedure.

The soil samples for fumigation were placed inside a desiccator in a fume hood with a 100 ml beaker containing 50 ml $CHCl_3$ and a few boiling chips.  The desiccator was sealed and evacuated until the $CHCl_3$ boiled vigorously for approximately one minute.  The desiccator was then sealed under vacuum, placed in the dark at 25 ºC for 24 hours.  After fumigation, the desiccator was repeatedly evacuated to remove all of the $CHCl_3$ from the samples.

To extract both the control samples and the fumigated samples, each sample was placed in plastic bottle.  To the bottle, 6 ml of 0.5 M $K_2SO_4$ was added to give an oven dry soil weight (g) : extraction volume (ml) of approximately 1:4.  The bottles were capped and put on a shaker for 1 hour.  After shaking the samples were filtered using Whatman No. 5 filter papers and stored at 4 ºC until they were ready for analysis.  Organic C in the extracts was measured using a TOC analyser (LiquiTOC, Elementar Analseneysteme, Hanau, Germany).  Total N was determined colourimetrically using an AutoAnalyser II system.

### 4.2.2 Moidach More soils

*Sampling site description*

To investigate the short-term effects of $SO_4$ and F on $CH_4$ production and oxidation, soils were also collected from Moidach More (57.46ºN, 3.62ºW), a pristine raised peat bog in Morayshire, NE Scotland.  This site was chosen because it has had low S deposition in the past (Gauci and Dise 2002) and was used for long term $SO_4$ addition field experiments investigating the effects of acid rain $SO_4$ on $CH_4$ emission (Gauci and Dise 2002).  The authors found that the addition of 25 Kg S $ha^{-1}$ $y^{-1}$ for 18 months suppressed $CH_4$ emission of treatment plots by 36 % when compared to control plots.

### *Soil sampling and sorting*

At the site, three soil pits were dug randomly where the vegetation was uniform. The vegetation layer was removed and soil was sampled in large chunks at 0-20 cm. The samples were tightly bagged to remove air and stored in cool boxes whilst transported back to the University of York. Peat samples from the centre of the soil chunks were sorted under anaerobic conditions in a glove bag to remove large roots and stones and then homogenised.

### *Treatment application*

Five different F and $SO_4$ treatments were applied to the peat to investigate the effects of volcanic deposition. These were: Control, Sulfate, Sulfate + High Fluoride, High Fluoride and Low Fluoride. The treatments were based upon ash leachate values found in the literature. Five replicates were used for each treatment.

### *Potential measurements*

Potential measurements were carried out using the same method as for the mesocosm soils but 30 g of peat was used in each bottle instead of 15 g and the treatments described in Table 4.3 were used to make the slurry rather than deionised water. Methane production rates for the Moidach more peat soils were much slower than the mesocosm peat soils and so bottles were sampled at t= 0, 1, 2, 3, 4, 5, 6 and 7 days. Methane oxidation bottles were sampled at t= 0, 2, 4, 6, 8 and 24 hours. Methane and $CO_2$ production rates were calculated in the same way as above.

**Table 4.3** Treatments applied to incubations of peat soil sampled from Moidach More, Scotland

| Treatment | Concentration (μmol) | |
|---|---|---|
| | $CH_4$ production bottles, 15 ml of: | $CH_4$ oxidation bottles, 2 ml of: |
| Control | Deionised water | |
| Sulfate | 2500 μM $Na_2SO_4$ | 18750 μM $Na_2SO_4$ |
| Sulfate + High Fluoride | 2500 μM $Na_2SO_4$ + 5000 μM NaF | 18750 μM $Na_2SO_4$ + 37500 μM NaF |
| High Fluoride | 5000 μM NaF | 37500 μM NaF |
| Low Fluoride | 50 μM NaF | 375 μM NaF |

### 4.2.3 Statistical analysis

To investigate whether treatment had an effect on potential $CH_4$ production and oxidation, $CO_2$ production and microbial biomass, U-ANOVA was used followed by a Tukey HSD post hoc test to look for differences between groups or a Dunnett 2 sided t test to compare treatment groups against Controls. The data were normally distributed and the variances equal and so no transformation was required ($p > 0.05$). The only exception was the mesocosm $CH_4$ production and oxidation results, which were analysed non-parametrically using the Kruskal Wallis test to assess whether concentrations of $CH_4$ in the treatment bottles were significantly different to the Control concentrations. If the test revealed a significant result, it was followed by a series of Mann-Whitney tests to test the treatment groups against the Controls to investigate what the significant differences were. All statistical analysis was performed with SPSS Statistics 17.0.

## 4.3 Results

### 4.3.1 Moor House mesocosm study incubations

*Methane production and oxidation potentials*

Potential $CH_4$ production was greatest in peat sampled at 0-10 cm for all incubations apart from those which received Sulfate + Low Fluoride treatments where greatest $CH_4$ production was observed at a depth of 10-20 cm (Fig. 4.1). At 0-10 cm, $CH_4$ production in the Sulfate + High Fluoride slurries was five times greater than that of the control. Methane production in the Sulfate + Low Fluoride soils was 90% lower than in the Controls. However, due to a large standard deviation statistical analysis reported no significant difference between treatments (H= 4.51, n=5, *p*=0.34) (Table 4.4). At 10-20 cm, $CH_4$ production rates from $SO_4$ mesocosms were approximately 50 % lower than that of the controls. Peat incubations from the High fluoride and the Sulfate + High Fluoride treated mesocosms also emitted less $CH_4$ when compared to the controls. These results were not significant (H=4.54, n=5, *p*=0.34).

Rates of potential $CH_4$ oxidation were greater at 10-20 cm than at 0-10 cm for all treatments apart from Sulfate, which oxidised half the amount of $CH_4$ of the controls at 10-20 cm (Fig. 4.1). At 0-10 cm and 10-20 cm all treatments had lower rates of $CH_4$ oxidation when compared to the controls. Peat soils treated with High fluoride oxidised approximately 50% less $CH_4$ than controls at both depths. There is very little difference between emission rates from peat which received Sulfate + Low Fluoride and the controls at 10-20 cm. There was no significant treatment effect at either depth (0-10 cm: *p*=0.24, 10-20 cm: *p*= 0.15) (Table 4.4).

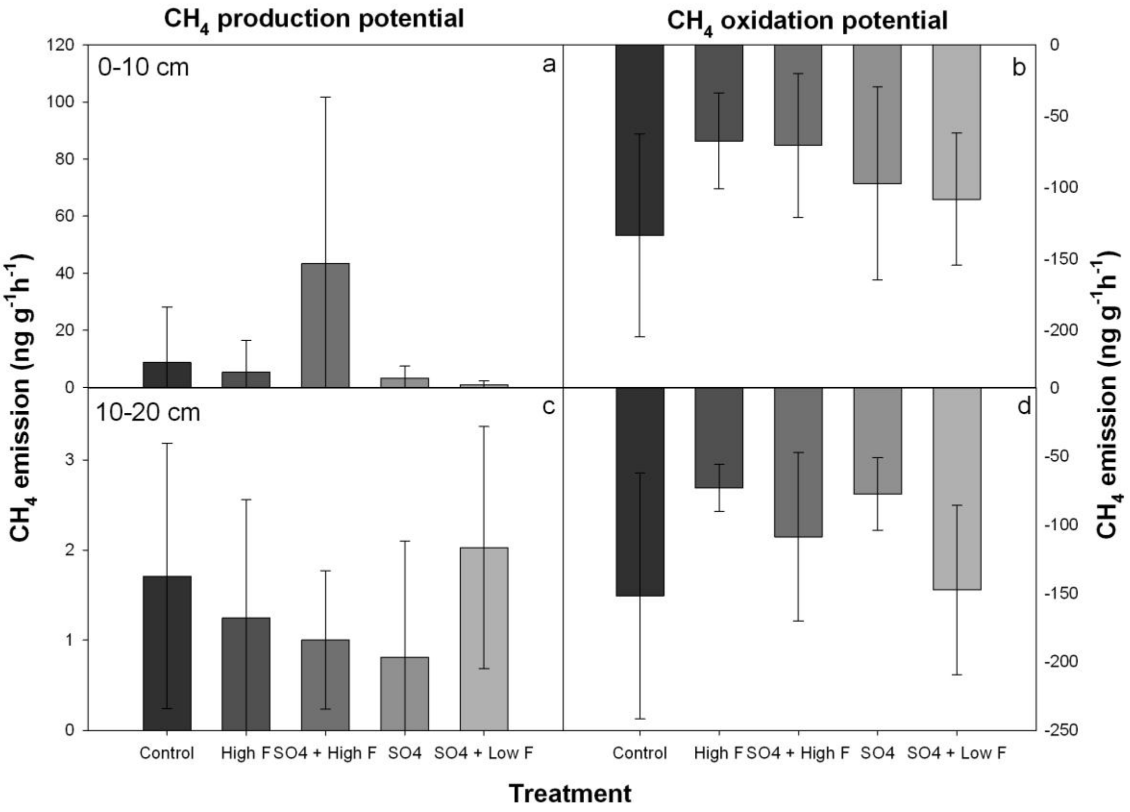


**Fig. 4.1** Potential $CH_4$ production and oxidation of mesocosm peat samples at the end of the treatment period. Samples taken at 0-10 cm (a and b) and 10-20 cm (c and d). Bars represent the average $CH_4$ emission of 6 replicates and errors bars represent standard deviation.

**Table 4.4** Summary of mesocosm potential $CH_4$ production and oxidation rates

| | Treatment | Mean $CH_4$ emission rates (ng $g^{-1}h^{-1}$) (± Std Dev) | Chi Square | $p^a$ |
|---|---|---|---|---|
| $CH_4$ production 0-10 cm | Control | 8.70 (19.47) | 4.51 | 0.34 |
| | High Fluoride | 5.40 (11.02) | | |
| | Sulfate + High Fluoride | 43.34 (58.32) | | |
| | Sulfate + Low Fluoride | 0.92 (1.40) | | |
| | Sulfate | 3.28 (4.19) | | |
| $CH_4$ production 10-20 cm | Control | 1.71 (1.47) | 4.54 | 0.34 |
| | High Fluoride | 1.25 (1.31) | | |
| | Sulfate + High Fluoride | 1.00 (0.77) | | |
| | Sulfate + Low Fluoride | 2.03 (1.34) | | |
| | Sulfate | 0.81 (1.29) | | |
| | | | | |
| $CH_4$ oxidation 0-10 cm | Control | -133.42 (71.24) | 5.50 | 0.24 |
| | High Fluoride | -67.27 (33.70) | | |
| | Sulfate + High Fluoride | -70.45 (50.42) | | |
| | Sulfate + Low Fluoride | -108.11 (46.35) | | |
| | Sulfate | -97.14 (67.66) | | |
| $CH_4$ oxidation 10-20 cm | Control | -151.84 (89.85) | 6.79 | 0.15 |
| | High Fluoride | -72.99 (17.31) | | |
| | Sulfate + High Fluoride | -108.59 (61.60) | | |
| | Sulfate + Low Fluoride | -147.54 (61.78) | | |
| | Sulfate | -77.46 (26.64) | | |

[a] Values were generated using Kruskal-Wallis non parametric test.

*Aerobic and anaerobic respiration*

Aerobic and anaerobic respiration was greater at 0-10 than 10-20 cm (Fig. 4.2). Aerobic respiration was always greater than anaerobic respiration rates. Lowest respiration rates were recorded in the soils sampled from 10-20 cm under anaerobic conditions. There were no significant treatment effects on soil respiration $CO_2$ emission at either depth or under aerobic or anaerobic conditions (Table 4.5). However, respiration rates from the Sulfate + High Fluoride treated soils were 30% greater than from Control soils under anaerobic conditions, which was of borderline significance (p=0.058 (Dunnett 2-sided t-test)).

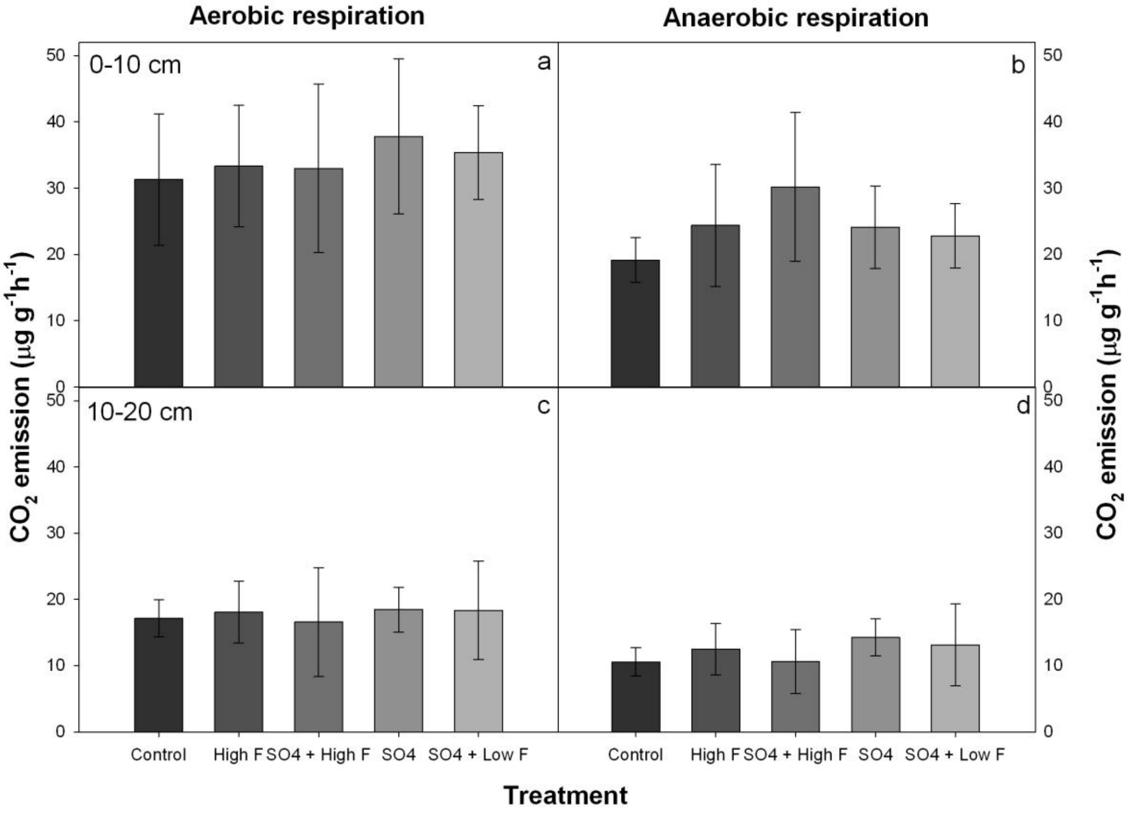


**Fig. 4.2** Aerobic and anaerobic respiration of mesocosm peat samples at the end of the treatment period. Samples taken at 0-10 cm (a and b) and 10-20 cm (c and d). Bars represent the average respiration rate of 6 replicates and errors bars represent standard deviation.

**Table 4.5** Summary of anaerobic and aerobic $CO_2$ production from mesocosm study

| | Treatment | Mean $CO_2$ concentration (µg $g^{-1}h^{-1}$) (± Std Dev) | Between subjects effects: Treatment | p value [a] Control Versus treatment |
|---|---|---|---|---|
| Anaerobic respiration 0-10 cm | Control | 19.14 (3.38) | F= 1.67<br>*P*= 0.19 | n/a |
| | High Fluoride | 24.37 (9.19) | | 0.75 |
| | Sulfate + High Fluoride | 30.19 (11.22) | | 0.11 |
| | Sulfate + Low Fluoride | 22.81 (4.85) | | 0.92 |
| | Sulfate | 24.10 (6.23) | | 0.79 |
| Anaerobic respiration 10-20 cm | Control | 10.57 (2.15) | F=0.88<br>*P*= 0.49 | n/a |
| | High Fluoride | 12.51 (3.90) | | 0.93 |
| | Sulfate + High Fluoride | 10.59 (4.83) | | 1.00 |
| | Sulfate + Low Fluoride | 13.12 (6.19) | | 0.83 |
| | Sulfate | 14.26 (2.81) | | 0.57 |
| | | | | |
| Aerobic respiration 0-10 m | Control | 31.31 (9.90) | F= 0.13<br>*P*= 0.97 | n/a |
| | High Fluoride | 33.34 (9.16) | | 1.00 |
| | Sulfate + High Fluoride | 32.99 (12.74) | | 1.00 |
| | Sulfate + Low Fluoride | 35.40 (7.09) | | 0.96 |
| | Sulfate | 37.83 (11.74) | | 0.81 |
| Aerobic respiration 10-20 cm | Control | 17.14 (2.82) | F= 0.36<br>*P*= 0.84 | n/a |
| | High Fluoride | 18.07 (4.68) | | 1.00 |
| | Sulfate + High Fluoride | 16.58 (8.24) | | 1.00 |
| | Sulfate + Low Fluoride | 18.36 (7.44) | | 1.00 |
| | Sulfate | 18.48 (3.38) | | 0.99 |

[a] *p* values indicate the significance of treatment effects on mean $CO_2$ concentration when compared to the control soils. Values were generated using univariate ANOVA Tukey HSD Post Hoc comparisons.

*Microbial biomass*

There were significant treatment effects for microbial biomass C (0-10 cm: F= 4.22, *p*= 0.01) and microbial biomass N (0-10 cm: F= 4.28, p= 0.01). A Tukey HSD post hoc comparison revealed the majority of differences to be between the Sulfate + Low Fluoride mesocosms and the mesocosms, which received additions of Sulfate + High Fluoride and High Fluoride alone (Fig. 4.3 and Table 4.6).

