

*Impacts of volcanic ash originating from the April 2010
eruption in Eyjafjallajökull (Iceland) on the
natural resources of Scotland*

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Executive Summary

The fall out of volcanic ash from the eruption of the Icelandic volcano Eyjafjallajökull caused significant travel disruption and raised concerns about the potential impacts on Scottish natural resources. This report provides an evaluation of these potential impacts on 3 main resource areas: (i) pastures and livestock; (ii) soils and (iii) surface water. This is based on current scientific opinion as well as post-eruption data collected from long-term monitoring sites. This report has been prepared as part of research funded by the Scottish Government.

Volcanic eruptions result in substantial emissions of gases and ash particles. The varying characteristics of ash between volcanoes and individual eruptions and the consequent transport patterns increase uncertainty of predicting the impact of ash fall on pasture, soils and waters across Scotland. According to the US Energy Information Administration, global human activity contributed 29,195 million tonnes of CO₂ to the air in 2006. Thus the Eyjafjallajökull eruption, although not insignificant at a maximum 30000 tonnes day⁻¹ will not make a substantial addition to global anthropogenic atmospheric CO₂ emission. The majority of the ash from the recent eruption appears to be fine grained glass particles, which can be dispersed widely. The main risks are to livestock through fluoride ingestion from volcanic ash on pasture. Initial indications are that the volcanic ash layer deposited in Scotland was thin (< 5 mm), and effects on pasture and soils are negligible. It is also clear that not enough ash was deposited to have a negative effect on water quality.

Initial data collected by the Macaulay Land Use Research Institute indicates that ash was present in Scottish rainfall and snow samples collected following the eruption. However, there were little measurable effects in surface waters in this instance compared to pre-eruption data. Measurable effects may have been associated with increased fluoride concentrations derived from ash that has fallen directly onto water surfaces and acidification episodes caused by increasing sulphate deposition in rainfall and snow that is then rapidly transported to rivers and lakes. Higher altitude and acid prone areas of Scotland are potentially more sensitive to increased inputs from the volcanic eruption leading to surface waters experiencing more acidic conditions than otherwise expected during snowmelt or high rainfall periods. Thus seasonality of deposition can have a major bearing on the associated risk of negative impacts, such as impacts that coincide with when freshwater fish, such as trout and salmon are most vulnerable or when crops are being planted.

Historic and continued post eruption monitoring of pH, sulphate, fluoride, dissolved organic carbon, trace metals, and particulate material in rainfall/snow and surface waters from sensitive upland areas will ensure that any unforeseen changes from the norm are detected. This will be important in the event of more substantial Icelandic volcanic eruptions e.g. Katla which would be expected to produce from 10-100 times more ash than the recent eruption at Eyjafjallajökull.

Introduction

The fall out of volcanic ash from the eruption of the Icelandic volcano Eyjafjallajökull in April 2010 caused significant travel disruption and raised concerns about the effects of deposited ash on natural resources in Scotland, in particular vegetation, soils and water surfaces. On the basis of historical evidence and depending on the scale of the eruption and transport patterns in subsequent days, weeks and months, it is known that volcanic eruptions on Iceland, which result in substantial emissions of gases and particles, have the potential to impact on Scottish natural resources. The purpose of this report is to document the effects of this event.

Prior to the main eruption at Eyjafjallajökull, gaseous emission and chemical composition analyses of ash from earlier smaller eruptions, close by at Fimmvörðuháls, were undertaken by the Institute of Earth Sciences, University of Iceland on the 1st-2nd April (see **Table 1**). Data collected indicated lava was of an alkali-olivine basalt origin, similar to that for Eyjafjöll. Leachate tests on ash from Fimmvörðuháls were performed to assess solubilisation of potentially toxic fluoride, which has been a cause of concern following past volcanic eruptions. These tests were mainly on samples composed of coarse ash; it is anticipated that the amount of fluoride leached from ash particles will increase with distance from eruptions as deposited ash becomes dominated by more finely grained material with enhanced surface areas, although these finer ash particles will be dispersed over a wider area (<http://www.earthice.hi.is/page/IES-EY-CEMCOM>).

Table 1 Preliminary observation from eruptions at Fimmvörðuháls*

Gas composition and flux report

The SO₂ gas flux produced by the eruption was ~3000 tonnes per day .

Approximately 70% of this SO₂ flux was produced by the fissure which opened on 31st March, with ~30% emitted from the 21st March fissure.

The flux of hydrogen fluoride from the eruption was ~30 tonnes per day.

Gas compositions emitted from the two eruption fissures were broadly similar, being very rich in H₂O (>80% by mole), <15 % CO₂ and <3% SO₂.

Strong variations between 5 and 25 in the SO₂/HCl ratio were observed at the 31st March fissure on the two measurement days, with higher values observed on 1st April when the activity was apparently more intense than 2nd April.

*after [Burton et al. 2010, Institute of Earth Sciences, University of Iceland, 2010](#)

The main eruption at Eyjafjallajökull was visually confirmed on 14th April 2010 and has since been monitored on a daily basis. Furthermore, data on chemical composition (<http://www.earthice.hi.is/page/IES-EY-CEMCOM>) and ash grain size distribution (http://www.earthice.hi.is/page/ies_EYJO2010_Grain) are available from samples taken between 15th and 28th April 2010 ([Institute of Earth Sciences, University of Iceland](#)).

Part (i) Potential impacts on grazed pastures and livestock

Effect of rainfall on pastures

After the accident at the Chernobyl nuclear power station in 1986, it was found that the contamination to pastures in Scotland were primarily of a particulate nature, which upon deposition, became attached to the herbage leaf surfaces, posing an immediate threat to livestock, through ingestion. However, these particles were rapidly washed from the leaves into the soil by rainfall, dew and fog. The same dependency on prevailing weather conditions could be expected of the volcanic ash deposit. Once within soil, it could be expected that the volcanic ash residues would have little effect on the health of livestock.

Ingestion of ash from contaminated pasture

It is likely that pastures across Scotland will have received some atmospheric deposits of volcanic ash from Eyjafjallajökull. If so, grazing livestock (predominantly sheep and cattle) are likely to have ingested this material. There is also a possibility that animals may have inhaled fine ash particles. Furthermore, under circumstances of direct deposition on to the animals themselves, there may have been uptake of soluble materials coming from the ash via the skin of these animals. Whether exposure of grazing animals, via ingestion, inhalation or skin absorption to volcanic ash could adversely affect their health depends upon the physical and chemical characteristics of the ash particles and the level of deposition. There is a literature on the effects of volcanic eruptions on livestock health in different parts of the world. This, combined with information on the chemical composition of ash derived from Eyjafjallajökull, can help in assessing its impacts on grazing livestock in Scotland.

Past volcanic eruptions and effects on livestock

Although the chemical composition of volcanic ash can vary substantially, depending on the individual volcano and type of eruption, most ash consists mainly of siliceous materials, sulphate, chloride salts and oxides of common metallic elements, including aluminium, iron, sodium, calcium and magnesium; other trace elements may also be present. Although these materials are essentially non-toxic, the presence of the potentially toxic levels of fluoride (Solubilised fluoride and gaseous Hydrogen fluoride are amongst emissions from volcanic eruptions – **Table 1**) holds most concern for livestock health. However, results of investigations following a number of volcanic eruptions from various parts of the world have been very variable.

