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Fluoride in ash leachates: environmental implications at Popocatépetl volcano, central Mexico

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Abstract. Ash emitted by volcanic eruptions, even of moderate magnitude, may affect the environment and the health of humans and animals through different mechanisms at distances significantly larger than those indicated in the volcanic hazard maps. One such mechanism is the high capacity of ash to transport toxic volatiles like fluoride, as soluble condensates on the particles' surface. The mobilization and hazards related to volcanic fluoride are discussed based on the data obtained during the recent activity of Popocatépetl volcano in Central Mexico.

1 Introduction

Environmental and health effects of potentially toxic elements released from natural sources have gained much attention due to the high concentrations these elements may reach in air, soil and water. Active volcanoes are one of the important sources of such elements, not always imposing a considered hazard to near and remote settlements, as volcanic clouds may cover extended areas. In addition to the solid components, the gaseous eruptive column is typically composed of H_2O, CO_2, SO_2, HCl, HF, H_2S and volatile metal and metalloid compounds. Most of these gases may pose environmental and human health hazards. About 1700 were killed by CO_2 emission from lake Nyos in 1986, and more than 30 deaths were also attributed to CO_2 exposure at lake Monoun, Cameroon in 1984 (Kling et al., 1987; Baxter et al., 1989). Sulfur dioxide emissions from Kilauea volcano produced some increase in asthma cases in Hilo, Hawaii (Michaud et al., 2004). Exposure to hydrogen sulfide released from volcanoes and geothermal systems has also been linked to adverse health effects like nervous system and respiratory problems (Bates et al., 2002; Hansell and Oppenheimer, 2004).

The ash released by eruptions may also affect health, through different mechanisms. The respiratory system and the eyes comprise of the most vulnerable tissues to ash (Horwell et al., 2003; Horwell and Baxter, 2006). In addition, part of the erupted gases and volatiles are adsorbed on the ash particles and dispersed by them over extensive areas. Elements scavenged by ashes may then be mobilized to the environment posing a hazard to flora, fauna and human health beyond regions marked in the hazards maps (Fulignati et al., 2006; Kockum et al., 2006).

Popocatépetl is an active volcano surrounded by a large population in central Mexico (De la Cruz-Reyna and Tilling, 2008). It reawakened in 1994, after nearly 70 yr of quiescence with an episode of eruptive activity that continues to the date of this submission. This activity includes numerous ash emissions associated with phreatic and magmatic eruptions. Besides México City, other highly populated areas close to the volcano have been reached by ashes during the current eruptive episode. Although this episode has been limited to moderately explosive eruptions (VEI ≤ 3), the history of the volcano shows that it is capable of producing major plinian phases and ashfalls that could affect over 20 000 000 people living within 100 km of the volcano (Fig. 1) (De la Cruz-Reyna and Siebe, 1997). Furthermore, even with the moderate ongoing activity, total concentrations of water-soluble metals and fluoride at Popocatépetl have reached hazardous levels on some occasions (Armienta et

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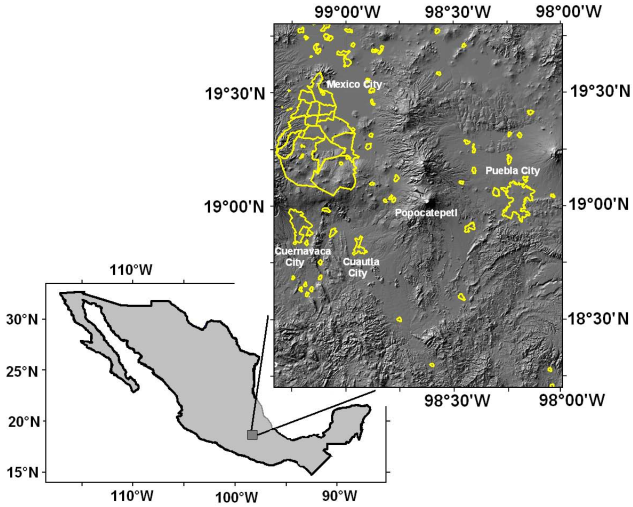

Fig. 1. Locations of Popocatépetl volcano and major cities and towns. About 20 million people could be potentially affected by tephra fallout produced by a major eruption.

al., 1998, 2002). This requires a careful assessment, for the actual environmental hazard of toxic elements depends not only on their concentrations and toxicity, but also on their chemical form and prevailing physico-chemical conditions. In this work, the potential environmental effects of fluoride carried by ashes emitted by Popocatépetl volcano are evaluated based on its concentrations in aqueous leachates, considering that environmentally available F in the tephras was primarily estimated by extraction in water (Cronin et al., 2003).

2 The impact of volcanic fluoride

Volcanic fluoride may cause detrimental impacts on the environment due to its toxicity, and to the large amounts that may be released by eruptions, the main natural atmospheric source of fluoride (Bellomo et al., 2007). Fluorine as fluorapatite is a constituent of teeth and bones and it is, thus, required for their health. However, an excess of fluoride causes diverse negative health effects such as dental or skeletal fluorosis, with mottled and harder teeth and bone calcification (Edmunds and Smedley, 1996). Crippling skeletal fluorosis is a significant cause of morbidity in a number of regions of the World. Chronic effects are reported to have been caused by the ingestion of groundwater contaminated by water-rock interaction processes (Fawell et al., 2006). The World Health Organization established a guideline of 1.5 $mg\,l^{-1}$ of fluoride in drinking water (WHO, 2004), a value that has been adopted in Mexico as the potable water standard (DOF, 2000).