For the microbial biomass C experiments at 0-10 cm there were no significant differences between the controls and the treatments however, there was a significant difference between two of the treatment groups (Fig. 4.3). The Sulfate + Low Fluoride treated mesocosms had significantly more C than the Sulfate + High Fluoride treated mesocosms, 7.98 mg $g^{-1}$ compared to 3.26 mg $g^{-1}$ respectively (Table 4.6). The Sulfate + Low Fluoride treated mesocosms also had greater concentrations of C than the High Fluoride treated mesocosms but this result was only of borderline significance (*p*= 0.06). At 10-20 cm, there was no significant difference between any of the treatment groups or the controls. The Sulfate + Low Fluoride mesocosms did have considerably higher C concentrations than the Controls (5.63 mg $g^{-1}$ compared to 3.07 mg $g^{-1}$) (Fig. 4.3) but this result was not statistically significant due to the large standard deviation of the Sulfate + Low Fluoride samples (Table 4.6).

The results of the microbial biomass N analysis at 0-10 cm showed no significant difference between either of the controls and the treatments (Table 4.6). One comparison was of borderline significance (*p*= 0.06) this was the Control versus Sulfate + Low Fluoride. This treatment had approximately double the N concentration of the Control. There were significant differences in N concentrations between treatment groups as with the microbial biomass C concentrations at 0-10 cm. The concentrations of microbial biomass N in the High Fluoride and the Sulfate + High Fluoride treated mesocosms were significantly lower than the N concentration in the Sulfate + Low Fluoride mesocosms (*p*= 0.01 and 0.02 respectively). At 10-20 cm, there were no significant differences between treatment groups and controls.

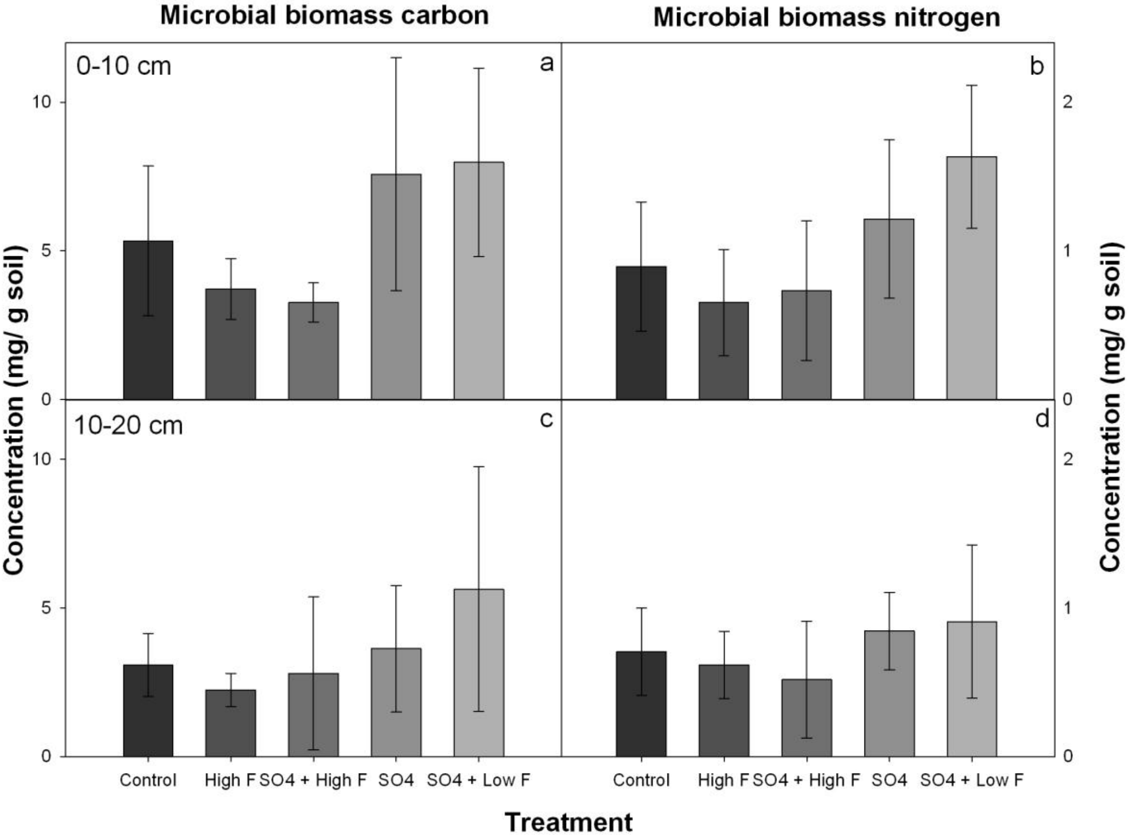


**Fig. 4.3** Microbial biomass carbon and nitrogen of mesocosm peat samples at the end of the treatment period. Samples taken at 0-10 cm (a and b) and 10-20 cm (c and d). Bars represent the average microbial biomass of 6 replicates, errors bars represent standard deviation.

**Table 4.6** Summary of average microbial biomass carbon and nitrogen from mesocosm study

| | Treatment | Mean concentration (mg $g^{-1}$ soil) (± Std Dev) | Between subjects effects: Treatment | *p* value [a] Control Versus treatment |
|---|---|---|---|---|
| Microbial biomass carbon 0-10 cm | Control | 5.33 (2.52) | F = 4.22<br>*p* = 0.01 | n/a |
| | Sulfate | 7.58 (3.91) | | 0.57 |
| | Sulfate + High Fluoride | 3.26 (0.66) | | 0.64 |
| | High Fluoride | 3.71 (1.03) | | 0.81 |
| | Sulfate + Low Fluoride | 7.98 (3.17) | | 0.41 |
| Microbial biomass carbon 10-20 cm | Control | 3.07 (1.06) | F = 1.73<br>*p* = 0.17 | n/a |
| | Sulfate | 3.63 (2.13) | | 1.00 |
| | Sulfate + High Fluoride | 2.80 (2.57) | | 1.00 |
| | High Fluoride | 2.24 (0.56) | | 0.98 |
| | Sulfate + Low Fluoride | 5.63 (4.12) | | 0.38 |
| Microbial biomass nitrogen 0-10 cm | Control | 0.89 (0.43) | F = 4.28<br>*p* = 0.01 | n/a |
| | Sulfate | 1.21 (0.53) | | 0.80 |
| | Sulfate + High Fluoride | 0.67 (0.59) | | 0.94 |
| | High Fluoride | 0.61 (0.45) | | 0.86 |
| | Sulfate + Low Fluoride | 1.63 (0.48) | | 0.11 |
| Microbial biomass nitrogen 10-20 cm | Control | 0.70 (0.29) | F = 1.23<br>*p* = 0.32 | n/a |
| | Sulfate | 0.84 (0.26) | | 0.96 |
| | Sulfate + High Fluoride | 0.52 (0.39) | | 0.89 |
| | High Fluoride | 0.62 (0.23) | | 0.99 |
| | Sulfate + Low Fluoride | 0.91 (0.51) | | 0.86 |

[a] *p* values indicate the significance of treatment effects on mean microbial biomass C when compared to the control soils. Values were generated using univariate ANOVA Tukey HSD Post Hoc comparisons. Values in bold show where the mean difference is significant at the 0.05 level.

## 4.3.2 Moidach more incubations

*Methane production and oxidation potentials*

Potential $CH_4$ production of the High Fluoride treated soils was significantly greater than from Controls (p= 0.002) (Fig. 4.4 and Table 4.7). The average $CH_4$ production potential from these soils was 0.72 ng $g^{-1}h^{-1}$, which is 7 times greater than $CH_4$ production rates from Control soils, which emitted 0.1 ng $g^{-1}h^{-1}$. Methane production potential from the High Fluoride treated soils was also significantly higher than from all other treatments (Low Fluoride p= 0.006, Sulfate p= 0.003, Sulfate + High Fluoride p= 0.01) (Tukey HSD). All treatments had a higher potential $CH_4$ production than Controls. Potential $CH_4$ oxidation was not significantly different for any of the treatments when compared to the Controls (p= 0.07) (Table 4.7). Soils treated with Sulfate + High Fluoride and High Fluoride alone oxidised 16 and 13% less $CH_4$ than Control soils respectively (Fig. 4.4), although neither result was statistically significant (p= 0.27 and 0.48 respectively).

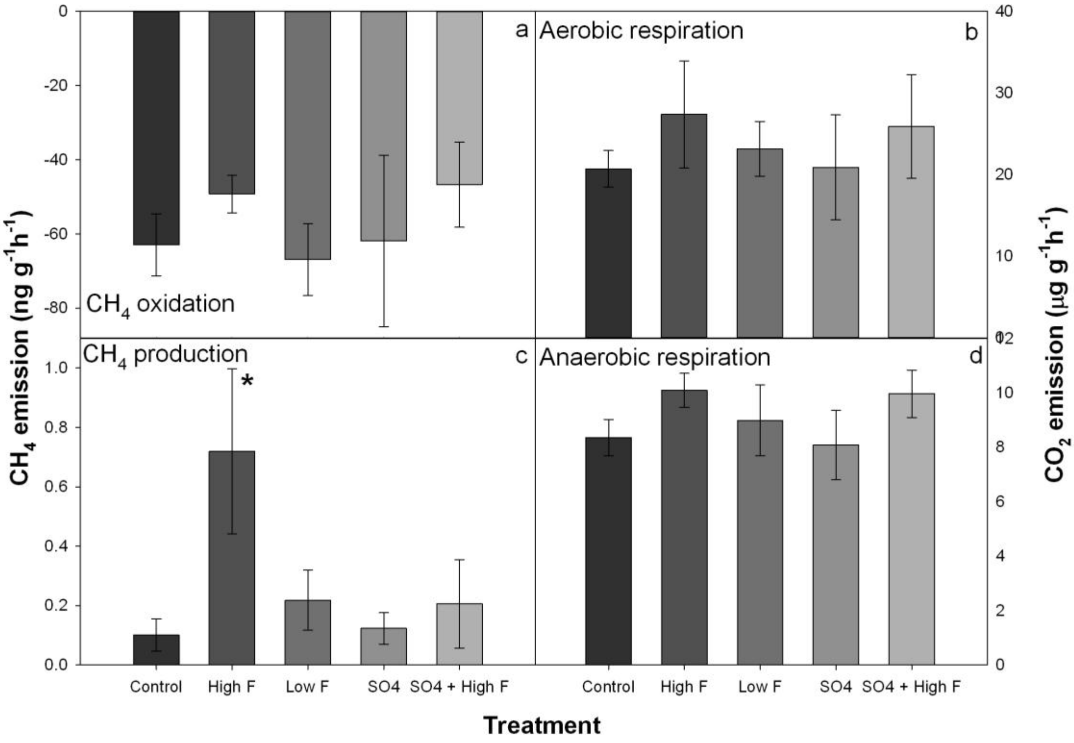


**Fig. 4.4** Potential $CH_4$ production (a) and oxidation (c) and aerobic (b) and anaerobic (d) respiration in peat incubations from Moidach More. Bars represent average $CO_2$ emission of 4 replicates and error bars represent standard deviation. * indicates $p< 0.05$.

**Table 4.7** Summary of potential $CH_4$ production and oxidation from Moidach More peat

| | Treatment | Mean $CH_4$ concentration (ng $g^{-1}h^{-1}$) (± Std Dev) | Between subjects effects: Treatment | p value [a] Control Versus treatment |
|---|---|---|---|---|
| Potential $CH_4$ production | Control | 0.10 (0.06) | F= 9.29<br>P= **0.001** | n/a |
| | High Fluoride | 0.72 (0.28) | | **0.002** |
| | Low Fluoride | 0.22 (0.10) | | 0.88 |
| | Sulfate | 0.12 (0.15) | | 1.00 |
| | Sulfate + High Fluoride | 0.21 (0.28) | | 0.92 |
| Potential $CH_4$ oxidation | Control | -62.94 (8.34) | F= 2.62<br>P= 0.07 | n/a |
| | High Fluoride | -49.24 (5.08) | | 0.48 |
| | Low Fluoride | -66.93 (9.72) | | 0.99 |
| | Sulfate | -61.91 (23.15) | | 1.00 |
| | Sulfate + High Fluoride | -46.68 (11.46) | | 0.27 |

[a] *p* values indicate the significance of treatment effects on mean $CH_4$ concentration when compared to the control soils. Values were generated using univariate ANOVA Tukey HSD Post Hoc comparisons. Values in bold show where the mean difference is significant at the 0.05 level.

### *Aerobic and anaerobic respiration*

There were no significant treatment effects on aerobic respiration (Table 4.8). The F containing treatments had the highest rates of aerobic respiration with High Fluoride having a greater influence on respiration rates than Low Fluoride (Fig. 4.4). Respiration rates were 32, 25 and 11% greater than Controls for the High Fluoride, Sulfate + High Fluoride and Low Fluoride treatments respectively. These differences were not statistically significant (p=0.23).

There was a significant treatment effect upon anaerobic respiration (p=0.01) (Table 4.8). The High Fluoride and Sulfate + High Fluoride treated soils had significantly greater respiration rates than the soils treated with Sulfate alone, p= 0.032 and 0.048 respectively.

**Table 4.8** Summary of anaerobic and aerobic $CO_2$ production from Moidach More peat

| | Treatment | Mean $CO_2$ concentration ($\mu g\ g^{-1}h^{-1}$) (± Std Dev) | Between subjects effects: Treatment | p value [a] Control Versus treatment |
|---|---|---|---|---|
| Anaerobic respiration | Control | 8.35 (0.67) | F= 3.86<br>*p*= **0.01** | n/a |
| | High Fluoride | 10.09 (0.63) | | 0.08 |
| | Low Fluoride | 8.98 (1.30) | | 0.85 |
| | Sulfate | 8.07 (1.27) | | 0.99 |
| | Sulfate + High Fluoride | 9.96 (0.87) | | 0.12 |
| Aerobic respiration | Control | 20.70 (2.23) | F= 1.54<br>*p*= 0.23 | n/a |
| | High Fluoride | 27.36 (6.56) | | 0.30 |
| | Low Fluoride | 23.15 (3.37) | | 0.95 |
| | Sulfate | 20.89 (6.43) | | 1.00 |
| | Sulfate + High Fluoride | 25.90 (6.36) | | 0.54 |

[a] *p* values indicate the significance of treatment effects on mean $CO_2$ concentration when compared to the control soils. Values were generated using univariate ANOVA Tukey HSD Post Hoc comparisons. Values in bold show where the mean difference is significant at the 0.05 level.

## 4.4 Discussion

### 4.4.1 Moor House mesocosm study incubations

*Methane production and oxidation potentials*

There were no significant treatment effects on $CH_4$ production or oxidation potentials in the Moor House peat soils used in the mesocosm experiment. This is in agreement with the results presented in Chapter 3, which showed no change in $CH_4$ emissions over the treatment period with the addition of $SO_4$ and F. There were a few interesting trends from the mesocosm peat incubations that were not statistically significant but still deserve consideration. Firstly, average $CH_4$ production rates of soils sampled at 10-20 cm in the Sulfate treated bottles were 50% lower than rates from Control soils. This result was not significant due to the large standard deviation of both the Control and the Sulfate bottles. It could indicate that in some soils sampled from 10-20 cm depth there was a suppression of $CH_4$ by $SO_4$, but due to the natural variation in conditions in each mesocosm the same result was not seen for all soils where $SO_4$ was added. Secondly, $CH_4$ production in the Sulfate + Low Fluoride soils was 90% lower than in the Controls at 10-20 cm, which also suggests that at this depth, microbial communities were more sensitive to $SO_4$ additions in some of the mesocosms.

A number of peat incubation experiments similar to the one carried out here have found no effect or variable effects of $SO_4$ addition on $CH_4$ production rates dependent upon the location of the peat in the soil profile (Table 4.1). Vile et al. (2003) observed no suppression of $CH_4$ production in peat taken from treatment plots that received 25 kg S $ha^{-1}$ $y^{-1}$. Eriksson et al. (2010) found no inhibition of $CH_4$ production at the depth of maximum $CH_4$ production in incubations of peat sampled from experimental plots that were treated with 20 kg S $ha^{-1}$ $y^{-1}$ for 12 years, but suppression was seen elsewhere in the profile. The authors concluded that methanogenic populations were unaffected by long-term S deposition at that depth. Blodau and Moore (2003) saw both $CH_4$ stimulation and suppression with the addition of $SO_4$ depending upon the location of the sample in the soil profile. Addition of 500 mM $SO_4$ increased potential $CH_4$ production rates in the surface layers by ~ 50 % and reduced it by ~ 40% in the deep peat layers. The opposite result was observed in a study by Yavitt et al. (1987), when $CH_4$ production was suppressed in the surface peat layers and stimulated in the deep peat layers where a 4-fold increase in $CH_4$ production occurred. These results suggest that microbial communities are different in the surface layers than in the deeper peat and that sulfate reducing bacteria (SRB) do not compete for substrates everywhere. Blodau and Moore (2003) speculated that methanogenic and sulfidogenic communities can adapt to coexist in different zones within surface layers of peatlands due to $SO_4$ pulses from the remineralization of organic S and reoxidation of iron sulfides. It is possible that $SO_4$ addition did not affect $CH_4$ emission in the mesocosm experiment because the methanogenic communities have adapted to a high S environment either through zonation or the utilisation of alternative substrates to SRB. In this study, $CH_4$ production rates were measured at 0-10 and 10-20 cm depths. Methane sampling over smaller depth increments could have shown a suppression of $CH_4$ emission at some depths and not at others as was reported in other investigations (Blodau and Moore 2003; Eriksson et al. 2010; Yavitt et al. 1987).