In August 1991, volcanic ash from an eruption from Mount Hudson in Chile, was apparently responsible for the deaths of thousands of sheep. Although the volcanic ash was found to contain high levels of fluoride, a subsequent investigation found that there were no signs of fluorosis in grazing sheep or humans which had been exposed. Thus, it was concluded that the sheep had died from factors (unexplained) relating to the physical characteristics of the volcanic ash, and not the fluoride content ([Rubin et al.](#)

1994). Fluorosis is a disease that damages the bones and joints (skeletal) and teeth (dental); the mineral tolerance of domestic animals to fluoride is described in the appendix A. **Table 2** describes maximum tolerable levels of fluoride for different livestock.

Adverse effects on grazing livestock were reported following eruptions from Mount Ruapehu, New Zealand (<http://volcanoes.usgs.gov/ash/agric/index.html#livestock>), during 1995-1996. Over 2000 grazing ewes and lambs were reported to have been killed in the Rangitaiki Plain (Taupo) from the Ruapehu eruption in October 1995 as a result of grazing pasture contaminated with 5 mm of ash. Post-mortem examinations suggested fluoride toxicity and pregnancy toxemia as the main causes of death. A few cattle and feral deer were also reported to have been killed from fluoride poisoning over the 1995-1996 period of the Ruapehu eruptions. It was suggested that the relatively high degree of soil ingestion by sheep in early spring would have exacerbated the effect (Cronin et al. 2003). Other effects of the volcanic ash were reduced soil pH due to the high sulphur content of the ash, and potential effects on copper metabolism from high sulphur intakes by sheep. The potential of other disturbances in trace element metabolism due to high sulphur intakes, e.g. molybdenum, selenium and zinc were not mentioned. It is noteworthy that Cronin et al. (2003) did not suggest the cause of the pregnancy toxemia deaths occurring after the Ruapehu eruptions. Pregnancy toxemia occurs most commonly from insufficient energy intake, leading to glucose deficiency in pregnant sheep. It is possible that many Ruapehu sheep deaths occurred as a result of the animals refusing to eat contaminated pasture.

Table 2: Recommended maximum tolerable levels of fluoride for a range of livestock

Receptor	Max tolerable level (ppm dw)	Notes
Calves	40	Minor lesions in teeth seen at 20 ppm, but relationship to animal performance not established
Dairy cattle	40	Mature dairy cattle consume more feed in relation to bodyweight than beef cattle
Beef cattle	50	
Finishing cattle	100	
Horses	40	Extrapolation – no direct evidence
Rabbits	40	Extrapolation – no direct evidence
Breeding sheep	60	Lifetime exposure of sheep, swine and poultry is less than for cattle and horses
Finishing sheep	150	
Pigs	150	
Turkey	150	
Chickens	200	

Implications for effects of the current eruption on livestock

From the preliminary data on the composition of volcanic ash from the Eyjafjallajökull eruption, silica is the most abundant component, followed by alumina and compounds of iron, calcium, sodium and magnesium. Information on fluoride emissions from an

earlier eruption at Fimmvörðuháls (**Table 1**) suggested that hydrogen fluoride emission was approximately 30 tonnes per day and samples of soluble fluoride in ash and fluoride in snow, contaminated with ash were 92 ppm fluoride and 112 ppm fluoride, respectively (ppm = mg soluble fluoride kg⁻¹ ash). It was noted that the ash particles from which this data was obtained, were relatively large (0.2-1 mm) and, because it can be expected that finer particles will contain higher concentrations of extractable fluoride, and will be dispersed over a wider area, fluoride levels in ash deposited on the Icelandic Mid-southern lowlands could be as high as 500 ppm fluoride. The recommendation (for affected Icelandic farmers) was to evacuate animals from ash-contaminated fields and meltwater. The maximum leachable fluoride found after the Ruapehu eruption was 95.6 ppm; therefore, fluoride levels for the Eyjafjallajökull ash can be considered to be high.

Because the Eyjafjallajökull eruption occurred beneath a glacier, the rapid cooling effect of the ice resulted in the majority of the ash being in the form of very fine grained glass particles, which could be dispersed widely. Although such fine particles would be expected to have higher levels of extractable fluoride and other materials, the high degree of dispersal over the UK and Western Europe would lead to lower local deposition rates.

According to Cronin et al. (2003), sheep can tolerate 60 ppm fluoride, and cattle, 40 ppm fluoride in the diet before experiencing symptoms of sickness; a dietary level of 100 ppm fluoride is considered to be an immediate toxic level for ruminants. In relation to the 1995-96 Ruapehu eruptions, Cronin et al. (2003) suggested that a deposition 'as little as' 1 mm could lead to symptoms of fluoride toxicity. If it is assumed that the ash from the Eyjafjallajökull volcano contains 500 mg fluoride kg⁻¹ ash with a density of 1 g cm⁻³, a 1 mm deposit covering 1 m² would represent 1 kg of ash, equivalent to 10 tonnes ash ha⁻¹. It is inconceivable that such deposition levels could be experienced in Scotland from the Eyjafjallajökull eruption. However, if Scotland were to experience even a 0.1mm deposit (100 g m⁻² or 1 tonne ha⁻¹), a sheep eating 1.6 kg dry mass herbage day⁻¹ on a pasture at 4000 kg dry mass herbage ha⁻¹ would be eating the equivalent of 4 m² of herbage, and 400 g volcanic ash, if all of the ash was deposited on the herbage. Under such circumstances the sheep would receive fluoride at toxic levels.

It is clear that knowledge of the fluoride concentrations of deposited ash would be crucial in establishing whether there would be a risk to the health of grazing livestock. Although it has been predicted that smaller particles would have higher concentrations of extractable elements than larger particles, there appears to be little, if any, information on whether the extractable element concentration is affected by 'age' of the particle. Does a particle driven to high altitudes in the atmosphere lose extractable elements due to its association with water droplets and ice particles? If so, extractable element concentrations (including fluoride) may be very much lower in particles deposited at large distances (and many days later), compared with particles deposited very close to the volcano. If, following chemical analysis, fluoride concentrations in

volcanic ash deposited in Scotland are found to be low, the health hazard to grazing sheep and cattle could be considered to be much reduced. However, any adverse effect on dietary intake of grazed herbage must be taken seriously.

Part (ii) Potential impacts on soils

As with the livestock and their habitat, the main impact of the volcanic eruption on soil would be expected from the amount of fluoride that enters the soil environment. The chemical element fluorine (which is a gas at normal temperature and pressure) belongs to the halogen group of reactive elements that comprise Group VII of the periodic table (others include, chlorine, bromine and iodine). Fluorine is the most electronegative which means it is the most reactive, and does not exist in nature in an elemental state but forms chemical compounds with other elements as fluoride anion (F⁻) in mineral salts, solutions and gases.