The addition of the High Fluoride treatment during the mesocosm experiment did not significantly affect $CH_4$ production rates at 0-10 or 10-20 cm. However, the $CH_4$ production rates of soils treated with Sulfate + High Fluoride were five times greater than Control rates. This trend was not significant due to the large variation in production rates between the six replicates. Methane production in the Sulfate + High Fluoride bottles was in the range of 0.07-143 ng $g^{-1}$ $h^{-1}$ with 3 of the bottles showing signs of stimulation of $CH_4$ production and 3 of the bottles having similar $CH_4$ production rates as the Controls.

### *Aerobic and anaerobic respiration*

There were no treatment effects on aerobic respiration from the mesocosm soils. There were however, treatment effects on anaerobic respiration. The addition of High Fluoride stimulated respiration resulting in increased rates of $CO_2$ production in the anaerobic bottles. Anaerobic respiration in mesocosms treated with Sulfate + High Fluoride was 30% greater than in Controls at 0-10 cm. Other experimental work has been carried out to investigate the effects of F on respiration, but the results have been varied (Tscherko and Kandeler 1997, and references therein). Wilke (1987) found no effect of F additions of up to 3700 mg $kg^{-1}$ to mull, moder and mor soils on respiration or $CO_2$ production. This is in contrast to findings by Van Wensem and Adema (1991) who found an increase in respiration rate and total $CO_2$ production with the addition of 170 μmol $g^{-1}$ F to poplar litter. The increase in anaerobic respiration in the mesocosm incubations was not translated to the mesocosm study where the addition of high concentrations of F had no effect on $CO_2$ fluxes (Section 3.3.2).

### *Microbial biomass*

Microbial biomass C and N were measured for the mesocosm soils but no significant differences between treatments and Controls were observed. There were however differences between the treatment groups. In peat sampled from 0-10 cm, microbial biomass C and N was significantly greater in the Sulfate + Low F soils than the Sulfate + High F and High F alone soils. Mesocosms which received the Sulfate + Low Fluoride treatments had higher concentrations of microbial biomass C and N than Control mesocosms. Mesocosms which received the High Fluoride and Sulfate + High Fluoride treatments had a lower microbial biomass than Controls. This could possibly indicate that low levels of F have a stimulating effect on micro-organisms and high concentrations of F have a toxic effect. These differences in microbial biomass do not appear to have an effect on $CH_4$ or $CO_2$ emissions from the mesocosm soils (lab incubations or field measurements). Measurements of potential $CH_4$ production were not significantly lower in the High Fluoride and Sulfate + High Fluoride bottles when compared to Controls and despite the lower microbial biomass, rates of anaerobic respiration were greater in these bottles compared to Controls. In the vicinity of an aluminium smelter where concentrations of F in the soil exceeded 100 mg F kg$^{-1}$, microbial biomass was only 20% of that in the unpolluted control and microbial activities were decreased to 5-20% of those in the control (Tscherko and Kandeler 1997). Concentrations of F in the mesocosm soils, which received the High Fluoride treatments, were six times greater than in the experiment by Tscherko and Kandler (1997) but still no significant effect on microbial biomass was observed. In soils around a disused phosphate fertilizer plant, which contained high concentrations of F and Cd, microbial biomass was decreased (Langer and Gunther 2001). The reason why no change in microbial biomass was observed in the mesocosms is unknown but is likely to be due to the fact that it is a peat soil and not a mineral soil as in the other studies.

### 4.4.2 Moidach more incubations

*Methane production and oxidation potential*

The addition of $SO_4$ to the incubations of the pristine Moidach More peats had no effect on potential $CH_4$ production rates. This is a surprising result as the same site was used by Gauci and Dise (2002). They added 25 kg S ha$^{-1}$ y$^{-1}$ for 18 months and saw a 36% average reduction in $CH_4$ emission in the last 12 months of the experiment. Here, the addition of $SO_4$ to the Moidach peat did not suppress $CH_4$ production but actually resulted in higher average $CH_4$ production rates than Control soils.

In the pristine Moidach more peat soils, the High Fluoride treatment significantly increased $CH_4$ production in the soils sampled from 0-10 cm. In the High Fluoride bottles, $CH_4$ production rates were seven times greater than production rates from Control soils. The same effect was not observed in the bottles treated with Sulfate + High Fluoride, which suggests that $SO_4$ inhibited the stimulating effect of the addition of F alone. The addition of F in the mesocosm experiment resulted in an increase in pore water concentrations of acetate and Fe (Section 2.3.1.2). Acetate is a substrate for methanogenesis and so could cause the observed increase in $CH_4$ production rates. However, Fe and $SO_4$ can inhibit methanogenesis as they are alternative electron acceptors (Zinder 1993). Reduction of $Fe^{3+}$ and $SO_4$ supplies more energy than methanogenesis making these pathways more favourable (Segers 1998; Zehnder and Stumm 1988). The complex balance between these species in solution is likely to be a controlling factor in $CH_4$ production rates. These results suggest that changes in $CH_4$ production rates due to F addition may not be directly due to F itself but the indirect effects are more important as F alters the chemical conditions of the peat to provide more substrates for methanogenesis.

There were no significant differences in $CH_4$ oxidation rates between treatments and controls. Although, soils treated with Sulfate + High Fluoride and High Fluoride alone oxidised 16 and 13% less $CH_4$ than control soils.

## 4.5 Conclusions

Results from the soil incubation experiments indicated that the addition of F and $SO_4$ during the mesocosm experiment did not have any effect upon the individual processes of $CH_4$ production or $CH_4$ oxidation at 0-10 or 10-20 cm. These results were also confirmed by the measurement of microbial biomass, which was not significantly different in the treated mesocosms when compared to the controls. The addition of similar treatments to a pristine peat soil produced surprising results, as the addition of $SO_4$ did not suppress $CH_4$ production rates as had been expected. As the addition of $SO_4$ did not suppress $CH_4$ production in the pristine or polluted soil, this suggests that soil heterogeneity is a more important factor than $SO_4$ deposition and that the previous pollution history of the Moor House site was not the inhibiting factor of the suppression of $CH_4$. The production of $CH_4$ in peat soils depends on so many varied factors that local conditions within the peat play a major role in the emission of C gas fluxes from peat soils.

Another interesting result that deserves further attention is the increase in $CH_4$ production due to the addition of high concentrations of F in the pristine soil, which is possibly due to changes in soil chemistry caused by the presence of F e.g. and increase in acetate concentrations.  This suggests that the addition of F in volcanic deposition may increase $CH_4$ emissions from some peat soils. Field studies should be carried out on a number of different peat soils, both pristine and polluted, to further investigate the effects of F on $CH_4$ and $CO_2$ emissions.

# Chapter 5: The effect of volcanic ash deposition on ecosystem respiration from an Icelandic mineral soil

## 5.1 Introduction

Ecosystem respiration (ER), gross photosynthesis (GP) and net ecosystem exchange (NEE) were measured in the mesocosm experiment described in Chapter 3, where the addition of F and $SO_4$ at concentrations likely to be leached from volcanic ash had no effect on $CO_2$ fluxes from peat mesocosms. However, there are other aspects of ash deposition that should be considered when investigating the potential impact of volcanic deposition on soil $CO_2$ fluxes. Firstly, volcanic ash contains other chemical species than F and $SO_4$ (Fruchter et al. 1980), which may impact upon soil microbial processes and therefore soil respiration. Dahlgren and Ugolini (1989) reported that the primary constituents in the leachate of ash from the Mt St Helens eruption in 1980 were $SO_4$, Ca, Mg, Na, K and Al. Dethier et al (1981) found Cl, $SO_4$, Ca, Na, Mg, K, $SiO_2$ and $NO_3$ in ash leachates from the same eruption. Fruchter et al (1980) also working on Mt St Helen's ash, found considerable amounts of Cl, $SO_4$ and $NO_3$ along with elevated levels of trace element cations such as Fe, Mn, Cu, Zn, and base cations Mg and Na. Over 55 soluble compounds have been identified in ash leachate studies (Witham et al. 2005). The leaching of these compounds in to soil may cause toxicity to microorganisms, changes in soil pH, salinity, nutrient availability and the solubility of heavy metals. These factors can have adverse effects on microbial activity resulting in reduced rates of $CO_2$ emission (Baath 1989; Pathak and Rao 1998; Sitaula et al. 1995). Soil pH affects the growth and proliferation of soil microbes (Rastogi et al. 2002) and therefore, a positive correlation between pH and ecosystem respiration has been reported in several studies (Hall et al. 1998; Reth et al. 2005; Rousk et al. 2009; Sitaula et al. 1995).

The second aspect of volcanic ash deposition that should be considered when investigating potential effects to soil respiration rates is the physical impact of ash on the soil surface. The physical effect of volcanic tephra deposition on the environment received considerable attention following the 1980 eruption of Mt St Helens in Washington, USA. The eruption impacted upon agriculture as plants were buried and damaged under the weight of the ash. Wet ash caused salt damage to leaves and fruit and photosynthesis was slowed due to reduced light intensity and the clogging of leaf stomata (Cook et al. 1981; Hinkley and Smith 1982). After the eruption of Volcano El Paricutin, Mexico (1943), the deposited ash layer prevented the germination and growth of seedlings in the underlying soil. The presence of ash on the soil surface also restricted gas exchange, reducing the supply of oxygen to plant roots (Eggler 1948). There are strong links between vegetation productivity and soil respiration (Janssens et al. 2001; Raich and Schlesinger 1992; Raich and Tufekciogul 2000) and so damage to vegetation through volcanic ash deposition may impact soil respiration rates. It is estimated that 30-70% of soil respiration directly stems from the vegetation via root or rhizosphere respiration (Reichstein et al. 2003).

Deposition of ash from the 1980 Mt St Helens eruption changed the colour of the soil surface and therefore its radiative properties. A layer of pale grey ash caused a greater reflectance of solar radiation and resulted in a lowering of soil temperature (Black and Mack 1986; Cook et al. 1981). A 2-3 cm ash layer reduced soil temperature by 6-10 °C (Cook et al. 1981). Temperature is one of the main regulating factors of soil respiration (Luo and Zhou 2006; Rustad et al. 2000; Schlesinger and Andrews 2000). The sensitivity of respiratory processes to an increase in temperature is described by the quotient $Q_{10}$. At the biochemical level, the $Q_{10}$ is approximately 2, which means that respiration rate doubles for every 10ºC increase in temperature (Luo and Zhou 2006). If ash deposition changes the surface albedo and therefore the temperature of the soil, the emission of $CO_2$ may also be affected.

Another physical effect of ash deposition is a change in the soil moisture regime. The ash layer reduces evaporation rates of water from the soil keeping it wet for longer during rainless periods (Cook et al. 1981). As such, volcanic ash deposition can play an important role in regulating soil moisture and is known to benefit agriculture in arid climates when applied as mulch to the surface of the soil (Diaz et al. 2005; Tejedor et al. 2003). Soil moisture also plays a major role in the regulation of $CO_2$ release from the soil. High moisture levels limit aeration and thus the diffusivity of air, reducing $CO_2$ transport from the soil. However, low levels of moisture can also reduce ecosystem respiration as it puts stress on microbial communities and root respiration (Rey et al. 2002). As there is a strong link between ash deposition, soil moisture content and respiration, it is likely that the presence of ash on the soil surface can have an effect upon ER.

Only one previous study has investigated the effects of volcanic ash deposition on soil respiration. Elliott (1982) mixed a mineral soil with volcanic ash and incubated for 30 days measuring $CO_2$ and $O_2$ uptake at regular intervals. There was no change in $CO_2$ evolution from the soils mixed with ash and so it was concluded that the deposition of volcanic ash would have little effect on microbially-controlled soil processes. The ash treatments used in this study were mixed with the soil rather than layered on the soil surface as would happen after a volcanic eruption and therefore the potential physical effects on soil moisture and $CO_2$ transport are not included. The effect of layers of tephra deposited on the soil surface on soil $CO_2$ fluxes has never before been assessed and may be important for areas in close proximity to volcanic eruptions as they receive large volumes of ash which may persist in the environment for long timescales (Wilson et al. 2011).

To assess the potential physical and chemical effects of volcanic ash on soil respiration, an experiment was set up on a grassland site in Iceland. Ash from the 2010 Eyjafjallajökull eruption was added to the site in different thicknesses (5cm and 10cm) and grain sizes (fine and coarse) to investigate the physical effects. Ash from the 2000 eruption of San Cristóbal, Nicaragua was applied to assess the chemical effects. This ash was chosen because it was fresh, i.e., it had not been rained upon, and leachate studies have shown that it contains high concentrations of soluble $SO_4$ and Cl salts on the ash particle surfaces (Delmelle et al. 2007). Five different treatments were added to the soil collars. These were: Control (which did not receive ash), 5 cm coarse ash, 10 cm coarse ash, 5 cm fine ash and 5 cm San Cristóbal ash. The experiment was designed to investigate the following hypotheses:

- Ash deposition reduces ecosystem respiration because of its physical effect on the soil environment causing an increase in soil moisture levels, impeding the transport of $CO_2$ and/or due to the burial of vegetation under the ash layer, lowering photosynthesis rates and therefore substrate supply to microbes,

- Ash deposition has a chemical effect upon soil microorganisms either through direct toxicity of leachates containing metals (e.g. Al, Fe, Cu) or a decrease in pH, which would reduce ecosystem respiration.

## 5.2 Methodology

### 5.2.1 Sampling site

The sampling site was located in the rural area of Smáratún (N 63º 43.558`, W 20º 00.323`), 13 km from the town of Hvolsvöllur in southern Iceland (Fig. 5.1). It is approximately 38 km north-west of the 2010 Eyjafjallajökull eruption location. This site was not subjected to heavy ash fall as the predominant direction of the plume movement was to the south-east of the eruption location (Davies et al. 2010). The sampling site was an area of grassland, which had recently been harvested for hay (Fig. 5.2). The soil type of the area is classified as a Brown Andosol (BA) (Arnalds 1999). Examination of the soil profile indicated the presence of distinct A1, B1, C1, B2 and C2 horizons and also distinct ash layers from previous volcanic events (Fig. 5.3). The dominant vegetation present at the site was *Poa trivialis*. This experiment was carried out on a mineral soil because Icelandic peats are located to the North of the country. It would not have been practical to travel North each day to take measurements and so a grassland site was chosen near to the experimental base where other data were being collected.

The sampling location within the grassland site was chosen carefully to ensure that it would be appropriate for the study. The location had a $CO_2$ flux greater than 1.5 µmol $m^{-2}$ $s^{-1}$, ensuring that $CO_2$ concentrations were well above the IRGA detection limits, thereby providing a good baseline to add treatments to. The area was flat so that the soil collars were inserted level to allow accurate calculation of the headspace volume. The vegetation was homogenous and there was approximately the same vegetation species and density in each collar.

**Fig. 5.1** Map showing the location of the sampling site (Smáratún), the Eyjafjallajökull eruption and where ash for the treatments was sampled. (Map adapted from Google maps)

**Fig. 5.2** Photograph of the grassland sampling site at Smáratún with Eyjafjallajökull in the background

**Fig. 5.3** Photograph of the soil profile of the grassland soil at Smáratún. A distinct ash layer can be seen at 30 cm depth.

### 5.2.2 Experimental design

*Experimental set up*

Twenty PVC collars (inner diameter: 10 cm, outer diameter: 11cm, depth: 20 cm) were inserted 5 cm in to the soil (Fig. 5.4). To prevent compaction of the soil and damage to the vegetation, a serrated knife was used to cut vertically down around the collar through the surface vegetation. A piece of wood was placed on top of the collar and a large mallet was used to drive the collar into the soil to a depth of 5 cm. The collars were inserted in four rows of five and were numbered from 1 to 20. The collars were then left overnight to allow the system to stabilise after the disturbance caused.

**Fig. 5.4** Photograph of the experimental set up at Smáratún. Twenty PVC collars inserted 5 cm into the soil with the IRGA and automatic survey chamber.

**Fig. 5.5** Photograph of pre-treatment $CO_2$ flux measurement from soil collar number 11 using the IRGA and automatic survey chamber.

### 5.2.3 Treatment loads and application

The treatments applied to the soil collars were chosen to investigate both the physical and chemical effects of volcanic ash upon ER. Ash collected from the 2010 eruption of Eyjafjallajökull was used to assess the physical effects. Two different grain sizes were collected within 20 km of the vent (Fig. 5.1) to assess whether the size of the ash particles has an important effect upon $CO_2$ flux. A coarse ash with a median particle size of 169 µm was sampled from Seljavellir (N63º 33.537360, W19º 37.321619). This was compared with a fine ash that has a median particle size of 18 µm, which is a windblown fraction that was sampled close to the Gigjökull glacier (N63º 40.900019, W19º 42.129660) (Particle size analysis results are presented in Appendix I). This ash was collected on 30th July 2010, 3 months after the main phase of the eruption. It had already been exposed to precipitation, and the water-soluble $F^-$, $Cl^-$ and $SO_4^{2-}$ salts which usually coat the surface of freshly erupted ash were washed away. Two different depths of ash, 5 and 10 cm, were applied to assess whether the thickness of the ash layer had an effect on ER, with the thicker layer almost completely covering the vegetation layer. To assess the potential chemical effect of volcanic ash on respiration, ash from the January 2000 eruption of San Cristóbal, Nicaragua, was applied to the soils. This ash was chosen because it was fresh, i.e., it had not been rained upon, and leachate studies have shown that it contains high concentrations of soluble $SO_4$ and Cl salts on the ash particle surfaces (Delmelle et al. 2007). The ash used is a composite sample (median particle size of 32 μm) collected from the village of Las Rojas, which is approximately 2 km from the crater.