Sources of fluoride in soils

Fluoride in soils can be derived from fluorine containing minerals in soil parent materials but it is also a contaminant originating from various industrial processes (e.g. aluminium smelters). Soils can also become contaminated from deposition of fluorine containing particles resulting from volcanic eruptions (Pyle & Mather 2009). Total fluorine concentrations in rocks and soils are variable (**Table 3**).

Table 3: Fluorine concentrations in rock and soils

Rock/soil type	Fluorine mg kg ⁻¹		Reference
	Range	Mean	
Granite	520-850		Kabata-Pendias, & Pendias, 2001
Basalt, gabbros	300-500		Kabata-Pendias, & Pendias, 2001
Limestones	50-350		Kabata-Pendias, & Pendias, 2001
Soils		200	Lindsay, 1979
Soils	110-700	462	Ure et al. 1979

Literature values given for total fluoride concentrations in soils are in the range 10-1000 mg kg⁻¹ on a dry weight basis (Kabata-Pendias, & Pendias 2001). Lindsay (1979) has reported an average value for soils of 200 mg kg⁻¹. For soils in the UK, values range between 110-700 mg kg⁻¹; a mean of 462 mg kg⁻¹ have been reported by Ure et al. (1979). In addition to sites receiving volcanic ash deposits, contamination can arise from industrial sources. For contaminated soils much larger concentrations have been reported, e.g. mining areas in the UK have concentrations of 2000 mg kg⁻¹ (Davis 1980). During the 20th century, fluoride release was one of the major air pollutants originating from industrial processes (e.g. aluminium smelting). Today little fluoride escapes beyond the factory limits; consequently the main source of fluoride to the wider environment is volcanic in origin (Belloma et al. 2007).

Monitoring studies following volcanic eruptions have provided an indication of the fluoride concentrations deposited on land and the accumulated concentrations in soils. [Belloma et al. \(2007\)](#) provided data on the environmental impact of fluoride emissions in the Mount Etna area. This study reported ash and total fluoride data within a 25 km radius of the volcano. Quantities of ash deposited ranged from as much as 21830 g m⁻² at 3.3 km from the volcano to 900 g m⁻² at 23 km. At distances greater than 22 km from the volcano the quantity of fluoride deposited was less than 0.06 g m⁻². These figures are cited to give some indication of the values close to the centre of an eruption and must be considered far greater than the amount deposited over Scotland over the period 14-21st April 2010.

Fluoride concentrations in soil and soil solution

In soil solution, fluorine can exist as a number of chemical species. Important species are the fluoride anion and a series of complexes formed with aluminium (e.g. AlF²⁺, AlF₂⁺, AlF₃⁰). In many natural waters, most of the fluoride could exist as Al-F complexes especially in acidic waters. When considering the solubility of fluoride in soils, it is important to distinguish between the total soluble concentration of the element and the activity of the free fluoride ion. Examples of fluoride reactions with soil components are described in the appendix B.

From the preliminary data on the composition of volcanic ash from the Eyjafjallajökull eruption (sampled on 15 April 2010), as noted previously, we can assume that the maximum fluorine content of ash is 500 mg kg⁻¹ and a deposit of 1 mm with a bulk density of 1 g cm⁻³ would deposit 1 kg of ash over an area of 1 m². To convert this amount to a soil concentration, we need to calculate the mass of soil within a square metre to some specified depth. If we assume a soil bulk density of 1 g cm⁻³, a 10 cm depth of soil would contain 100 kg and a 1 cm depth would have 10 kg. From these numbers, a 1 mm deposit of ash would raise the fluorine content to 50 mg F kg⁻¹ of soil if it reacted with the top 1 cm layer, however if the deposited fluorine reacted with the soil down to a depth of 10 cm the added fluorine would yield a concentration of only 5 mg F kg⁻¹ of soil. These values are well within the range of background soil concentrations.

Implications for effects of the current eruption on soils

The US Geological Survey have indicated that there are little detrimental effects provided ash falls are <5 mm deep, as the ash can be mechanically incorporated into agricultural soil and rehabilitation of land is not necessary. Recovery maybe slower in uplands where there is no tillage. Many Scottish soils, particularly podzolic soils are likely to contain sufficient amorphous iron and aluminium minerals to adsorb any leached fluoride from the surface soil horizons. However, if ash was deposited in greater quantities, it may be possible for fluoride to be transported through shallow sandy subsoils to surface waters. Any risk would need to be assessed with more detailed geochemical modelling analysis combined with site-specific soil data and quantitative information on the composition of deposited ash.

In organic soils, fluoride is likely to be more mobile than in mineral soils, although there is little available data in the literature on fluoride retention by organic soils. One possible consequence of soluble fluoride deposition on organic soils would be increased solubility of aluminium and some enhanced solubility of soil organic carbon (Elrashidi & Lindsay 1987). Wilke (1987) has also reported greater leaching of organic matter induced by fluoride in soils. Furthermore, a recent study (Romar et al. 2009) to investigate the influence of fluoride addition to acid soils reported high concentrations of fluoride (100 mg l^{-1}) brought about the mobilisation of soluble organic matter. It could be predicted that with a more severe eruption in Iceland and the deposition of greater quantities of ash onto peaty soil surfaces, there is a likely risk of increased loss of dissolved organic carbon in surface run off.

Part iii) Potential impacts on surface waters

Gaseous Emissions

As noted in **Table 1**, one of the main gases produced during volcanic eruptions is **Sulphur Dioxide** (SO_2). Increasing levels of atmospheric gases such as SO_2 have been shown to enhance the natural acidity (*ca* pH~5.6-6.0) of precipitation (rain and snowfall). In the atmosphere, the emitted SO_2 can oxidize to sulphate (SO_4). This can then react to form sulphuric acid and SO_4 -salts (e.g. with Ca, Na, Mg,) or be absorbed within ash particles (NIVA Communication 2010). As emissions come into contact with the soil and vegetation (as wet, dry or mist/cloud deposition), it eventually passes through the soil before reaching surface waters. Most of the sulphur from precipitation or leached from ash particles will be present in soil as negatively charged sulphate (SO_4^{2-}) ions. As increased amounts of sulphate are added to soil, its capacity to bind sulphate will decrease and excess sulphate leaches out to surface waters, associated with positively charged cations to maintain ionic balance. In poorly buffered acidic soils, such as organic rich upland soils in Scotland, most of these positive ions will be acidic (H^+) or potentially toxic aluminium (Al^{3+}) ions, reducing the pH of surface waters. In less acidic soils, mobilisation of base cations, such as calcium, will buffer surface waters (Brady 1990). Thus, physico-chemical characteristics of individual catchment soils will determine how much sulphate load is required before an effect on surface water chemistry would be noticeable. Moreover, varying ash characteristics (including leachate) between volcanoes and eruptions, increase the uncertainty of predicting the impact of ash fall and associated acid rain on soils and their receiving waters.

Large-scale research experiments in Norway (the RAIN project 1983-1992) have been undertaken to determine the impact on surface waters of sulphuric acid that has been artificially applied across a catchment scale. "Acidification of the runoff water was achieved gradually by small additions of acid with each watering and the increase in acidification took about 5 years. Small acid "episodes" occurred with each watering, but

these were caused by the acid that fell directly on open water surfaces in the catchment” (NIVA Communication 2010).

Therefore, SO₂ emitted from the volcanic eruptions on Iceland could contribute to increased acid precipitation over the UK, which in turn could affect the aquatic chemistry of watercourses. In the past, long-term effects of increased anthropogenic acidic precipitation had resulted in acidic lakes and streams, forest dieback and acidification of freshwaters. However, even short-term acidification episodes have been shown to result in episodic fish kills and reduced juvenile numbers if they coincide with the time when freshwater fish, such as trout and salmon are most vulnerable (Hesthagen 1989). Other acidic episodes can occur naturally during high flow conditions when water is rapidly routed via shallow sub-surface or overland flow paths with acidic chemistry that dominates the hydrograph. Thus, large depositions of sulphuric acid with snow can also cause acid impacts during snowmelts (Cadle et al. 1987; Mörth et al. 2008). This is because some of the melted snow rapidly bypasses the majority of the soil, running overland from patches of snow directly into lakes, streams and watercourses. Therefore, it is possible that higher altitude and acid prone areas of Scotland could receive increased sulphur inputs from the volcanic eruption, such that during snowmelt, surface waters may experience more acidic conditions than otherwise expected for a given catchment conditions.

There is an assumption that the SO₂ quantity from Eyjafjallajökull is an order of magnitude larger than that of Fimmvörðuháls (NIVA Communication 2010), suggesting 30,000 tonnes of SO₂ day⁻¹ have been produced; this would approximately result in 10 million tonnes per year. Thus, emissions from Eyjafjallajökull would equate to ca. 70% of current European emissions. However, other estimates have suggested that Eyjafjallajökull has only emitted between 3,000-4,000 tonnes of SO₂ a day (NIVA Communication 2010). It is also assumed that gaseous emissions will continue for a longer time period than emissions of ash particles.

Thus, there is a need to monitor the chemical composition of precipitation at this time, including snowfall and compare to the average concentrations expected pre-eruption. Measurements of pH in precipitation over Bergen, Norway on the 16th-18th April had normal pH-values, and thus there was assumed to be no significant acidification from eruption-derived sulphuric acid in this instant (NIVA Communication 2010). Measurements of pH and other acid-sensitive determinants in fresh snowfall and post-eruption rainfall from the Cairngorm plateau and Scottish Environmental Change Network (ECN) sites (Glensaugh and Sourhope) are described later.

Volcanoes also emit **Carbon Dioxide** (CO₂) during an eruption. Carbon dioxide is one of the gases that have been implicated in increasing global temperatures and climate change. The volcano Pinatubo (erupted 1991 in the Philippines) was estimated to have released approximately 15 million tonnes of SO₂ and 42 million tonnes of CO₂ to the

atmosphere in 1991. However, the US Energy Information Administration estimated that global human activity contributed 29,195 million tonnes of CO₂ to the air in 2006. Thus the Eyjafjallajökull eruption, although not insignificant at a maximum 30000 tonnes day⁻¹ will not make a substantial addition to anthropogenic atmospheric CO₂ emissions. Increasing temperatures can be mitigated by the particles emanating from eruptions by temporarily limiting sunlight provided they can reach the stratosphere (<http://www.abc.net.au/environment/articles/2010/04/16/2874939.htm>).

Particles

The majority of the ash from the Eyjafjallajökull eruption consists of volcanic glass, which will not easily solubilise in water. It is composed of mainly silica and aluminium oxides with lesser proportions of other oxides (<http://www.earthice.hi.is/page/IES-EY-CEMCOM>; NIVA Communication 2010). The amount of deposited ash across Scotland will be dependent on the extent of eruption and meteorological patterns. The majority of ash will fall directly or indirectly (via leaching from vegetation) onto soil. However, ash that falls directly onto natural watercourses can potentially “harm and irritate the gills of fish” and increased particle concentrations (turbidity) could be harmful to functioning within aquatic ecosystems. However, this would need a relatively high concentration of particles (>150 mg l⁻¹) for potentially detrimental effects to occur. In terms of aquaculture, water treatment systems are used which should filter out ash particles (NIVA Communication 2010). Determination of turbidity combined with analyses of size and shape of volcanic particles in surface water samples are useful indicators of water quality impacts.

Fluoride

The main impacts of high fluoride deposition are on vegetation and pastures including fluorosis amongst grazing animals, as detailed previously. Experiments involving watering with fluoride solutions have shown that the ion is easily absorbed in soils and “for all practical purposes immobile” (NIVA Communication 2010). As noted previously from the Fimmvörðuháls eruption, leaching of fluoride from ash could potentially increase concentrations if enough ash falls directly onto water surfaces. Although it is unlikely that enough ash was deposited over Scotland to have a negative effect on water quality in terms of fluoride.

Trace metals

The Eyjafjallajökull eruption has discharged relatively small amounts of trace metals (<http://www.earthice.hi.is/page/IES-EY-CEMCOM>). Emissions of trace elements will mainly bind within soils and make no significant addition to the annual anthropogenic deposition of trace metals that already occurs over the UK uplands. Consequently, in surface waters, there were unlikely to be measurable effects from this eruption. Characterisation of any surface water impacts across Scotland would be indicated by stochastic increases in fluoride and/or trace metal concentrations above that of EQS and potable water standards. Acidification sensitive parameters in surface waters, such as

pH and alkalinity, are influenced by many other factors including discharge and are difficult to assess with individual post-eruption samples. However, selected water quality parameters (pH, conductivity, fluoride, chloride, sulphate, dissolved organic carbon (DOC) and trace metals) of both pre and post-eruption are described later to assess potential impacts of SO₄ deposition and transported ash on surface waters at different sites across Scotland. The nature of long-term monitoring at the ECN sites has allowed for these comparisons of pre and post eruption chemical data in receiving water bodies.

Possible short and long term effects and the significance of a Katla eruption

The Norwegian Institute for Water Research has composed the following summary of possible short and long-term effects of the Eyjafjallajökull eruption incorporating the main contaminants emitted from a volcanic eruption i.e. SO₂, particles, fluoride and trace metals (**Table 4**). They have also assessed potential impacts if the Katla volcano erupts ([NIVA Communication 2010](#)). This volcano, also situated in Iceland would be expected to be 10-100 times larger than the recent eruption at Eyjafjallajökull.

There are many uncertainties, including the actual concentrations of emissions and unknown micro-scale effects (e.g. on aquatic biota). However, the main effect is expected to be potential acidification episodes caused by increasing SO₄ deposition. Continued monitoring of both dissolved as well as particulate fractions has enabled an assessment of these impacts.

Table 4: Summary of anticipated effects on aquatic chemistry and aquatic biology with three different scenarios for sulphur, particles, fluoride and trace metals*.