Five different treatments were added to the soil collars with 4 replicates of each, at 2 pm on 1st August 2010. These were: Control (which did not receive ash), 5 cm coarse ash, 10 cm coarse ash, 5 cm fine ash and 5 cm San Cristóbal ash. Treatments were allocated randomly; the experimental design is presented in Fig. 5.6. Ash was poured into the collars carefully using a beaker to the desired depth. The San Cristóbal ash was weighed before it was applied to the collars so that the leachate composition could be calculated. Each replicate received 211 g of San Cristóbal ash, which equated to an ash layer of approximately 5 cm thickness.

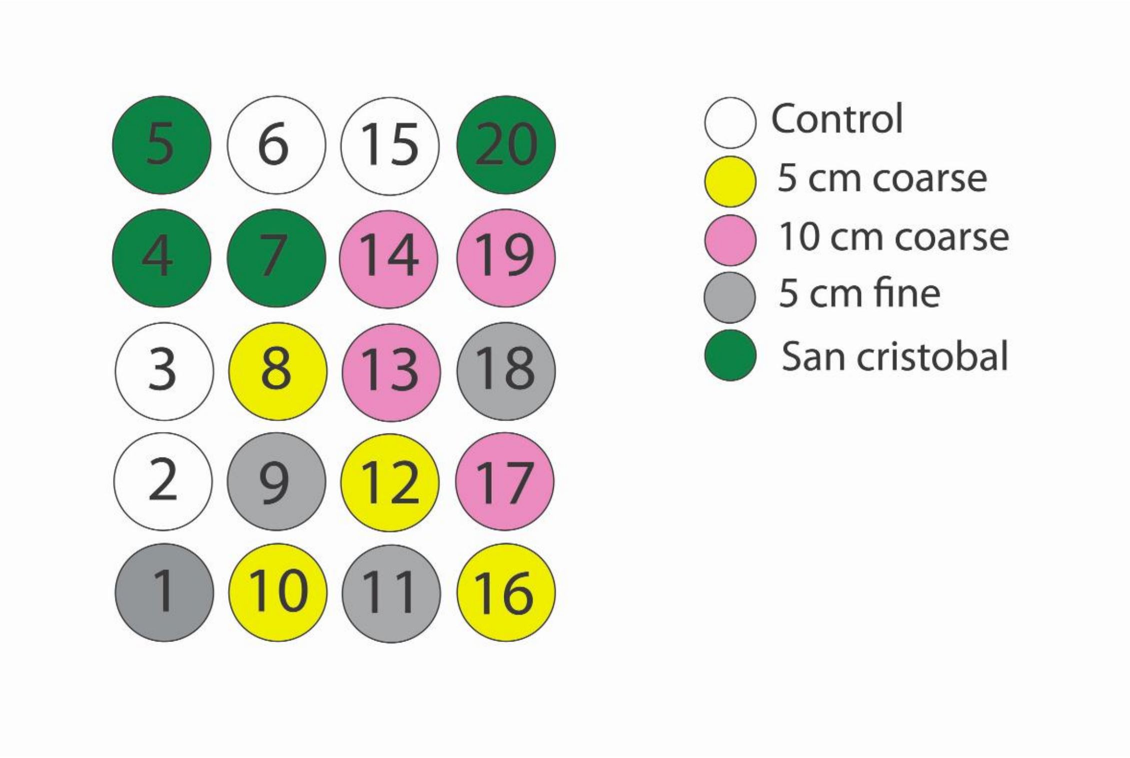


**Fig. 5.6** Experimental design showing the allocation of treatments between the 20 soil collars

When the ash layers had been applied, they were wetted with deionised water. Each soil collar received 225 ml of deionised water at the start of the experiment. This quantity of water represents the average weekly amount of rainwater collected at the Eyrarbakki weather station in southern Iceland (Data available from www.en.vedur.is). The collars were then left under natural conditions and only received water during rainfall events.

### 5.2.4 Ecosystem respiration measurements

On the morning of 1st August 2010, pre-treatment $CO_2$ flux was measured. The next measurements were taken one hour after treatments had been applied. Carbon dioxide fluxes were then measured twice per day for 5 days, once every morning and then again in the evening. Ecosystem respiration was measured using a portable IRGA (LICOR LI-8100) coupled with a 10 cm automated survey chamber (LICOR LI-8100-102) (Fig. 5.5). The chamber is opaque and so created dark conditions over the soil. This prevented photosynthesis from occurring and allowed the measurement of ER alone. ER includes respiration from the soil, vegetation, roots and micro-organisms within the ecosystem. Each $CO_2$ measurement took 3 minutes. The first minute was an equilibration period, which allowed the air to mix in the chamber. This is important as the IRGA only uses a small volume of air to measure the $CO_2$ concentration and so it needs to be well mixed. During the following two minutes $CO_2$ concentration in the chamber was measured once every second. The chamber was then moved onto another collar during a programmed one-minute delay between sampling measurements, this allowed ambient $CO_2$ concentrations to return. The chamber works on a pneumatic system which contracts and expands a bellows to raise and lower the chamber over the soil collar, which eliminates the disturbance that would occur if this were to be done manually (LI-COR 2010). The chamber is also vented to reduce changes in chamber pressure, which could affect $CO_2$ diffusion rates from the soil. This is important as $CO_2$ movement from the soil is driven by diffusion. The $CO_2$ flux is calculated by linear regression of the $CO_2$ concentrations measured over time.

### 5.2.5 Additional measurements

At the same time as the $CO_2$ flux measurements, measurements of air temperature, soil temperature, soil moisture and rainfall were also recorded. Prior to the treatment addition, soil temperature and soil moisture were measured in each collar. Both of these variables are important regulators of soil respiration (Rustad et al. 2000). Soil temperature was measured using a digital soil thermometer probe (Fisher Scientific Traceable Lollipop) inserted 5 cm into the soil. Soil moisture was measured using a moisture meter coupled with a theta probe (Delta-T Devices Ltd. HH2 Moisture Meter Version 2.3). After the last $CO_2$ measurement on Day 5, the ash layer was removed from each collar and the temperature and moisture content of the soil underneath was measured again. Soil temperature probes were also inserted into one replicate per treatment and remained in situ to monitor changes in temperature over the 5 days. A reading was taken from each of these probes each time $CO_2$ flux was measured. It was not possible to monitor soil moisture content over the sampling period because the prongs on the theta probe were too short to take an accurate reading of moisture in the soils covered by ash without causing major disturbance to the ash layer. It was decided that pre-treatment and after-treatment measurements would be more appropriate than disturbing the ash in the collars which could affect the pathways of rainfall inputs and $CO_2$ emissions.

Air temperature was measured every time each soil collar was sampled for $CO_2$. Changes in air temperature can cause changes in air pressure and volume within the chamber, which can affect gas fluxes into and out of the soil. The LICOR chamber is vented to prevent this but measurements were taken anyway as fluctuations in air temperature can affect soil temperature which can regulate respiration rates.

A rain gauge was installed at the sampling site before treatments were applied. Rainwater samples were collected every evening and the amount of rainfall collected was recorded each day. The rainwater samples were filtered to 0.2 µm using syringe filters (Nalgene, Surfactant-free cellulose acetate membrane in acrylic housing) and refrigerated until ready for analysis. The samples were analysed by Ion Chromatography for F, Cl, $NO_3$, $SO_4$ and $PO_4$

using a Dionex ICS 2000 fitted with an AS18 column coupled with an AS40 automated sampler. A Potassium Hydroxide eluent was used with a gradient of 1 to 38 mM over 40 minutes to produce optimum peak resolution (Flow rate: 0.25 ml/min; Suppressor current: 24 mA; Column temperature: 30 ºC). The species chosen for analysis are likely to be present in both the rainwater and the ash leachate, which will allow assessment of the above-background inputs from the ash. To determine concentrations of Al, Fe, Ca, Na, Mg, K, Mn, P, S, Si, and Zn, 6 ml samples were acidified with 60 µl of nitric acid (70%) and then frozen. Samples were sent for analysis by inductively coupled plasma- atomic emission spectroscopy (ICP-AES) (IRIS Intrepid II, Thermo Electron Corporation, Franklin, MA) at Radboud University Nijmegen, the Netherlands.

When the ash layer had been removed from the soil collars and soil temperature and moisture had been measured, a small sample of soil was taken from the top 5 cm of the profile for pH analysis. This soil was returned to the laboratory, air-dried and sieved to < 2 µm. The soil pH was measured by weighing 10 grams of soil, to which 25 ml of water was added. The solutions were shaken for 15 minutes and the pH was measured using a glass/calomel electrode and pre-calibrated Thermo Orion pH meter (model 420A+).

### 5.2.6 Ash leaching experiment

To analyse the chemical effect of ash deposition on soil respiration, the San Cristobal ash that was used in the field experiment was leached in the lab to determine its composition. Although the Eyjafjallajökull ash had already been leached by rainwater it was leached again in the laboratory to assess the potential chemical impacts on the soil. Four columns of ash were prepared to represent the different ash treatments used in the soil respiration experiment (San Cristóbal, 5cm Fine, 5cm Coarse and 10cm Coarse). The columns consisted of a 25 cm length of PVC pipe (Outer diameter: 4cm, inner diameter: 3.4cm) sealed at the bottom with a Whatman N$^{o}$41 filter paper and a PVC cap with drainage holes (~1mm diameter). The columns were held in place vertically using a clamp and stand, over a funnel and sample collection tube (Fig. 5.7). To each column, 20 g of the appropriate ash was added followed by a thin layer of chemically inert plastic beads, which prevented disturbance of the ash surface during water addition. The 10 cm Coarse ash column received 40 g of ash to create a realistic ash to water ratio as occurred in the field. In the soil respiration experiment, the collars initially received 225 ml of deionised water, which was poured onto the ash surface; subsequent water addition was via natural rainfall (155.5 ml). To replicate this in the leaching experiment, the columns initially received 21 ml of water, which was poured by hand onto the ash. After the initial leachate was collected from the bottom of the column, a Watson Marlow 205S pump (with Marprene tubing) was used to replicate the water addition by rain. Over a period of 6 hours and 15 minutes, 15 ml of water was added to the columns at a flow rate of 0.04 ml $min^{-1}$. When the columns had drained, the second batch of leachate was collected. After collection, the ash leachates were immediately filtered and analysed for base cations (Na, K, Ca, Mg), anions (F, $SO_4$, Cl) and trace elements (Al, Fe, Mn, P, Si, Cr, Ni, Cu, Cd, Pb, Zn) using the same methods as for the rainwater analysis. These elements were chosen as they are either key nutrients or micronutrients which are likely to be present in volcanic leachates and may prove beneficial or toxic to soil microorganisms.

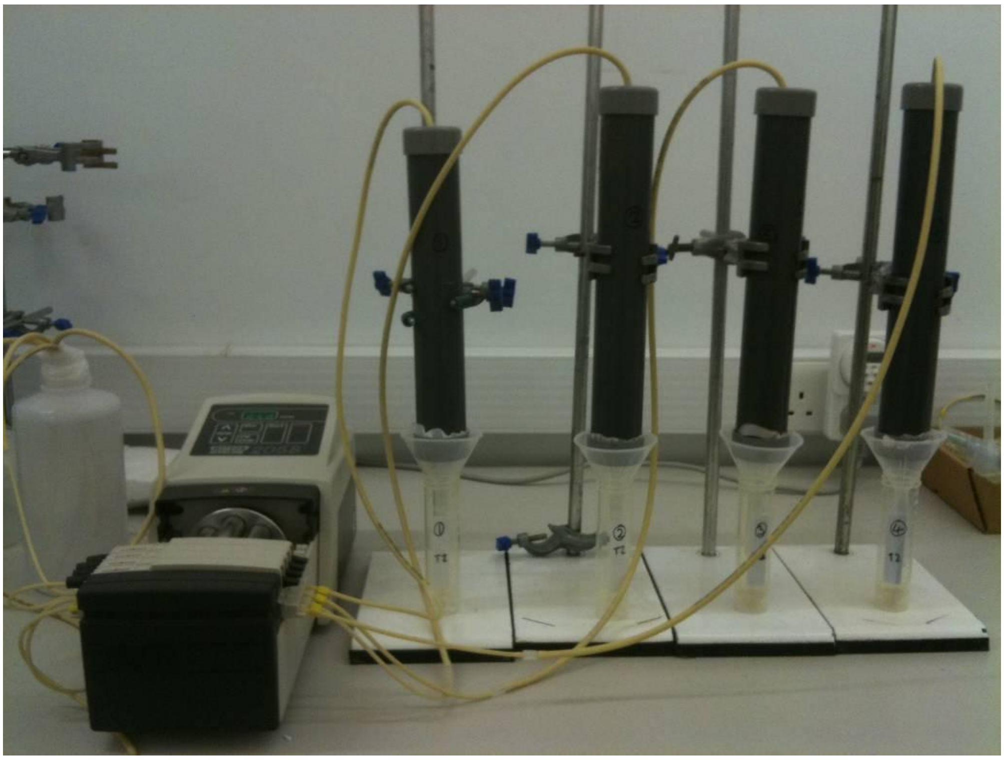


**Fig. 5.7** Photograph of the ash leaching experiment where deionised water is continually added to columns of ash via the pump to replicate the leaching of ash by rainfall, which occurred in the field during the soil respiration experiment.

### 5.2.7 Statistical analysis

To compare the effects of treatments on $CO_2$ emissions, the data were split into pre-treatment and post-treatment groups. The $CO_2$ data were first tested for normality using the Kolmogorov-Smirnov tests of normality ($p > 0.05$) and for homogeneity of variances with Levene's test of equality of error variances ($p > 0.05$). The $CO_2$ flux data met the requirements of these tests and so transformation was not required. Repeated-measures multivariate analysis of variance (RM-MANOVA) (Pillai's trace) were used to analyse the post-treatment effects of the treatments on the $CO_2$ fluxes, with sampling time as the within-subject factor and treatment as the between-subjects factor. A number of covariates were tested in the model to explain within-treatment variability but were only included if $p < 0.1$. Final soil temperature, moisture and pH were tested as covariates for the RM-ANOVA post-treatment period but showed no correlation to $CO_2$ flux ($p$=0.76, 0.93 and 0.83 respectively) and therefore $CO_2$ fluxes were analysed with no covariates. RM-MANOVA also allowed examination of within treatment variability (time effect and interactions between time and treatment (time times treatment)). Post Hoc comparisons were included if treatment was a significant factor (Tukey HSD) or to test if the fluxes from the treated mesocosms were significantly different to those of the control mesocosms (Dunnett t-tests). As pre-treatment $CO_2$ data were only available for one sampling time, the RM-MANOVA was unsuitable and so was replaced with U-ANOVA instead. Treatment was a fixed factor with $CO_2$ flux as the dependant variable. This test was followed by Post Hoc comparisons (Tukey HSD and Dunnett t-tests as above) if treatment effect was a significant factor. Pre-treatment soil temperature and moisture were tested as covariates but neither was significant ($p$= 0.598 and 0.722 respectively) therefore these data were not included in the analysis. All analyses were performed with SPSS Statistics 17.0.

## 5.3 Results

### 5.3.1 Ecosystem respiration

*Pre-treatment*

Pre-treatment $CO_2$ emissions were within the range of 544-926 mg $m^{-2}h^{-1}$. There were no significant differences between ER of the Control collars and any of the treatment groups (F=0.232, *p*= 0.916).

*Post-treatment*

Over the post-treatment period (1-94 hours) there was a significant treatment effect on $CO_2$ emissions (*p*=0.048) as soils treated with San Cristóbal ash had lower $CO_2$ emissions than the control soils (*p*=0.031 (Simple Contrasts test)) (Table 5.1 and Fig. 5.8). During the period of 20-94 hours after treatment, average ER was consistently lower from soils treated with San Cristóbal ash than the Control soils. At 94 hours after treatment, average $CO_2$ flux from the soils that received the San Cristóbal ash layer was 30% lower than Control $CO_2$ fluxes.

All soils treated with volcanic ash had reduced ER 1 and 20 hours after application of the ash (Fig. 5.8), which coincide with the times when the soil was wet due to the initial water addition and a period of heavy rain (Fig. 5.9). Statistical analysis of $CO_2$ fluxes from this wet period (1-20 hours) highlighted a significant treatment effect of the 10 cm Coarse ash layer on ER (*p*=0.008). One hour after treatment, average $CO_2$ flux was 86% lower in these soils when compared to Control fluxes, 20 hours after treatment fluxes were 76% lower. Although all of the ash treatments show this pattern, it is only statistically significant for the 10 cm Coarse treatment. Throughout the remainder of the sampling time, weather conditions were dry and no other sudden reductions in ER were observed.