Component	Short-lasting eruption of the volcano under Eyafjellajökull	Long-lasting eruption of the volcano under Eyafjellajökull	Eruption of Katla
Sulphur	Little or no effect, but a possibility of episodic acidification under special conditions	Effect on aquachemistry in areas vulnerable to acidification and that are already acidic	Fish death in areas that are vulnerable to acidification and areas that are already acidic
Particles	Little or no effect	Little or no effect	Little or no effect (?)
Fluoride	No effect	No effect	No effect
Trace Metals	No effect	No effect	No effect

*after [NIVA Communication, 2010](#)

Short-term (up to four weeks) impacts on surface waters

Sulphate: No major effect on aquatic chemistry and thus neither for biology in the short-term. The reason is that potential increased acid deposition is buffered by soil before it

runs into streams, rivers and lakes. In areas that are currently covered in snow, there could be an acidity episode during the snowmelt period as sulphate that has been deposited during the entire period will be released rapidly. If the sulphate deposits are mainly concentrated on the acid vulnerable organic-rich soils in Scotland, a noticeable negative effect cannot be dismissed (in the form of increased sulphate and reduced pH). Even if this does not lead to fish death there could be impacts on other organisms in running water, for instance on ephemerids (mayflies).

Particles: Particle concentrations in the UK should not be sufficiently severe in surface waters for there to be negative effects on fish or other aquatic organisms.

Fluoride: No effects on surface waters because most of this will be retained by the soil.

Trace metals: No effects because potential increases will probably be retained by soil.

Longer term impacts on surface waters

If prolonged eruptions occur, there may be increased contributions to deposits to what currently occurs naturally and by long-distance anthropogenic pollution.

Sulphate: In case of a long-term eruption, there would potentially be an escalation of acidification episodes in the most sensitive and vulnerable parts of Scotland and the UK. These areas are currently undergoing recovery from acidification because non-marine sulphate deposition has diminished in recent decades. This “extra dose of sulphate in precipitation from any eruption of increased duration” may retard recovery processes.

Particles: It is doubtful that particle concentrations will be sufficiently high in surface waters to enable observation of negative effects on fish or other aquatic organisms.

Fluoride: No major effects because most of this will still be retained by soil.

Trace metals: No major effects because the amounts deposited will probably be diluted and whatever does get deposited will mostly be retained by the soil.

Monitoring of precipitation (snow and rain) and surface waters:

Surface water and precipitation have been monitored in order to address potential affects of the volcanic eruption on higher altitude and acid prone areas of Scotland, where surface waters may experience more acidic conditions than otherwise expected for given catchment conditions. An additional site in the Cairngorms has been added to standard monitoring sites across Scotland. Standard water chemistry measurement parameters have and will continue to be carried out (including F, Cl, DOC, SO₄-S, pH, conductivity, major cations and typical trace elements e.g. Al, Si, Cu, Zn, Mn). NM SO₄-S is the contribution of sulphate in water that is derived from non-marine sources.

A surface water autosampler was deployed in mid-May 2010, immediately post eruption, on the loch outflow at Lochnagar, Cairngorm (elevation of 780 m) adjacent to a routinely monitored (fortnightly) site (Acid Waters Monitoring Network then ECN). At this time, this site was still influenced by melt from significant snow patches in the corrie. Surface water samples are collected on a daily basis and analytical data will be compared with long term, pre-eruption data that is available from the established site. The sampler will remain in place for another year for assessment of snowmelt from spring 2011. Fresh snow fall occurred across the Cairngorms shortly after the eruption. Surface snow samples were collected at 5 different sites from the Cairngorm plateau on 18th and 24th April towards the end of a period of significant snowfall and parameters determined (**Table 5**) as with rainfall and surface waters.

Table 5: Post eruption fresh snowfall data from the Cairngorm plateau, NE Scotland

Site	Collection Date	pH (-)	Cond. ($\mu\text{S cm}^{-1}$)	F (mg L^{-1})	Cl (mg L^{-1})	SO ₄ -S (mg L^{-1})	NM SO ₄ -S (mg L^{-1})	DOC (mg L^{-1})
@1141 m	18-Apr-2010	5.50	12.9	0.06	1.06	0.16	0.11	0.70
@740 m	18-Apr-2010	5.63	12.4	<0.05	1.10	0.15	0.10	3.10
@1120 m	18-Apr-2010	6.20	24.7	0.10	4.31	0.36	0.16	1.30
@1240 m	24-Apr-2010	6.33	9.67	<0.05	0.32	0.24	0.23	0.50
@1190 m	24-Apr-2010	6.51	13.1	<0.05	0.70	0.32	0.29	0.70

Rainfall and surface water samples were collected at two ECN sites; Glensaugh in NE Scotland and Sourhope in the Borders as part of ongoing standard weekly monitoring programme. Comparative data is available from pre-eruption samples that have been collected within the past 10 years (Rainfall - **Table 6**; Surface water - **Table 7**).

In terms of particulate material within precipitation, 2 fresh snow samples (Cairngorm) and one rainfall sample (Lunan) were also analysed and found to contain particulate material that could be identified as volcanic glass shards originating from the Eyjafjallajökull eruption (Images from Scanning Electron Microscopy (SEM) data). Initial data indicates that ash was present in Scottish rainfall samples collected following the eruption but at lower concentrations than in snow. As can be expected, the rainfall samples also contain significant amounts of pollen and dust.

Sample collection and measurement is on-going at designated sites in Scotland to ensure that the results of continuing or future volcanic activity can be derived. Moreover, data from established long term monitoring sites across the UK within the ECN can be accessed to assess a wider coverage of potential impact. Precipitation and surface water samples have been routinely collected at the ECN for over 15 years. Filter papers used during sample processing post-eruption have been retained and will be viewed using SEM to quantify the spatial and to some extent temporal spread of the ash over the UK (data processing ongoing).

Table 6a: Pre-eruption rainfall data 2000-2005 (mean and 99 percentile range)

Site	pH (-)	Cl (mg L ⁻¹)	SO ₄ -S (mg L ⁻¹)	NMSO ₄ -S (mg L ⁻¹)	DOC (mg L ⁻¹)
Glensaugh	4.90 (3.90-6.80)	3.58 (0.20-18.2)	0.68 (0.10-2.70)	0.50 (0.05-2.30)	1.77 (0.31-6.19)
Sourhope	4.90 (3.98-7.20)	3.20 (0.20-20.9)	0.58 (0.12-2.34)	0.40 (0.05-1.96)	1.88 (0.33-6.20)
Site	Na (mg L ⁻¹)	K (mg L ⁻¹)	Ca (mg L ⁻¹)	Mg (mg L ⁻¹)	Al (mg L ⁻¹)
Glensaugh	2.254 (0.045-10.1)	0.334 (0.024-4.93)	0.329 (0.039-1.68)	0.270 (0.024-1.11)	0.018 (0.004-0.130)
Sourhope	2.110 (0.143-9.90)	0.193 (0.026-2.17)	0.444 (0.039-5.06)	0.260 (0.002-2.20)	0.021 (0.004-0.136)
Site	Si (mg L ⁻¹)	Fe (mg L ⁻¹)	Cu (mg L ⁻¹)	Mn (mg L ⁻¹)	Zn (mg L ⁻¹)
Glensaugh	0.037 (0.003-0.284)	0.007 (0.001-0.047)	0.020 (0.001-0.123)	0.007 (0.001-0.043)	0.012 (0.001-0.062)
Sourhope	0.058 (0.009-0.253)	0.016 (0.001-0.080)	0.015 (0.001-0.129)	0.004 (<0.001-0.043)	0.010 (0.001-0.100)