**Table 5.1** Summary of results from RM-MANOVA and Dunnett Post-Hoc comparisons where a significant Control Vs. treatment result occurred.

| Time | Source | Type III sum of squares | df | Mean Square | F | Sig. | Post Hoc comparison Control Vs |
|---|---|---|---|---|---|---|---|
| Pre-treatment | Intercept | 1.13E7 | 1 | 1.13E7 | 1065.64 | 0.000 | - |
| | Treatment | 9797.03 | 4 | 2449.26 | 0.23 | 0.916 | |
| | Error | 158661.77 | 15 | 10577.45 | | | |
| After treatment (1-94 hours) | Intercept | 5.82E7 | 1 | 5.82E7 | 963.64 | 0.000 | - |
| | Treatment | 748387.35 | 4 | 187096.84 | 3.10 | **0.048** | |
| | Error | 905775.22 | 15 | 60385.02 | | | |
| After treatment wet (1-20 hours) | Intercept | 1.50E7 | 1 | 1.50E7 | 311.83 | 0.000 | 10cm Coarse *P*= 0.008 |
| | Treatment | 737323.49 | 4 | 184330.87 | 3.83 | **0.024** | |
| | Error | 721489.78 | 15 | 48099.32 | | | |
| After treatment dry (31-94 hours) | Intercept | 4.33E7 | 1 | 4.33E7 | 1274.58 | 0.000 | - |
| | Treatment | 864115.27 | 4 | 216028.82 | 6.36 | **0.003** | |
| | Error | 509860.62 | 15 | 33990.71 | | | |
| After treatment dry (55-94 hours) | Intercept | 3.15E7 | 1 | 3.15E7 | 1299.65 | 0.000 | San Cristóbal *P*=0.047 |
| | Treatment | 693287.15 | 4 | 173321.79 | 7.15 | **0.002** | |
| | Error | 363428.79 | 15 | 24228.59 | | | |

During the sampling period when the weather conditions were dry (31-94 hours after treatment), collars receiving coarse ash (5cm and 10cm) showed a trend of higher rates of ER when compared to Control soils (Fig. 5.8). Those that were treated with the 5cm Fine and San Cristóbal ash had lower rates of ER than Controls. These trends were not statistically significant, however significant differences in $CO_2$ emissions were measured between the coarse and fine ash treatments. During the period of 31-94 hours after treatment, ER from the 10cm Coarse collars was significantly greater than from the 5cm Fine and San Cristóbal treated collars (*p*= 0.042 and 0.008 respectively). Similarly, ER from the 5cm Coarse soils was greater than from the San Cristóbal treated soils (*p*= 0.012) over the same time period. At the individual time points of 1 and 20 hours after treatment, when the soils were wet, t-tests revealed significant differences between treatments and controls. One hour after treatments were added, soils that received the 10cm Coarse, 5cm Fine and San Cristobal ash layers had significantly lower rates of ER than Controls (Table 5.2). Twenty hours after treatment application soils that received the 10cm Coarse and 5cm Fine ash layers had significantly lower rates of ER than Controls.

Statistical analysis revealed significant time x treatment interactions over the post-treatment period (*p*=0.003). This indicates that the differences between treatments were not consistent throughout the sampling period. This is to be expected as water inputs varied over time and affected the ash layers differently, which had knock-on effects to $CO_2$ fluxes.

**Table 5.2** Summary of results from independent samples t-tests at 1 and 20 hours after treatment where control samples were tested against treatment groups.

| Time (hours after treatment) | Treatment | Mean $CO_2$ flux (Std dev) (mg $m^{-2}h^{-1}$) | Independent samples t-test Controls Vs treatment | | |
|---|---|---|---|---|---|
| | | | t | df | *p* |
| 1 | Control | 817.95 (92.05) | - | - | - |
| | 10cm Coarse | 108.08 (35.72) | 14.38 | 6 | **0.00** |
| | 5cm Coarse | 573.67 (342.87) | 1.38 | 6 | 0.22 |
| | 5cm Fine | 446.59 (135.19) | 4.54 | 6 | **0.00** |
| | San Cristobal | 470.73 (244.36) | 2.66 | 6 | **0.04** |
| 20 | Control | 438.67 (18.10) | - | - | - |
| | 10cm Coarse | 100.96 (15.37) | 28.44 | 6 | **0.00** |
| | 5cm Coarse | 295.34 (158.30) | 1.80 | 6 | 0.12 |
| | 5cm Fine | 298.52 (113.87) | 2.43 | 6 | **0.05** |
| | San Cristobal | 261.30 (182.78) | 1.93 | 6 | 0.12 |

*p* values in bold indicate treatment groups that have $CO_2$ fluxes which are significantly different from controls at the 0.05 level.

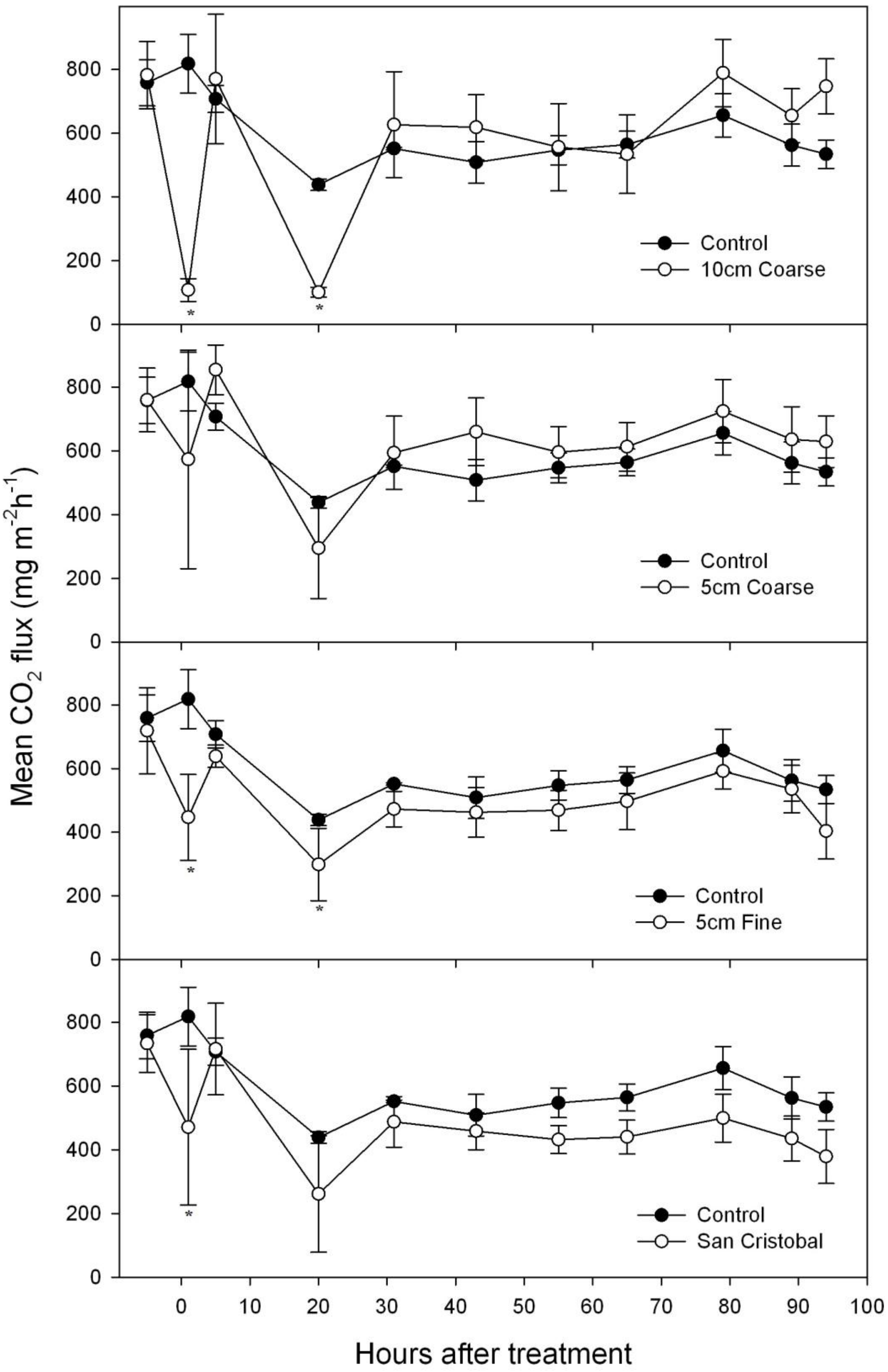


**Fig. 5.8** Carbon dioxide emissions from treated collars against emissions from control collars. Each point represents the mean flux from 4 replicates. Error bars represent standard deviation. * indicates $p < 0.05$ treatments compared to controls.

### 5.3.2 Climate data and Rainwater analysis

Over the treatment period, the air temperature at the sampling site was in the range of 11-18 °C (Fig. 5.9). The highest temperatures were recorded during the pre-treatment sampling and 94 hours after treatments were applied. Lowest temperatures were recorded at 9pm on 03/08/2010 (55 hours after treatments were applied) where average temperatures during $CO_2$ measurement were 11.9 °C.

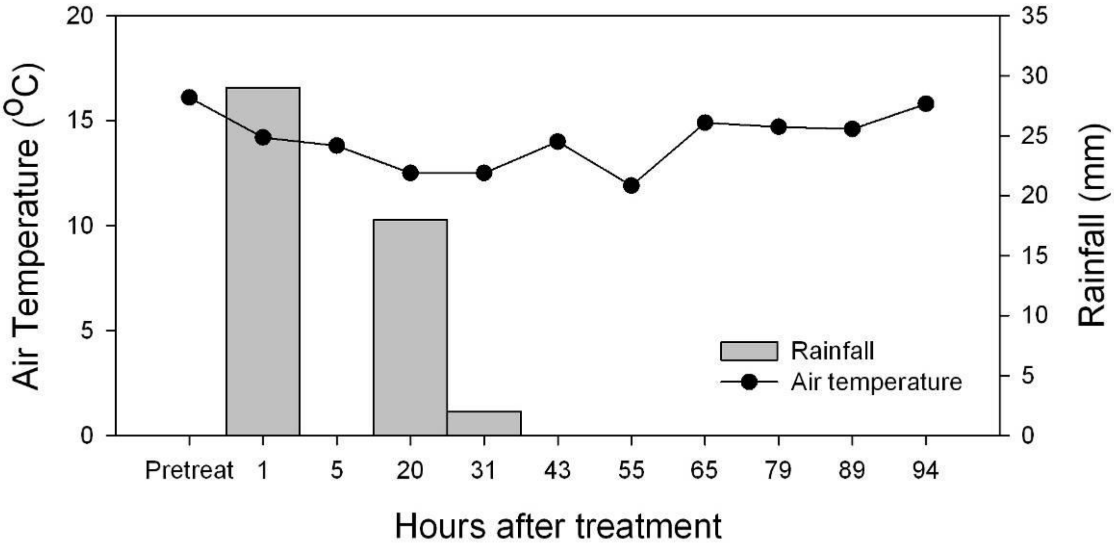


**Fig. 5.9** Daily rainfall amounts (mm) and average air temperature (°C) over the sampling period

After the ash treatments were applied, there was an initial water addition of 225 ml per core, which is the equivalent of 29 mm of rainfall. Over the next day, 18 mm of natural rain fell (~140 ml) which was followed by 2 mm 31 hours after treatments had been applied (~15 ml) (Fig. 5.9). There was no more rain over the rest of the sampling period. The chemical composition of the natural rainwater collected over the sampling period is presented in Table 5.3. Fluoride was not present in the rainwater solutions.

**Table 5.3** Chemical composition of rainwater sampled over the treatment period

| Date | mm of rain | Concentration ($\mu mol\ l^{-1}$) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Al | Ca | Fe | Mg | Na | P | S | Si | Zn | $SO_4$ | Cl |
| 02/08 | 18 | 0.2 | 16.5 | 0.2 | 2.3 | 11.3 | 1.1 | 6.7 | 0.3 | 0 | 12.7 | 27.9 |
| 03/08 | 2 | 0.9 | 33.3 | 0.4 | 3.9 | 19.1 | 0.6 | 13.6 | 1.4 | 0 | 11.4 | 24.3 |

### 5.3.3 Soil temperature, moisture and pH

There were no differences in pre-treatment soil temperatures between any of the treatments or the controls (Fig. 5.10). At the end of the experiment however, the soils treated with a 10 cm Coarse ash layer were significantly warmer than the Control soils and those treated with San Cristóbal ash (*p*=0.014 and 0.029 respectively). Although the difference in temperatures was statistically significant, the actual increase in temperature was small (0.25ºC warmer than Controls, 0.23ºC warmer than San Cristóbal), compared to the natural variation in temperature observed in the soils pre-treatment.

After-treatment soil moisture content was greater than pre-treatment moisture content for all treatment groups (Fig. 5.10). The average moisture content of the Control soils increased from 29 to 41% over the treatment period. Soil moisture increased in the range of 6-21% volume for all collars over the period of the experiment. This is to be expected due to the initial 225 ml water input and rainfall over the first two days. However, there was no significant difference in soil moisture content between treatment groups either pre-treatment or post-treatment (*p*= 0.276 and 0.510 respectively).

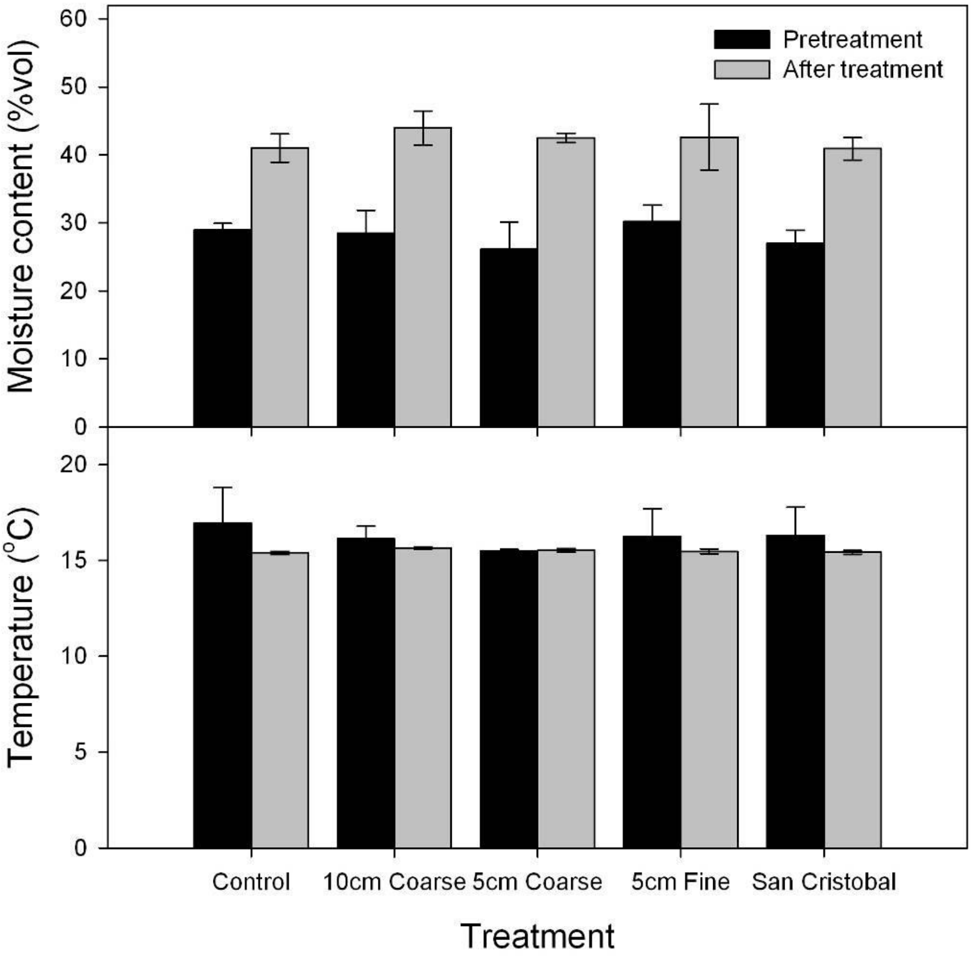


**Fig. 5.10** Temperature (°C) and moisture content (% vol.) measured pre-treatment and after treatment. Bars represent the mean of 4 replicates. Error bars represent standard deviation

At the end of the experiment, the ash layer and vegetation were removed from each collar and the pH of the topsoil was measured. The soils in the Control collars had an average pH of 5.98 (Fig. 5.11), which is similar to that of the 5cm Coarse, and 5cm Fine treated soils (6.06 and 6.01 respectively). However, soils that received the 10 cm Coarse and San Cristóbal ash layers had a lower average pH (5.64 and 5.57 respectively) although only the San Cristóbal soils had significantly lower pH than the Controls (*p*=0.036).