Table 6b: Post-eruption rainfall data (mean and 99 percentile range)

Glensaugh	pH (-)	Cond. (µS cm ⁻¹)	F (mg L ⁻¹)	Cl (mg L ⁻¹)	SO ₄ -S (mg L ⁻¹)	NMSO ₄ -S (mg L ⁻¹)	DOC (mg L ⁻¹)			
Median	4.82	18.1	0.01	0.85	0.39	0.33	2.16			
Mean	4.80	20.3	0.01	1.41	0.44	0.37	2.63			
Range	4.38-5.17	7.30-42.3	<0.01-0.06	0.20-4.93	0.12-0.97	0.11-0.90	0.90-5.70			
<i>n</i>	18	18	17	18	18	18	18			
	Na (mg L ⁻¹)	K (mg L ⁻¹)	Ca (mg L ⁻¹)	Mg (mg L ⁻¹)	Al (mg L ⁻¹)	Si (mg L ⁻¹)	Fe (mg L ⁻¹)	Cu (mg L ⁻¹)	Mn (mg L ⁻¹)	Zn (mg L ⁻¹)
Median	0.976	0.100	0.190	0.119	0.002	0.009	0.015	<0.001	0.002	0.005
Mean	1.291	0.135	0.265	0.164	0.004	0.015	0.021	0.001	0.005	0.007
Range	0.300-5.32	0.100-0.200	0.100-1.15	0.024-0.709	0.001-0.023	0.004-0.068	0.015-0.040	<0.001-0.002	0.001-0.027	0.002-0.014
<i>n</i>	18	18	18	18	18	18	18	18	18	18

Sourhope	pH (-)	Cond. (µS cm ⁻¹)	F (mg L ⁻¹)	Cl (mg L ⁻¹)	SO ₄ -S (mg L ⁻¹)	NMSO ₄ -S (mg L ⁻¹)	DOC (mg L ⁻¹)			
Median	5.41	24.3	0.01	1.20	0.55	0.40	4.10			
Mean	5.60	27.7	0.02	2.17	0.59	0.49	4.40			
Range	4.52-7.08	7.60-63.0	<0.01-0.06	0.25-8.97	0.28-1.37	0.13-1.25	1.20-10.5			
<i>n</i>	19	19	19	19	19	19	19			
	Na (mg L ⁻¹)	K (mg L ⁻¹)	Ca (mg L ⁻¹)	Mg (mg L ⁻¹)	Al (mg L ⁻¹)	Si (mg L ⁻¹)	Fe (mg L ⁻¹)	Cu (mg L ⁻¹)	Mn (mg L ⁻¹)	Zn (mg L ⁻¹)
Median	1.485	0.304	0.431	0.186	0.010	0.223	0.015	0.001	0.004	0.008
Mean	2.085	0.609	0.530	0.269	0.016	0.667	0.024	0.002	0.007	0.010
Range	0.390-5.21	0.100-3.40	0.090-1.35	0.068-0.454	0.001-0.101	0.038-2.97	0.015-0.040	<0.001-0.006	0.001-0.029	0.002-0.033
<i>n</i>	19	19	19	19	19	19	19	19	19	19

F and conductivity not routinely measured pre-eruption

Due to diminishing concentrations of NM SO₄-S at some long term monitoring sites (anthropogenic atmospheric inputs of SO₂ have decreased), measurement of this variable ceased as the values were approaching analytical detection limits.

Table 7a: Pre-eruption surface water data 2000-2005 (mean and 99 percentile range)

Site	pH (-)	Cl (mg L ⁻¹)	SO ₄ -S (mg L ⁻¹)	NM SO ₄ -S (mg L ⁻¹)	DOC (mg L ⁻¹)
Glensaugh	6.83 (5.37-7.38)	7.10 (4.57-10.6)	1.72 (0.90-3.29)	1.39 (0.72-2.79)	6.58 (2.17-24.1)
Sourhope	7.40 (6.69-7.86)	7.53 (4.85-19.3)	2.26 (1.15-2.74)	1.89 (0.63-2.37)	2.41 (0.85-21.2)
Site	Na (mg L ⁻¹)	K (mg L ⁻¹)	Ca (mg L ⁻¹)	Mg (mg L ⁻¹)	Al (mg L ⁻¹)
Glensaugh	6.141 (3.84-7.89)	0.420 (0.050-0.968)	4.200 (1.79-7.06)	1.316 (0.757-1.91)	0.115 (0.002-0.516)
Sourhope	7.298 (3.87-8.46)	3.795 (1.48-5.18)	10.880 (3.58-15.7)	3.795 (1.49-5.18)	0.027 (0.004-0.160)
Site	Si (mg L ⁻¹)	Fe (mg L ⁻¹)	Cu (mg L ⁻¹)	Mn (mg L ⁻¹)	Zn (mg L ⁻¹)
Glensaugh	4.300 (1.96-5.68)	0.179 (0.033-0.614)	0.018 (0.001-0.059)	0.008 (0.001-0.035)	0.003 (0.001-0.019)
Sourhope	6.418 (2.62-7.30)	0.011 (0.001-0.059)	0.003 (0.001-0.023)	0.002 (<0.001-0.015)	0.001 (0.001-0.008)

Table 7b: Post-eruption surface water data (mean and 99 percentile range)

Glensaugh	pH (-)	Cond. (μS cm ⁻¹)	F ⁻ (mg L ⁻¹)	Cl ⁻ (mg L ⁻¹)	SO ₄ -S (mg L ⁻¹)	NM SO ₄ -S (mg L ⁻¹)	DOC (mg L ⁻¹)			
Median	7.30	70.0	0.03	5.48	1.52	1.29	5.21			
Mean	7.25	68.6	0.03	5.36	1.48	1.23	6.28			
Range	6.70-7.40	44.8-79.2	0.02-0.03	4.09-5.87	0.86-1.59	0.67-1.50	3.80-21.9			
<i>n</i>	20	20	20	20	20	20	20			
	Na (mg L ⁻¹)	K (mg L ⁻¹)	Ca (mg L ⁻¹)	Mg (mg L ⁻¹)	Al (mg L ⁻¹)	Si (mg L ⁻¹)	Fe (mg L ⁻¹)	Cu (mg L ⁻¹)	Mn (mg L ⁻¹)	Zn (mg L ⁻¹)
Median	6.840	0.433	5.632	1.645	0.064	3.892	0.232	0.001	0.027	0.003
Mean	7.079	0.452	5.725	1.696	0.079	3.676	0.277	0.001	0.027	0.004
Range	5.86-9.62	0.350-0.600	4.12-8.55	1.16-2.56	0.024-0.169	2.60-4.73	0.110-0.590	<0.001-0.004	0.001-0.055	<0.001-0.016
<i>n</i>	20	20	20	20	20	20	20	20	20	20
Sourhope	pH (-)	Cond. (μS cm ⁻¹)	F ⁻ (mg L ⁻¹)	Cl ⁻ (mg L ⁻¹)	SO ₄ -S (mg L ⁻¹)	NM SO ₄ -S (mg L ⁻¹)	DOC (mg L ⁻¹)			
Median	7.66	141	0.04	5.98	2.04	1.76	1.10			
Mean	7.66	137	0.04	6.00	2.06	1.78	1.15			
Range	7.50-7.80	110-152	0.04-0.07	5.82-6.23	1.90-2.29	1.64-1.99	0.90-1.80			
<i>n</i>	19	19	19	19	19	19	19			
	Na (mg L ⁻¹)	K (mg L ⁻¹)	Ca (mg L ⁻¹)	Mg (mg L ⁻¹)	Al (mg L ⁻¹)	Si (mg L ⁻¹)	Fe (mg L ⁻¹)	Cu (mg L ⁻¹)	Mn (mg L ⁻¹)	Zn (mg L ⁻¹)
Median	8.506	0.657	13.940	4.656	0.003	5.553	0.020	<0.001	<0.001	<0.001
Mean	8.742	0.693	14.143	4.886	0.003	5.439	0.020	<0.001	<0.001	<0.001
Range	6.37-11.29	0.60-0.87	9.22-19.04	3.43-6.54	0.001-0.007	4.59-5.79	0.002-0.020	<0.001-<0.001	<0.001-0.001	<0.001-0.001
<i>n</i>	19	19	19	19	19	19	19	19	19	19

F and conductivity not routinely measured pre-eruption

Implications for effects of the current eruption on surface waters

The initial findings from analytical data at the routinely monitored sites (Glensaugh and Sourhope), suggest that post-eruption rain samples were within the “normal” range of pH values when compared to long-term data ranges. Surface waters also show pH values at the higher end (less acidic) of the normal ranges with potential variability attributed to standard stream discharge responses.

Sulphate levels in rainfall were slightly raised from 14th-28th April (individual data points are not shown) and then decreased into May. However, these values were still within the long-term ranges observed at these sites. In the surface waters, sulphate concentration increases were less noticeable suggesting buffering by soil. Pre-eruption, atmospheric sulphate deposition was initially monitored at all ECN sites, however this ceased at most sites due to falling concentrations, (sample concentrations in many cases being less than detection limits) and also cost implications of continuing to monitor at the required frequency. Given recent events this could be re-started should funding become available. The concentration of fluoride in precipitation (both fresh snow and rainfall) and surface water has been determined. Most samples contained relatively low fluoride concentrations close to the analytical detection limits (<0.006 mg l⁻¹), however some exceptions occurred. Notably, fluoride was detected in the surface snow sample with the greatest ash concentration (**Table 5**) and also in some post-eruption rainfall samples. However, fluoride (not routinely measured routinely at ECN sites) is also detected at similar levels in a few pre-eruption rainfall samples analysed recently from Glensaugh (**Table 8**) and thus a small concentration of fluoride cannot be just attributed to volcanic activity. Post-eruption, major cations and a selection of trace metals were within their pre-eruption ranges for each respective site, the exception being Si in rainfall at Sourhope but this was not evident in surface water (**Tables 6 and 7**).

Table 8: Pre-eruption rainfall samples at Glensaugh

Site	F (mg L ⁻¹)	Cl (mg L ⁻¹)	SO ₄ -S (mg L ⁻¹)	DOC (mg L ⁻¹)
Glensaugh	0.05	2.21	0.23	2.40
Glensaugh	0.03	2.81	0.25	1.50
Glensaugh	0.07	3.73	0.39	2.80

Consequently, there are unlikely to be measurable effects in surface waters in this instant. However, historic and continued post eruption monitoring of pH, sulphate, fluoride and trace metals in rainfall, surface water and soil solution in sensitive upland areas will ensure that any unforeseen changes from the norm are detected. This will be important in the event of more substantial Icelandic volcanic eruptions with their consequential ash clouds.

Conclusions

The main risks associated with volcanic ash and gaseous emissions on natural resources in Scotland are to livestock by fluoride ingestion from volcanic ash on pasture and surface water quality. Initial indications are that the volcanic ash layer deposited in Scotland was thin (< 5 mm), and effects on pasture and soils are negligible. It is also clear that not enough ash was deposited over Scotland to have a negative effect on water quality.

Initial data collected in this study indicates that ash was present in Scottish rainfall and snow samples collected following the eruption. However, there were little measurable effects in surface waters in this instance compared to pre-eruption data. Measurable effects may have been associated with increased fluoride concentrations leached from ash that has fallen directly onto water surfaces and acidification episodes caused by increasing sulphate deposition in rainfall and snow that is then rapidly transported to receiving waters bypassing mitigating mechanisms within soils.

Historic and continued post eruption monitoring of pH, sulphate, fluoride, dissolved organic carbon, trace metals, and particulate material in rainfall/snow and surface waters from sensitive upland areas will ensure that any unforeseen changes from the norm are detected. This will be important in the event of more substantial Icelandic volcanic eruptions e.g. Katla which would be expected to be 10-100 times larger than the recent eruption at Eyjafjallajökull.

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Appendix A: Mineral tolerance of domestic animals to fluoride

Sources: Active volcanoes and fumaroles may contribute significantly to local concentrations of fluoride in one of three principal forms: hydrofluoric acid, silicon tetrafluoride, or fluoride-containing particulate matter. Direct inhalation of fluoride containing compounds does not contribute significantly to fluoride accumulation in domestic animals (National Research Council 1980). However, these emissions may contaminate plants, soil, and water. Gaseous fluoride compounds may be absorbed and incorporated into plant tissues. Particulate fluorides may accumulate on plant surfaces and be ingested when plants are eaten. The particles themselves are usually quite inert, with toxicity related largely to solubility (National Research Council 1980).

Essentiality: There is little weight of evidence to suggest essentiality of fluoride. Non-fluoride diets have been associated with low body weight in rodents (McClendon & Gershon-Cohen, 1953) and low fluoride has been associated with impairment of fertility in female mice fed 0.1-0.3 ppm fluoride (Messer et al. 1972, 1973). It is well established that fluoride has significant anti-carcinogenic properties (National Research Council 1971, 1974).

Metabolism: Absorption of fluoride is presumed to be a largely passive process (National Research Council 1974), although some *in vitro* studies with rat intestine have suggested active transport (Stookey et al. 1964; Parkins et al. 1966; Parkins 1971). Soluble fluorides (e.g. NaF) and small amounts of poorly soluble fluorides (e.g. CaF₂) in solution are rapidly and efficiently absorbed (90 %). Calcium, aluminium, sodium chloride, and high fat levels are dietary factors that depress fluoride absorption and can be used as a protective measure (National Research Council 1974).