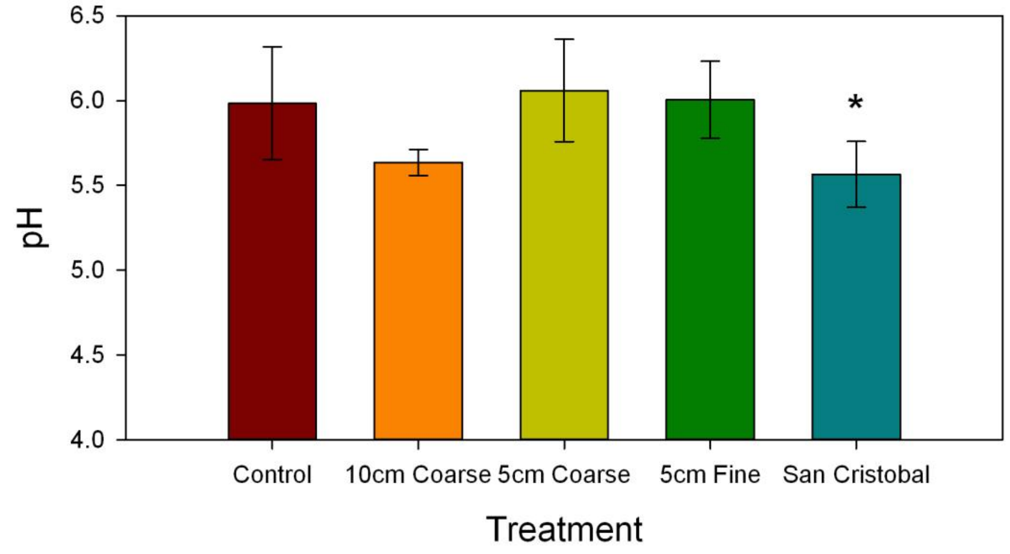
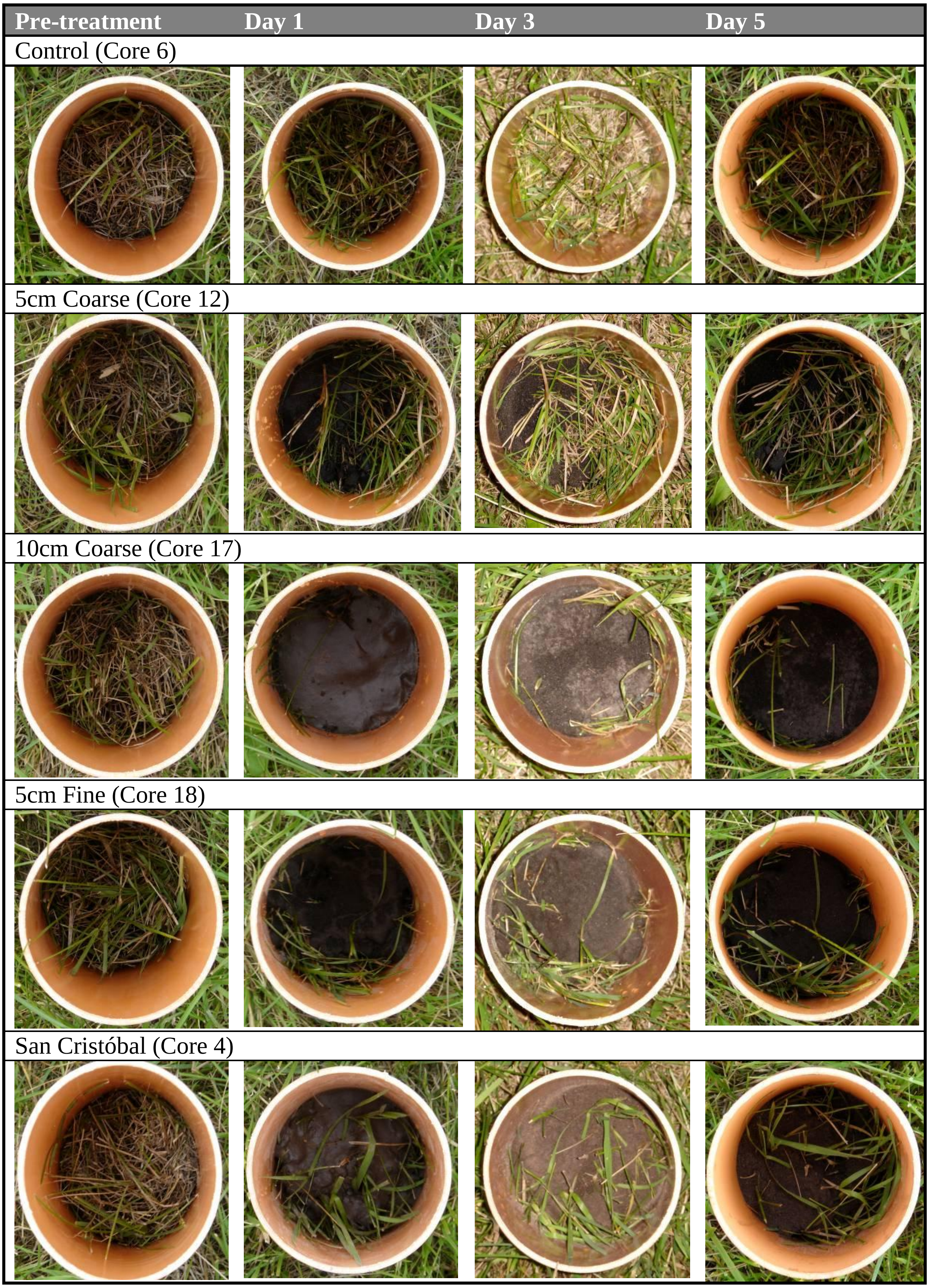


**Fig. 5.11** Soil pH measured at the end of the experiment. Bars represent the mean of 4 replicates. Error bars represent standard deviation. * indicates $p < 0.05$.

### 5.3.4 Effect of ash on vegetation

Application of ash to treatment collars caused the partial burial of vegetation, with a larger proportion of the vegetation being buried under the 10 cm ash layer (Fig. 5.12). There were no visible signs of injury to the vegetation.

**Fig. 5.12** Photographs of soil collars (one from each treatment group) over the sampling period. Note: collars appear lighter in day 3 but this is due to the camera flash.



### 5.3.5 Ash leaching experiment

After the first water addition (by hand), the San Cristóbal and Coarse ash columns started to drain instantly. However, the Fine ash drained much slower with water pooling on the ash surface immediately after addition. Approximately 65% of the added water was collected from the bottom of each column containing 20g of ash. Half of this amount was collected from the 10 cm Coarse column which contained 40g of ash. After the second water addition, approximately 90% of the water added was collected for all columns. When the ash was removed from the columns after leaching, there was a distinct difference in the physical characteristics of the different ash types. The San Cristóbal ash had a soft malleable, clay-like texture whereas the Eyjafjallajökull fine ash particles had cemented together to form a hard solid block of ash. This cementing was not seen in the Eyjafjallajökull coarse ash, which had the texture of wet sand.

*Chemical composition*

A summary of the ash leachate composition from the column leaching experiment can be found in Table 5.4. Unsurprisingly, concentrations of the chemical species leached from the San Cristóbal ash were greater than from the Eyjafjallajökull ash, which had previously been leached by rain. In both the San Cristóbal and Eyjafjallajökull leachates, concentrations of each of the chemical species were greater in pulse 1 than pulse 2, with the exception of Al, K, Si and P where concentrations were greatest in pulse 2.

*pH*

There was a significant difference in the pH of the San Cristóbal leachate and the Eyjafjallajökull leachate with the former being more acidic (Fig. 5.13). Following the initial water addition, the pH of the leachate from the San Cristóbal column was 3.88. The leachate from the other three columns containing Eyjafjallajökull ash had a higher pH of ~6.75. The pH increased slightly in the second leachate when compared to the first with a pH of 4.17 in the San Cristóbal leachate and a pH closer to 7 from the Eyjafjallajökull columns.

**Table 5.4** Summary of ash leachate composition. Values are the sum of results from pulse 1 and pulse 2.

| | Total amount (μmol $l^{-1}$) | | | |
|---|---|---|---|---|
| | San Cristóbal | 5 cm Fine | 5 cm Coarse | 10 cm Coarse |
| F | 5877.83 | 302.79 | 67.93 | 339.13 |
| Cl | 116958.82 | 758.53 | 308.04 | 532.58 |
| $SO_4$ | 56698.60 | 509.79 | 82.69 | 180.38 |
| Al | 223.73 | 218.18 | 74.52 | 144.13 |
| Ca | 669.46 | 275.75 | 227.45 | 172.06 |
| Fe | 3.10 | 4.13 | 1.46 | 3.45 |
| K | 23.92 | 158.07 | 66.76 | 98.04 |
| Mg | 558.60 | 43.54 | 30.40 | 24.63 |
| Mn | 14.92 | 0.43 | 0.22 | 0.21 |
| Na | 55.25 | 335.97 | 23.96 | 123.58 |
| P | 3.59 | 20.86 | 8.98 | 14.56 |
| Si | 65.42 | 76.30 | 44.68 | 64.65 |
| Cr | 1.15 | 0.18 | 0.11 | 0.12 |
| Ni | 3.95 | 0.37 | 0.07 | 0.23 |
| Cu | 303.67 | 9.12 | 3.13 | 5.02 |
| Cd | 0.80 | 0.01 | 0.00 | 0.01 |
| Pb | 0.58 | 0.05 | 0.01 | 0.03 |
| Zn | 52.68 | 8.13 | 1.14 | 2.60 |

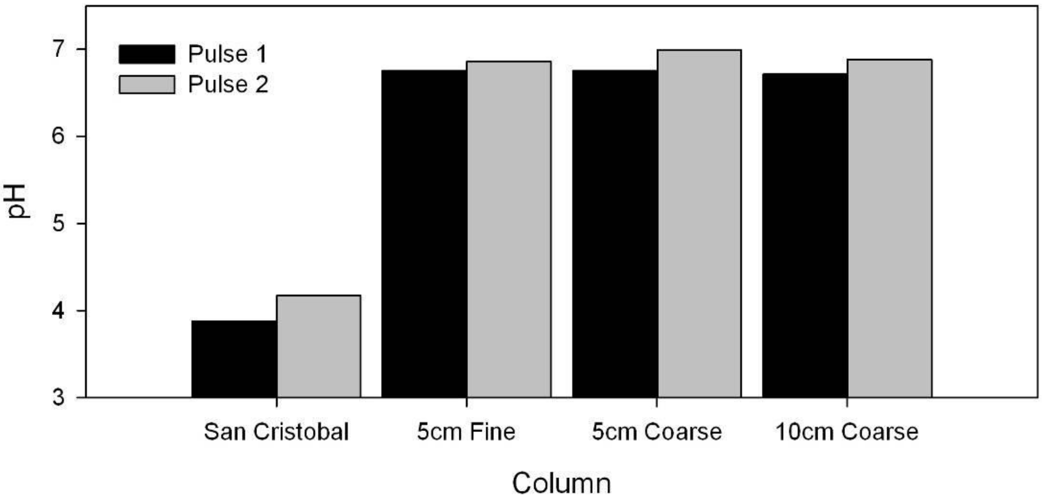


**Fig. 5.13** pH of ash leachate collected after initial water addition (pulse 1) to ash columns and continuous addition using a pump (pulse 2).

*Anions*

Concentrations of major anions in the San Cristóbal and Eyjafjallajökull ash leachates followed the order: Cl > $SO_4$ > F with the exception of the 10 cm Coarse column leachates in which concentrations of F were greater than $SO_4$. In the San Cristóbal ash leachate, the Cl concentration in the first pulse was 105 mmol $l^{-1}$ which was reduced by ~ 90% in the second pulse with concentrations of ~ 11mmol $l^{-1}$. Similarly, concentrations of $SO_4$ and F were lower in the second pulse by 40 and 70%. The total concentrations of Cl, $SO_4$ and F were 150, 110 and 17 times greater respectively than in the Eyjafjallajökull ash leachates.

Chemical speciation modelling of the ash leachate data was carried out using the CHEAQS PRO model (See Chapter 2 Section 2.2.5 for details). The results showed that all of the Cl in solution was present as free Cl. Between 97-99% of the $SO_4$ was present as free $SO_4$ with 2-3% as $Ca(SO_4)_{(aq)}$. The amount of free F in solution varied in each of the leachates between 56 and 99% with the remainder of the F being present as Al-F complexes.

*Basic cations*

The greatest concentrations of base cations in the San Cristóbal ash leachate were found in the order: Ca > Mg > Na > K. The total concentration (pulse 1 + pulse 2) of Ca was 670 µmol $l^{-1}$ which is 27 times greater than the concentration of K. Fifty percent of the Ca and Mg present in the leachate was in the form of free $Ca^{2+}$ and $Mg^{2+}$ ions. The remaining 50% of Ca and Mg in the leachate was paired with the $SO_4$ counter-ion as $Ca(SO_4)$ and $Mg(SO_4)$. Concentrations of Ca and Mg were more than 50% lower in the Eyjafjallajökull ash leachates than the San Cristóbal leachates and almost 100% of the Ca and Mg present in solution were in the form of free ions. Concentrations of Na and K however, were greater in the Eyjafjallajökull ash leachates than the San Cristóbal leachates with 178 µmol Na $l^{-1}$ in the first pulse of the 5cm Fine ash column leachate compared to 55 µmol $l^{-1}$ in the San Cristóbal leachate. All of the Na and K in the Eyjafjallajökull leachates was present as free $Na^+$ and $K^+$ ions. The speciation of Na and K in the San Cristóbal leachates was slightly different. Approximately

90% of the Na and K was present as free ions, the remaining 10% was split between $SO_4$ and Cl counter-ions as $Na_2SO_4$, NaCl, $K_2SO_4$ and KCl.

### *Metals*

There were similar concentrations of Al and Fe in the San Cristóbal and Eyjafjallajökull leachates with ~220 μmol Al $l^{-1}$ and ~3 μmol Fe $l^{-1}$ in the leachate from the San Cristóbal and 5cm Fine ash columns. However, concentrations of heavy metals such as Zn, Cu, Ni and Sr were considerably higher in the San Cristóbal ash leachates with greater concentrations being released in the first pulse than the second pulse. The highest concentrations of these heavy metals in the San Cristóbal leachate were found in the following order: Cu > Zn > Ni > Cr. Approximately 192 μmol $l^{-1}$ Cu was leached from the ash in the first pulse of water which was followed by a further 111 μmol $l^{-1}$ in the second pulse. In comparison, the total Cu concentration released from the 5cm fine ash column was 9 μmol $l^{-1}$. Chemical speciation modelling revealed that 50% of the Cu was in the form of free $Cu^{2+}$ ions and the rest was in the form of $CuSO_4$. The speciation of Cu in the Eyjafjallajökull leachates was 75-85% free $Cu^{2+}$ with the remaining Cu as copper hydroxides. The same speciation results were given for Zn, Sr, Ni and Pb in the Eyjafjallajökull leachates. The San Cristóbal speciation results showed less free metal ions in solution and a greater percentage of $SO_4$ compounds (Zn: 40% free $Zn^{2+}$, 60% $Zn(SO_4)$. Sr: 55% free $Sr^{2+}$, 45% $Sr(SO_4)$. Ni: 50% free $Ni^{2+}$, 50% $Ni(SO_4)$. Pb: 15% free $Pb^{2+}$, 85% $Pb(SO_4)$). The speciation of Al and Fe also differed between the leachates of the two different ash samples. Water leached through the Eyjafjallajökull ash contained mostly Al and Fe hydroxides whereas the San Cristóbal leachates contained only Al and Fe that was complexed with F.

## 5.4 Discussion

The results of this experiment suggest that tephra addition to soils may affect $CO_2$ production and transport through the physical effect of ash on the soil surface and the chemical effect of ash leaching into the soil. These results differ from Elliott et al. (1982) who mixed soil with volcanic ash from the 1980 eruption of Mt. St. Helens (Washington, USA) over a 20 day incubation period and found no change in $CO_2$ evolution or $O_2$ uptake from the soil mixtures. They concluded that volcanic ash deposition would have little effect on microbially controlled soil processes. However, the study only used laboratory incubations and was not carried out in the field under natural conditions as is reported here.

### 5.4.1 Physical effects of ash on $CO_2$ flux

Ash from the 2010 Eyjafjallajökull eruption was used to assess the physical effects of ash on $CO_2$ flux with a variety of treatments incorporating different grain sizes and ash layer thicknesses. The results show a significant reduction in $CO_2$ flux when the soils were wet due to the addition of a 10 cm Coarse ash layer and significant differences between the coarse and fine Eyjafjallajökull treatments between 31 and 94 hours. Payne and Blackford (2005) found no evidence of any physical effects of tephra on peatland ecosystems when they added tephra treatments of 1-700 g $m^{-2}$. However, Hotes et al (2004) reported that in the first two years after treatments of 6 cm layers of ash, the physical effect of tephra was more important for vegetation than chemical changes of the porewater. They reported that fine-grained material caused stronger vegetation change than coarse.

*Ash thickness*

Our study indicates that ash thickness can influence the $CO_2$ flux of soils during wet periods as a 10 cm layer of coarse ash significantly reduced the emission of $CO_2$ whereas a 5 cm layer of the same ash did not. There were no differences in $CO_2$ flux between the 5 and 10 cm Coarse treatments during the dry sampling period. This effect during wet periods is likely due to a physical effect of the ash on $CO_2$ transport from the soil to the atmosphere. Coarse ash has a higher permeability than soil (Goldin 1982) so water infiltrates through quickly and the soil forms a barrier, therefore the ash becomes saturated with water and gas cannot escape. One possible reason why a significant reduction in ER is seen in the collars treated with 10 cm of ash and not in those treated with 5 cm of ash may be due to the vegetation, enhancing transport routes for $CO_2$. The vegetation in the 10 cm ash collars was mostly buried by ash and a crust of ash may have formed at the surface (Schulte et al. 1985), acting as a barrier and preventing the escape of $CO_2$. The vegetation was only partially buried in the 5 cm ash collars so the ash surface was interrupted by vegetation (Fig. 5.12). This allows alternative pathways for $CO_2$ transport even if a crust is formed.

The partial burial of vegetation reduces the access of $O_2$ to plant roots and also causes suffocation and starvation. Ash coats leaves and stems, which reduces light intensity and clogs stomata thereby reducing photosynthesis (Eggler 1948). Although GP was not measured in this experiment, it is likely that the 10 cm Coarse treatment would reduce photosynthesis. Photosynthesis supplies C substrates for root metabolism and growth. Plant metabolism and recently produced organic material are key drivers of soil respiration (Ryan and Law 2005); 64-86% of root-borne substances are rapidly respired by micro-organisms (Luo and Zhou 2006). If photosynthesis were reduced as is reported in the literature (Cook et al. 1981; Eggler 1948; Hinkley and Smith 1982) this would reduce root exudate production and therefore substrate supply for respiration. In a tree girdling experiment where the supply of photosynthates to roots was terminated, decreases in soil respiration of up to 37% were detected within 5 days. This increased to 54% after 2 months (Hogberg et al. 2001). The link between soil respiration and substrate supply from photosynthesis has also been demonstrated using clipping and shading experiments on U.S. grasslands (Craine et al. 1999; Wan and Luo 2003). In the Great Plains, soil respiration decreased by nearly 70% within one week of shading (Wan and Luo 2003). If the respiration experiment in Iceland had been continued over a longer period, a decrease in $CO_2$ flux may have been observed from the soils covered with the 10 cm ash layer due to a reduction in photosynthesis.

At the end of the experiment, soil temperature was significantly higher in the 10 cm Coarse soils than the control soils. The same temperature rise was not observed for the soils treated with 5 cm of the same ash. It is therefore unlikely that the rise in temperature is due to the dark colour of the ash lowering the albedo of the surface and absorbing heat. It is more likely that the thicker ash was acting like a physical barrier, insulating the soil and trapping the heat in. The sensitivity of respiratory processes to an increase in temperature is described by the quotient $Q_{10}$. At the biochemical level, the $Q_{10}$ is approximately 2, which means that respiration rate doubles for every 10ºC increase in temperature (Luo and Zhou 2006). The increase in temperature of the soils receiving 10 cm of ash was only 0.25ºC over the course of the experiment. It is therefore not a large enough increase in temperature to significantly increase respiration rates of these soils.

*Grain size*

Soils treated with the coarse ash layers (5 and 10 cm) showed a trend of increased respiration when compared to controls. Although this was not statistically significant, the 10 cm Coarse treated soils did have significantly greater rates of ER than the 5cm fine and San Cristóbal treated soils which implies that grain size is an important factor in regulating $CO_2$ flux from ash covered soils. Hotes et al. (2004) speculated that fine-grained tephra could impede gas exchange between the soil and the atmosphere which could reduce $O_2$ saturation and possibly redox potentials. In a seedling study, soil oxygen levels were significantly decreased with increasing tephra thickness (Schulte et al. 1985). This could be true for the 5 cm Fine and San Cristóbal treatments, which are both fine grained (median grain size of 18 and 32 µm respectively) and both showed a trend of lower $CO_2$ flux than the Controls over the sampling period. Fine ash particles can move downwards with water and clog the underlying soil pore spaces (Sneva et al. 1982), which changes the porosity of the soil and the transport route of $CO_2$, potentially reducing the $CO_2$ flux at the surface. There was a noticeable difference in the physical characteristics of the ash that had been leached with water in the column leaching experiment. The fine ash had cemented together to form a hard and solid layer, which then shrank as it dried leaving gaps around the edges of the column. The cementing of fine ash has also been reported in other studies (Hotes et al. 2004; Mack 1987; Schulte et al. 1985). This may have occurred in the field experiment, which is a possible reason why ER was lower for the 5 cm Fine and San Cristóbal soils than the Controls. The reduction in $CO_2$ flux was not significant as preferential pathways for $CO_2$ emission were created around the edge of the collar. In reality the ash layer would not be interrupted in this way and therefore the deposition of fine-grained tephras may have a significant effect upon $CO_2$ fluxes. The effect of addition of fine-grained tephra over larger surface areas on $CO_2$ fluxes deserves further research.

Volcanic ash can play an important role in regulating soil moisture and is known to benefit agriculture in arid climates when applied as mulch to the surface of the soil (Diaz et al. 2005; Tejedor et al. 2003). The grain size of the ash is a key factor in the regulation of soil moisture. Coarse ash enhances infiltration and reduces evaporation when dried which replenishes soil moisture. Fine ash swells and seals when wet, retarding infiltration and increasing surface run-off (Sneva et al. 1982). These fine particles also clog underlying soil pore spaces further reducing infiltration and soil moisture entry (Black and Mack 1986; Cook et al. 1981; Sneva et al. 1982). Soil moisture did increase over the course of the experiment for all soil collars due to the initial water input and rainfall, but there were no significant differences in moisture content of soils covered by different grain sizes of ash as had been expected. If $CO_2$ flux had been measured over a longer time period, perhaps differences in soil moisture between the treatments would have evolved and had subsequent effects upon ER.

### 5.4.2 Chemical effects of ash on $CO_2$ flux

The chemical effect of ash leaching upon soil respiration was assessed using the San Cristóbal ash treatment as the Eyjafjallajökull ash had previously been leached by rain. Soils treated with San Cristóbal ash had significantly lower $CO_2$ fluxes throughout the post-treatment monitoring period. This is likely to be due to a chemical effect of leaching this ash. The San Cristóbal ash was leached in the laboratory column leaching experiment to investigate which chemical species would have been released from the ash in to the soil in the field experiment in

Iceland. The results showed acidic leachate solutions enriched in Cl, $SO_4$, F, Ca, Mg, Cu, Al and Zn. These acidic inputs from the ash layer resulted in a significant reduction of average soil pH by 7% when compared the Control soils. This is the pH of the soil not the soil solution, which is likely to reflect ash leachate pH values. The reduction in ER could be due to the low pH of the acidic ash leachates.

Soil pH regulates chemical reactions, the bioavailability of metals and the multiplicity of enzymes in micro-organisms (Luo and Zhou 2006). Most bacterial species grow within a pH range of 4–9; as such soil pH is an important factor controlling the growth and activity of soil microbes. Several studies have reported a positive correlation between pH value and soil $CO_2$ production (Hall et al. 1998; Reth et al. 2005; Sitaula et al. 1995). Rousk (2009) reported soil respiration rates that were 33% lower in a soil with a pH of 4.5 when compared to a soil with a pH of 8.0. Production of $CO_2$ is 2-12 times lower in soils with a pH of 3.0 compared to soils with a pH of 4.0 due to the adverse effect of low pH on soil microbial activity (Sitaula et al. 1995).

Soil pH not only affects soil microorganisms but also the availability of nutrients and the solubility of metals (Firestone et al. 1983; Rousk et al. 2009). The acidic San Cristóbal leachates (pH 3.88 and 4.17) contained high concentrations of heavy metals and Ca when compared to the Eyjafjallajökull ash leachates, which had a pH range of 6.7-7.0. In particular, concentrations of Cu and Zn were high in the San Cristóbal column leachates.

The adverse effect of heavy metals on soil biological and biochemical properties have been well documented (Baath 1989; Bardgett et al. 1994; Doelman and Haanstra 1984; Speir et al. 1999). Speir (1999) reported a sharp decline in soil respiration when three New Zealand soils were amended with separate additions of Cd, Cr, Cu, Ni, Pb and Zn (Concentration range of 10-100 mmol metal $kg^{-1}$ soil). Additions of Cr and Cu acidified the soil below pH 5.0, causing soil respiration to decline linearly with pH. These metals strongly hydrolyse in solution causing an increase in the concentration of $H^+$ ions in soil solution and thus pH. The results of the ash leaching experiment (Table 5.4) were used to estimate the amount of these metals transferred from the ash layer in the field experiment to the underlying soil (top 5 cm: soil mass ~0.5 kg). Rough calculations give concentrations of 0.4 μmol Cd kg$^{-1}$, 0.6 μmol Cr kg$^{-1}$, 160 μmol Cu kg$^{-1}$, 2.2 μmol Ni kg$^{-1}$, 0.3 μmol Pb kg$^{-1}$ and 30 μmol Zn kg$^{-1}$. Speir (1999) also found Ca to be an effective inhibitor of respiration when it was added at a concentration of 10 mmol kg$^{-1}$ soil. However, the authors concluded that a significant proportion of the inhibition of soil respiration was due to soil acidification rather than due to direct metal toxicity. Concentrations of Ca released from the ash were significantly lower that this value at 360 μmol Ca kg$^{-1}$. Although concentrations of metals in the ash leachates were lower than those reported in the literature, there was still a significant decrease in soil pH. It is therefore likely that the significant reduction in soil respiration recorded in the field in the soils, which received a 5 cm layer of San Cristóbal ash, is due to a combination of soil acidification and metal toxicity having an adverse effect on soil microbial activity. As tephra layers are repeatedly leached after deposition during every rainfall event, they will continue to release metals into the soil and therefore the effect on soil pH and consequently soil respiration may be prolonged. If the experiment had been continued over a longer time period the effect of the acidic inputs on soil pH may further reduce soil respiration from the San Cristobal collars.

## 5.5 Conclusion

The field study reported in this chapter is a first attempt at investigating the effect of tephra layers on $CO_2$ emissions from a grassland site in Iceland. This study highlighted some interesting findings that deserve further research. Firstly, the most significant finding was that the chemical effects of leaching volcanic ash can reduce ER by 30% when compared to Control soils. The cause of this effect is unknown but is likely to be due to a lowering of pH. In future experiments, changes in soil solution chemistry should be monitored alongside measurements of ER to give a better indication of how volcanic leachates affect the emission of $CO_2$. Secondly, there was evidence of a short-term physical effect of tephra deposition, which caused a decrease in ER but only when the ash was wet. Further work should be carried out on the effect of tephra thickness and grain size on the emission and transport of $CO_2$. Thirdly, no effect on vegetation was seen here but the experiment was carried out over a small surface area for just 5 days.  Effects on vegetation may take longer to appear.  This may deserve further research due to the strong relationship between photosynthesis providing substrates for soil respiration.

# Chapter 6: Conclusions

## 6.1 Gaps in knowledge identified

The objective of this thesis was to increase the understanding of the effects of distal volcanic deposition on peatland ecosystems, in particular the effects on peat soil chemistry and emissions of $CH_4$ and $CO_2$. A greater understanding of the effects of volcanic deposition on C cycling in peatlands has important implications for evaluating the role of volcanic activity in influencing the terrestrial C cycle. The aim of this research was to investigate the following gaps in current scientific knowledge:

- The effect of F addition on peat soil chemistry
- The effect of F addition on $CH_4$ and $CO_2$ emissions from peat soils
- The effect of co-addition of F and $SO_4$ on $CH_4$ and $CO_2$ emissions from peat soils
- The effect of layers of ash in the vicinity of an eruption on ecosystem respiration

## 6.2 Main findings of thesis

*The effect of F and $SO_4$ addition on peat soil chemistry*

- The addition of High F and $SO_4$ + High F treatments to peat mesocosms resulted in increased concentrations of F, Al, Fe and acetate in solution. There was no change in soil solution pH. In the soil, concentrations of F and Fe were increased and concentrations of S were decreased. In the *Eriophorum* shoots, concentrations of F and Al were increased.

- The addition of $SO_4$ resulted in no change in $SO_4$ or S concentrations in soil, soil solution and plant material. There was also no effect of treatment on soil solution pH. The only significant changes to peat mesocosms which received the $SO_4$ and $SO_4$ + Low F treatments were an increased in soil P concentrations and a decrease in soil Si concentrations.

*The effects of treatments on peat soil $CH_4$ emissions*

- The addition of F to peat mesocosms had no effect on $CH_4$ emissions over the 20 week study. Incubations of the same soils indicated that F did not have an effect on the individual processes of $CH_4$ production or $CH_4$ oxidation. The results were the same when F was added in combination with $SO_4$.

- The addition of $SO_4$ to peat mesocosms had no effect on $CH_4$ emissions and did not cause a suppression of $CH_4$ as has been reported in other studies.

- Laboratory incubations of a pristine peat soil (Moidach More) also showed no effect of $SO_4$ addition on $CH_4$ production rates. Interestingly, the addition of high concentrations of F resulted in a sevenfold increase in $CH_4$ production rates when compared to controls.

*The effects of treatments on peat soil $CO_2$ emissions*

- Additions of F, $SO_4$ and F+$SO_4$ had no effects on mesocosm $CO_2$ emissions.

*The effects of ash layers on ecosystem respiration*

- The chemical effect of leaching a volcanic ash layer significantly reduced ecosystem respiration by 30% when compared to controls.

- After precipitation events there was a short-term physical effect of ash deposition where soils covered with ash had lower rates of ecosystem respiration when compared to controls. This effect was most pronounced in the soils that were covered with the thickest (10cm) ash layer.

- The burial of vegetation had no effect on ecosystem respiration.

The results of Chapter 2 suggested that the deposition and subsequent leaching of F-containing tephra on distal peatlands may cause disruption to ecosystem functioning. Addition of treatments containing high concentrations of F to ombrotrophic peat mesocosms had significant effects upon concentrations of some elements present in the soil, vegetation and soil solution. In the soil solution, the addition of F increased the solubility of Al, Fe and acetate resulting in the accumulation of these species in solution near the peat surface. This build up of acetate, Al and Fe over the treatment period suggests that F breaks down organo-metallic compounds causing leaching of organic matter along with metal ions. This may have implications for microbial communities within the peat that are associated with decomposition of organic matter and carbon cycling. There was no significant increase in pH with the addition of F as has been reported previously which may indicate that F substitution for $OH^-$ on mineral surfaces is not the dominant sorption mechanism in the peat soils tested. In *Eriophorum* shoots, concentrations of F and Al increased indicating that a fraction of those species were bio-available in solution. However, there were no signs of toxicity that are sometimes observed due to the presence of F and Al and no change in sedge density, which provides further evidence to support the argument that Al-F complexes are less toxic than F and Al separately.

Application of $SO_4$ and F to the Moor House peat soils had no effect upon $CH_4$ and $CO_2$ gas fluxes. There was no evidence of $CH_4$ emission suppression with the addition of $SO_4$ at a rate of 73.7 Kg $ha^{-1}$ over 20 weeks. There are two possible reasons for this; firstly, it may be due to peat soil heterogeneity with local conditions, i.e., microbial communities and peat composition etc. playing a more important role in regulating $CH_4$ fluxes than S inputs. An alternative explanation may be that past anthropogenic S pollution at the sampling site may mean that the suppressive effect of sulfate on methane emission was already at its limit, i.e., $SO_4$ availability within the peat was such as to render $CH_4$ emissions insensitive to additional experimental $SO_4$ inputs. These findings highlight the complexity of the relationship between S deposition and $CH_4$ suppression and point to a very long period of $CH_4$ emission recovery in peats subjected to past high S deposition events. Consideration of this effect in climate models is required in order to be able to fully appreciate how volcanism causes environmental changes.

This study found no effect of F addition of 13.5 and 135 kg $ha^{-1}$ on C gas fluxes from the mesocosm peat soils, despite the potentially toxic and reactive nature of F. There was evidence of F uptake by *Eriophorum* shoots, but there were no signs of visible injury. Plant damage through F toxicity is species dependent therefore other peatland species may be more sensitive which would have implications for $CH_4$ transport to the atmosphere.

Results from the soil incubation experiments indicated that the addition of F and $SO_4$ during the mesocosm experiment did not have any effect upon the individual processes of $CH_4$ production or $CH_4$ oxidation at 0-10 or 10-20 cm. These results were also confirmed by the measurement of microbial biomass, which was not significantly different in the treated mesocosms when compared to the controls. The addition of similar treatments to a pristine peat soil produced surprising results, as the addition of $SO_4$ did not suppress $CH_4$ production rates as had been expected. As the addition of $SO_4$ did not suppress $CH_4$ production in the pristine or polluted soil, this suggests that soil heterogeneity is a more important factor than $SO_4$ deposition and that the previous pollution history of the Moor House site was not the inhibiting factor of the suppression of $CH_4$. The production of $CH_4$ in peat soils depends on so many varied factors that local conditions within the peat play a major role in the emission of C gas fluxes from peat soils.

Another interesting result that deserves further attention is the increase in $CH_4$ production due to the addition of high concentrations of F in the pristine soil, which is possibly due F effects on substrate availability e.g. acetate. This suggests that the addition of F in volcanic deposition may increase $CH_4$ emissions from some peat soils. The addition of High Fluoride and Sulfate + High Fluoride to the pristine peat also caused a significant increase in anaerobic respiration rates. The same trend was seen for the mesocosm soils but the results were not statistically significant. Field studies should be carried out on a number of different peat soils, both pristine and polluted, to further investigate the effects of F on $CH_4$ and $CO_2$ emissions.

The field study reported in Chapter 5 is a first attempt at investigating the effect of tephra layers on $CO_2$ emissions from a grassland site in Iceland. One previous study mixed tephra with soil and found no change in soil respiration rates (Elliott et al. 1982). The effect of layers of tephra deposited on the soil surface on soil $CO_2$ fluxes has never before been assessed and may be important for areas in close proximity to volcanic eruptions as they receive large volumes of ash which may persist in the environment for long timescales (Wilson et al. 2011). This study highlighted some interesting findings that deserve further research. Firstly, the most significant finding was that the chemical effects of leaching volcanic ash can reduce ER by 30% when compared to Control soils. The cause of this effect is unknown but is likely to be due to a lowering of pH. In future experiments, changes in soil solution chemistry should be monitored alongside measurements of ER to give a better indication of how volcanic leachates affect the emission of $CO_2$. Secondly, there was evidence of a short-term physical effect of tephra deposition, which caused a decrease in ER but only when the ash was wet. Further work should be carried out on the effect of tephra thickness and grain size on the emission and transport of $CO_2$. Thirdly, no effect on vegetation was seen here but the experiment was carried out over a small surface area for just 5 days. Effects on vegetation may take longer to appear. This may deserve further research due to the strong relationship between photosynthesis providing substrates for soil respiration.