Low levels of fluoride intake will result in appreciable (but harmless) accumulations of fluoride in skeleton and teeth. These accumulations can increase, within limits, over a period of time without morphological evidence of pathology. However, in some cases of high-fluoride intake, structural bone changes may develop (Shupe et al. 1963). Fluoride accumulation in animals does not tend to pose significant problems in the human food chain. Most soft tissue does not accumulate fluoride, even during high intakes. Tendon (Armstrong & Singer 1970), aorta (Ericsson & Ullberg 1958), and placenta have higher accumulations than other soft tissue due to their higher concentrations of calcium and magnesium. Kidneys also tend to exhibit high fluoride concentrations during high-fluoride intake simply because they contain urine that has high fluoride concentrations.

The relationship between dietary fluoride and concentrations of fluoride in milk is weak. Greenwood et al. (1964) found that Holstein cows fed 10, 29, 55, or 109 ppm fluoride from 3 months of age up to 7.5 years, had concentrations of fluoride in milk of only 0.06, 0.10, 0.14, or 0.20 mg l⁻¹, respectively. Fluoride crosses the placental barrier of cows and fluoride levels in the bones of offspring are correlated with the fluoride

concentration of the maternal blood ([National Research Council 1974](#)). However, concentrations of fluoride in bones of calves born to cows consuming 108 ppm fluoride (as NaF) were low ([Hobbs & Merriman 1962](#)), and it appeared that neither placental fluoride transfer nor milk fluoride concentrations were sufficient to adversely affect the health of calves.

Toxicosis: The dietary level at which fluoride ingestion becomes harmful is difficult to define. No single value (i.e. dose level) is appropriate as low-level toxicosis depends on duration of ingestion, solubility of the fluoride source, general nutritional status of the receptor(s), species of animal, age of receptor(s) when ingestion took place, and toxicity-modifying components of the diet. Diagnosis of fluoride toxicosis is difficult as there tends to be an extended interval between exposure and toxicity ([Shupe 1970](#)).

If excess fluoride ingestion is sufficiently high or for a long enough period of time, morphological abnormalities will develop. In livestock, clinically palpable (bilateral) lesions develop on the medial surface of the proximal third of the metatarsals. Subsequent lesions are seen on the mandible, metacarpals, and ribs. Radiographic evidence of osteoporosis, osteosclerosis, osteomalacia, hypertosis, and osteophytosis have all been described ([Johnson 1965](#); [Shupe & Alther 1966](#); [Shupe 1969](#)). Severely affected bones appear chalky white, are larger in diameter and heavier than normal, and have a roughened irregular surface. Movement may be impaired by intermittent periods of stiffness/lameness, associated with calcification of particular structures and tendon insertions. Primary adverse effects on reproduction and lactogenesis have not been demonstrated, although milk production may decrease during high fluoride intakes.

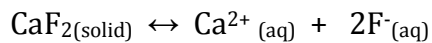
Cows first exposed to fluoride at four months of age can consume 40-50 ppm fluoride in their diet for two or three lactations without measurable effect on milk production ([National Research Council 1980](#)). Higher dietary fluoride levels (93 ppm) affected milk production in the second lactation slightly, and a significant yield reduction was seen in subsequent lactations. Acute fluoride toxicosis is rare and has usually resulted from accidental ingestion of compounds such as sodium fluosilicate (rodenticide). Toxic signs include high concentrations of fluoride in blood and urine, restlessness, stiffness, anorexia, reduced milk production, excessive salivation, nausea, vomiting, urinary and faecal incontinence, colonic convulsions, necrosis of gastrointestinal mucosa, weakness, severe depression, and cardiac failure. Death sometimes occurs within 12-14 hrs ([Krug 1927](#)).

Maximum tolerable levels ([National Research Council 1981](#)): Recommended maximum tolerable levels take into consideration the adverse biological and economic effects of excessive intakes of fluoride, plus the practical reality that many useful phosphorus supplements for livestock contain significant concentrations of fluoride (**Table 2**). While small intakes of fluoride are beneficial (possibly essential), prolonged intakes of fluoride concentrations above these maximum tolerable levels may result in

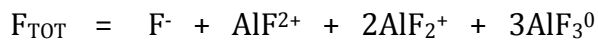
reduced performance. The maximum tolerable levels are expressed on a dry weight basis and based on tolerances to sodium fluoride. The assumption has been made that the diet is essentially the sole source of fluoride.

Appendix B: Fluoride reactions with soil components

When minerals are present that contain fluoride, the free ion activity is controlled by the solubility of the least soluble mineral. However if the fluoride ion can form soluble complexes with other elements the total amount of fluoride will be enhanced, e.g. in soils the activity of fluoride can be controlled by the solubility of fluorite (CaF_2), according to the reaction:



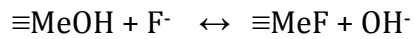
But in soil solutions where aluminium is always present, the total soluble fluoride (F_{TOT}) in soil solution will depend upon the extent of complex formation with aluminium.



The formation of fluoro-aluminium complexes will also mean that increased deposition of soluble fluoride will enhance total aluminium concentrations in soil solution. Other mineral phases that could control the activity of fluoride include, fluorite (CaF_2), fluorphlogopite ($\text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$) and fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$). If fluoride containing minerals are assumed to exist in soils, estimates of the soluble fluoride concentration can be made using geochemical modelling. In the presence of the mineral fluorite (often found in waste from lead mines), the concentration of fluoride can be calculated if the activity of calcium is known. For this calculation, to simulate natural soil conditions three activities of Ca^{2+} (0.05, 0.50, and 5.0 mM) can be used, representing calcium concentrations from infertile podzolic soils to fertile cultivated soils. At 5mM Ca^{2+} the fluoride concentration would be 1.5 mg l⁻¹, at 0.5 mM Ca^{2+} fluoride would be 4.77 mg l⁻¹ and at 0.05 mM the fluoride concentration would be 15.1 mg l⁻¹. These fluoride concentrations can be compared to the concentration of 1 mg l⁻¹ maintained in the U.K. water supply (Harrison 2005) by addition of soluble fluoride containing minerals such as H_2SiF_6 . From these calculations, it can be deduced that in all but the most fertile soils the formation of fluorite is not likely to attenuate fluoride concentrations. A similar calculation can be made for the mineral fluorphlogopite, in this case fluoride concentrations can be maintained at 0.42 mg l⁻¹ in the presence of 0.5 mM Mg^{2+} which may occur in a reasonably fertile soil.

When fluoride concentrations in soil solution are not large enough to form mineral precipitates, fluoride concentrations can be attenuated by adsorption onto the surfaces of amorphous iron and aluminium (oxy)hydroxide minerals (e.g. ferrihydrite,

allophane). This mechanism is particularly important in acid soils where the Ca and Mg concentrations may be too low to allow the formation of fluorite or fluorphlogopite. The quantity of reactive amorphous iron and aluminium (oxy)hydroxide minerals in soil can be estimated from acid ammonium oxalate extract of iron and aluminium and could be used to estimate a soil's ability to adsorb fluoride. The mechanism for fluoride surface adsorption on mineral surfaces is ligand exchange, ([Hingston et al. 1967](#); [Mohapatra et al. 2004](#)), which can be written as,



$\equiv\text{MeOH}$ represents iron and aluminium at the surface of (oxy)hydroxide minerals.