In conclusion, the addition of $SO_4$ to peat soils in the experimental works presented in this thesis did not suppress the emission of $CH_4$, even in the pristine Moidach More soil where this relationship has been verified before. This highlights the difficulty of working with natural systems, which have differing pollution histories, water tables levels, substrate quality, vegetation coverage and microbial communities. The mesocosm study further indicated that F deposition, at rates representative of tephra fallout does not interfere with C gas fluxes in peat soils, despite the well-established toxicity of F in the environment. This suggests that methanogens and methanotrophs may be tolerant to F at the doses applied. The lab incubations of pristine peat however, showed increased rates of $CH_4$ production where high concentrations of F had been added. This result suggests that F effect on C gas fluxes is still inconclusive and deserves further attention. The impact of tephra deposition on soil respiration from a grassland soil was also assessed. Over the duration of the experiment, inputs of acidic ash leachates reduced the soil pH lowering rates of ER. There was also a significant reduction in $CO_2$ flux when the ash-laden soils were wetted, the magnitude of this effect seemed to be influenced by the grain size characteristics of the ash particles. These results suggest that volcanic tephra deposition can impact upon the C cycle in the locality of the eruption site.

## 6.3 Future research

Although there was no effect of F on $CH_4$ emissions from Moor House peat soils, the results of the Moidach more peat incubations are intriguing. Further studies should:

- Investigate the effect of F in combination with $SO_4$ on fens and other peat types as F may have an effect on different pathways of $CH_4$ production, e.g., acetoclastic methanogenesis.
- Be carried out over a longer term to discover if F has any effects on vegetation that may impact on C fluxes either through changes in root exudates, changes in $CH_4$ emission pathways, respiration and photosynthesis or when F containing plant material is incorporated in to the litter.
- Add an ash layer treatment to investigate the effect of leachates containing F and other volcanic species e.g. heavy metals, which may affect pH.

Further research should also be carried out on the effects of $SO_4$ deposition on $CH_4$ suppression as the results presented here contrast with results presented in current literature. Sulfate addition to both the Moor House and Moidach more soils had no effect on $CH_4$ emissions, which is thought to be due to local peat conditions or previous site history. Further studies should:

- Be carried out on a large number of soils in order to discover trends between pristine sites and those which have previously been affected by $SO_4$ addition either volcanic or anthropogenic.
- Include soils with different $SO_4$ availabilities and $SO_4$ reduction rates.
- Use controlled environment cabinets to replicate field conditions.

The effect of ash layers on ecosystem respiration also deserves further research. Further studies should:

- Run over a longer time period to include vegetation effects and pH effects over time.
- Include measurements of soil solution and soil moisture throughout the sampling period.
- Have a larger number of replicates.
- Test a variety of soils including peats.
- Increase the number of ash layers thicknesses and grain sizes.

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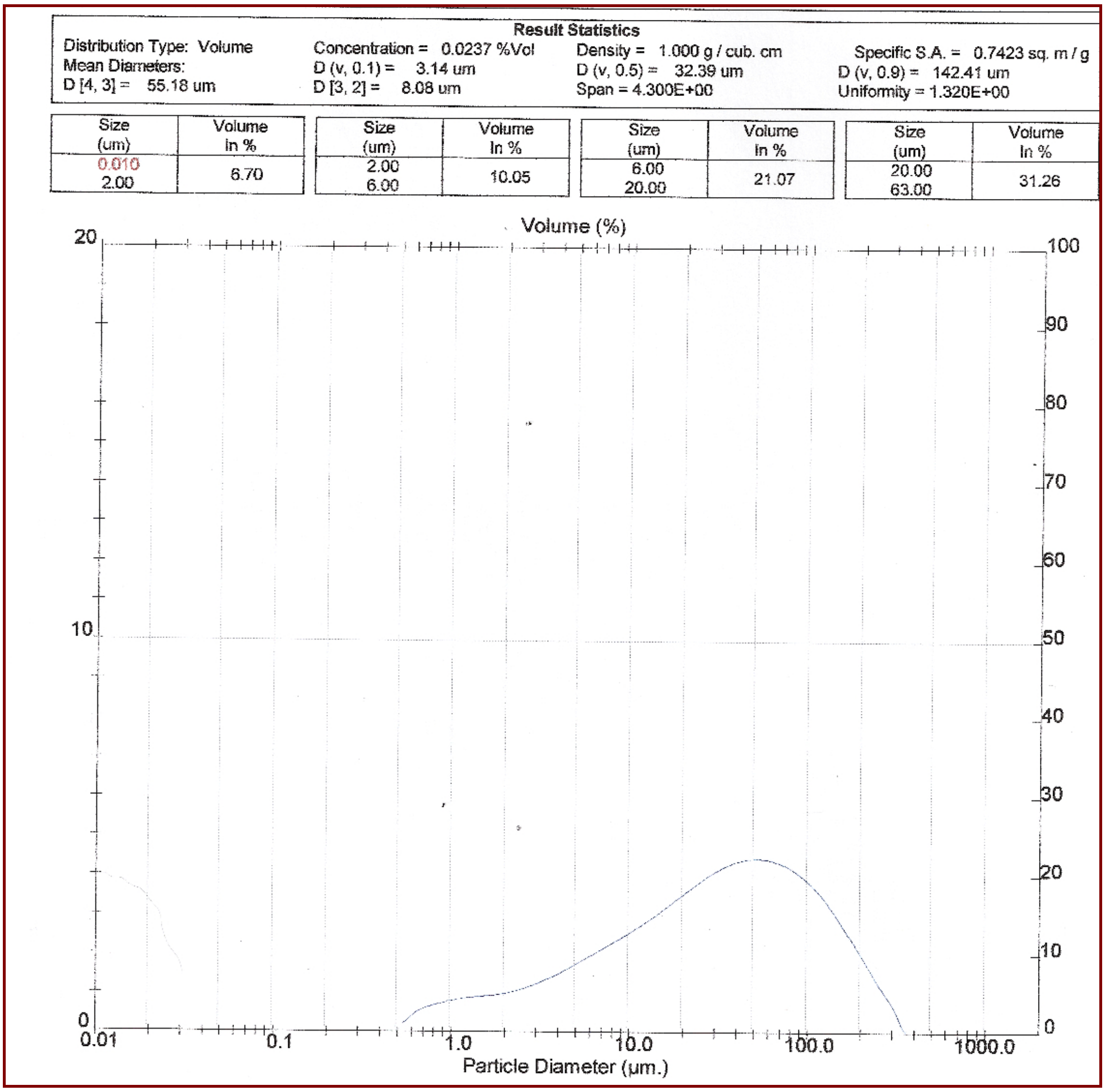
# *Appendix I*

## 1.1 Chapter 5 supporting information

*Particle size analysis results*



**Result Statistics**

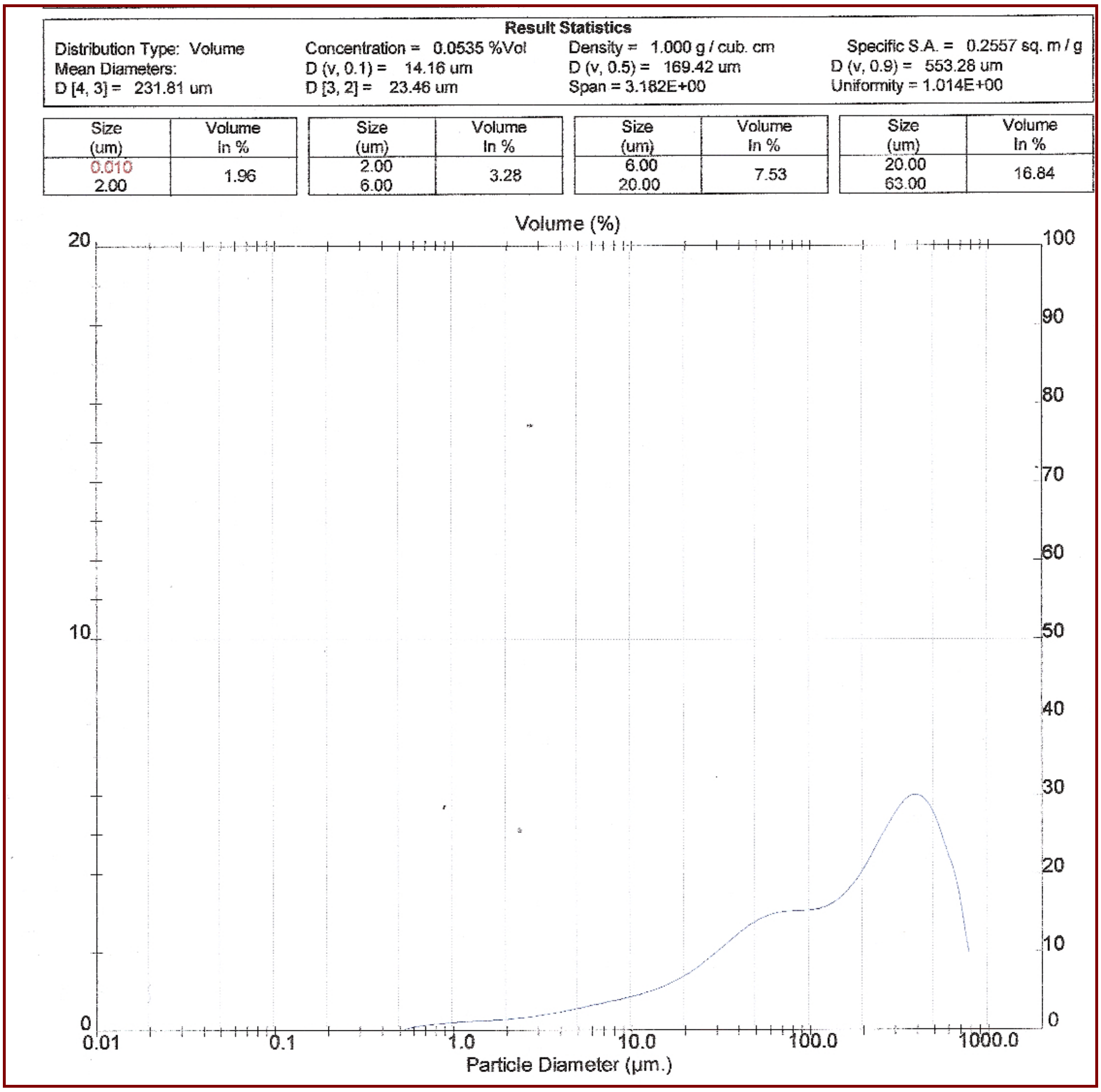
Distribution Type: Volume
Concentration = 0.0237 %Vol
Density = 1.000 g / cub. cm
Specific S.A. = 0.7423 sq. m / g

Mean Diameters:
D (v, 0.1) = 3.14 um
D (v, 0.5) = 32.39 um
D (v, 0.9) = 142.41 um

D [4, 3] = 55.18 um
D [3, 2] = 8.08 um
Span = 4.300E+00
Uniformity = 1.320E+00

| Size (um) | Volume In % | Size (um) | Volume In % | Size (um) | Volume In % | Size (um) | Volume In % |
|---|---|---|---|---|---|---|---|
| 0.010<br>2.00 | 6.70 | 2.00<br>6.00 | 10.05 | 6.00<br>20.00 | 21.07 | 20.00<br>63.00 | 31.26 |

**Fig. A.1** Particle size analysis results for the San Cristóbal ash sample



**Result Statistics**

Distribution Type: Volume
Mean Diameters:
D [4, 3] = 231.81 um

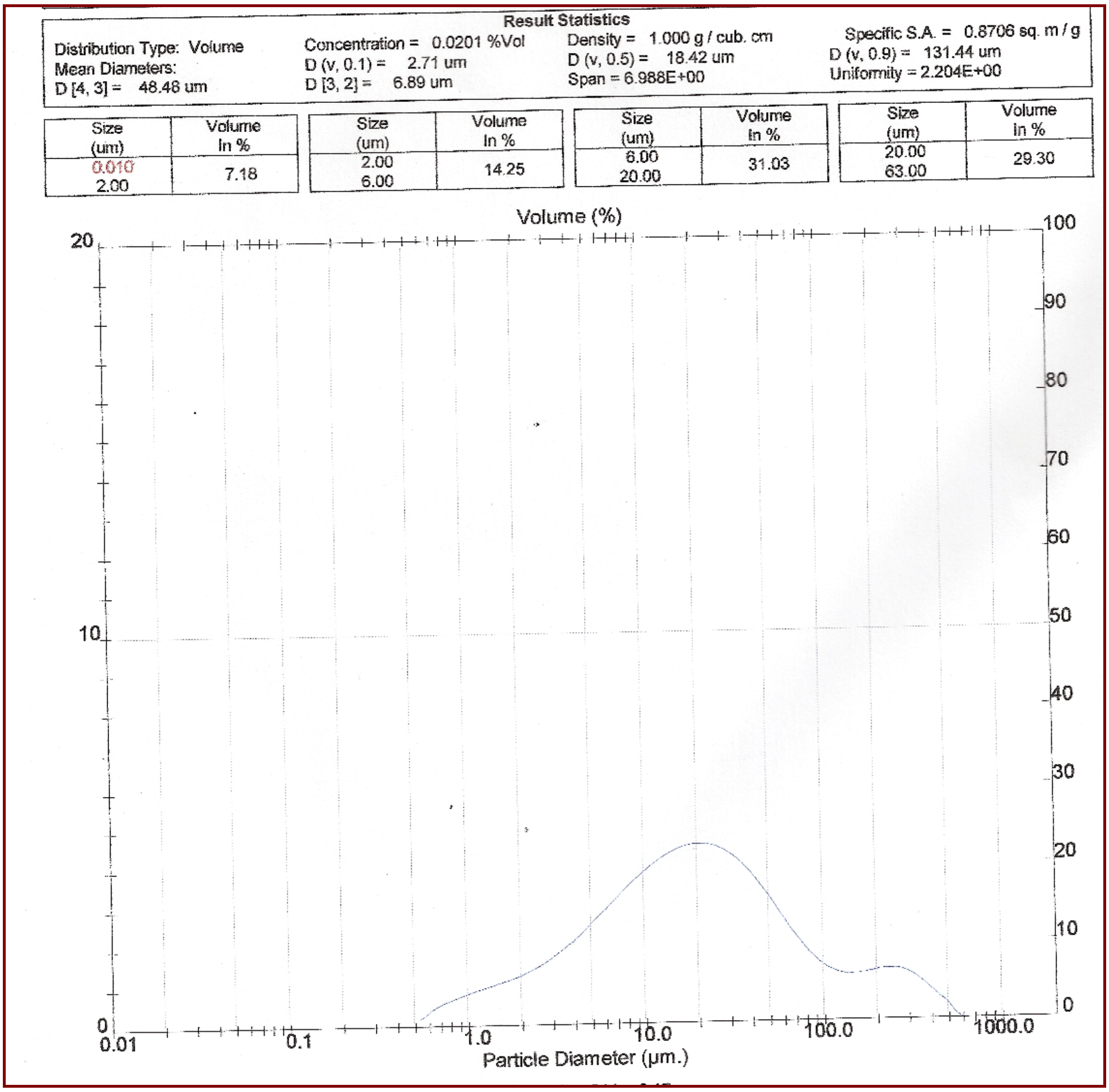
Concentration = 0.0535 %Vol
D (v, 0.1) = 14.16 um
D [3, 2] = 23.46 um

Density = 1.000 g / cub. cm
D (v, 0.5) = 169.42 um
Span = 3.182E+00

Specific S.A. = 0.2557 sq. m / g
D (v, 0.9) = 553.28 um
Uniformity = 1.014E+00

| Size (um) | Volume In % | Size (um) | Volume In % | Size (um) | Volume In % | Size (um) | Volume In % |
|---|---|---|---|---|---|---|---|
| 0.010<br>2.00 | 1.96 | 2.00<br>6.00 | 3.28 | 6.00<br>20.00 | 7.53 | 20.00<br>63.00 | 16.84 |

**Fig. A.2** Particle size analysis results for the coarse Eyjafjallajökull ash sample



Result Statistics

Distribution Type: Volume
Mean Diameters:
D [4, 3] = 48.48 um

Concentration = 0.0201 %Vol
D (v, 0.1) = 2.71 um
D [3, 2] = 6.89 um

Density = 1.000 g / cub. cm
D (v, 0.5) = 18.42 um
Span = 6.988E+00

Specific S.A. = 0.8706 sq. m / g
D (v, 0.9) = 131.44 um
Uniformity = 2.204E+00

| Size (um) | Volume In % |
|---|---|
| 0.010<br>2.00 | 7.18 |

| Size (um) | Volume In % |
|---|---|
| 2.00<br>6.00 | 14.25 |

| Size (um) | Volume In % |
|---|---|
| 6.00<br>20.00 | 31.03 |

| Size (um) | Volume In % |
|---|---|
| 20.00<br>63.00 | 29.30 |

**Fig. A.3** Particle size analysis results for the fine Eyjafjallajökull ash sample