Effects of large fluoride concentrations on livestock are comparable to those on humans (Weinstein and Davison, 2004). Fluoride excess caused by volcanic activity has also affected animals by direct ingestion of volcanic ash, or ingestion of contaminated water and crops (Bellomo et al., 2007). Iceland has been repeatedly affected by eruptions of fluoride-bearing ash. In 1693, the first fluorine intoxication of animals due to a volcanic eruption was reported from emissions of Hekla volcano (Thorarinsson, 1979). In 1783, ashfall and gases of Lakagigar volcano caused the death of tens of thousands of sheep, cattle and horses (Cronin et al., 2003). Fluoride concentrations from 350 to 4300 $\mu g\,g^{-1}$ on forage covered by ash, and ashes containing up to 2000 ppm water soluble fluorine emitted by Hekla in 1970, resulted in the death of about 1500 ewes and 6000 lambs (CSLP, 1971; Thorarinsson, 1979), and ash from the 1973 eruption of Eldfell, on the island of Heimaey caused vegetation damage.

High concentrations of fluoride released by other volcanoes have also produced serious environmental damage. In 1988, about 10 000 farm animals were affected by fluoride-bearing ashes from the Lonquimay volcano eruption in Chile (SEAN, 1989a), killing more than 4000 heads (goats, sheep, cattle and horses). Furthermore, dental fluorosis (incisors attrition and brown or black spotted discolouration) was observed in cattle near Lonquimay two years after the eruption (SEAN, 1989b, c; Araya et al., 1993). Similarly, ashfall from Ruapehu volcano eruptions caused the death of thousands of sheep in 1995–1996 probably by fluorosis. Enamel and dentine fluoride enriched bands were observed in immature surviving animals. In this case, ashes were enriched with fluorine not only by adsorption processes within the eruptive column, but also from the hydrothermal activity present in the volcano before the eruption (Cronin et al., 2003).

Fluoride doses about 100 $mg\,kg^{-1}$ of body weight are acutely lethal in most mammals (Weinstein and Davison, 2004). Concentrations above 250 $mg\,kg^{-1}$ dry weight in grass can kill sheep in 2 to 3 days (Thorarinsson, 1979). About 40 ppm dry weight has been considered as the maximum acceptable fluoride concentration for beef or dairy cattle to avoid chronic fluorosis (Araya et al., 1993; Weinstein and Davison, 2004).

Ingestion of fluoride may also pose a significant risk to wildlife. Deer affected by osteofluorosis were observed near aluminium smelters and other industrial facilities like thermal power plants in various countries (Kierdorf et al., 1999; Kierdorf and Kierdorf, 2003; Zemek et al., 2006). Other wild animals like field voles (*Microtus agrestis*), woodmice (*Apodemus sylvaticus*), moles (*talpa europaea*), shrews (*Sorex araneus*) and cotton rats (*Sigmodon hispidus*), were also affected by fluoride emission from an aluminium smelter in Wales (Boulton et al., 1994; Weinstein and Davison, 2004). Bison and mule deer showed osteofluorosis around hot springs of Yellowstone National Park, USA, and India (Dwivedi et al., 1997; Patra et al., 2000; Weinstein and Davison, 2004).

Vegetation may also be affected by excessive fluoride causing margin and leaf tip necrosis, chlorotic, red-brown points of leaves and deformation of fruits. Fluoride may affect plants either from gaseous emissions of HF or from absorption by roots from fluoride-enriched soils. However, the phytotoxicity of fluoride absorbed from soils by roots is much less significant than that from airborne fluoride as HF (Kabata-Pendias and Pendias, 2001; Weinstein and Davison, 2004). The effect of the continuous degassing of Mount Etna volcano in Italy on vegetation growing on the volcano flanks was studied by D'Alessandro et al. (2008). Surprisingly, the impact of this emission (considered as the main natural source of fluorine to the troposphere) on vegetation was only visible in pine needles. The authors ascribed this fact to the morphology and height of the volcano and the neutralizing action of Ca deposits derived from limestone dusts, as well as the possible development of plant resistance to volcanic gas exposure.

3 Environmental setting at Popocatépetl

Popocatépetl (5452 m a.s.l.) is located in central México (19.02° N, 98.62° W) in the eastern-central portion of the Mexican Volcanic Belt. It is the second highest volcano in México and the youngest within the Sierra Nevada, a volcanic range which extends in a roughly N-S direction. This range also includes a large complex of overlapping cones called Iztaccíhuatl volcano (19.18° N, 98.64° W, 5286 m a.s.l.).

Both, Popocatépetl and Iztaccíhuatl volcanoes have a pronounced altitudinal gradient with climates ranging from temperate to cold depending on height. Rapidly decaying glaciers partially cover the summit areas of both volcanoes. In 1947, the zone comprising Popocatépetl and Iztaccíhuatl volcanoes was officially declared "Natural National Protected Area" considering its unique flora and fauna, and is currently known as the Izta-Popo National Park. The Popocatépetl's height favours a flora and fauna diversity that changes with altitude. A temperate coniferous forest is dominated by oak (*Quercus rugosa*), cypress (*Cupressus lusitanica*), Oyamel or sacred fir (*Abies religiosa*) and pine (*Pinus hartwegii*), in the altitude range of 2850 to 3900 m. Grasslands (*Hilaria cenchroides, festuca amplissima*), oak, fir and pine are also found between 2300 and 2700 m, and alpine grassland predominates at the highest altitude (ca. 4000 m) where *Hagrostis tolucensis, Calamagrostis intermedia*, and *Arenaria bryoides*, among other species have been identified (Beaman, 1962, Rzedowski, 1979; Almeida et al., 1994; Velasquez et al., 2001; Sánchez-González and López-Mata, 2003; Hernández-García and Granados-Sánchez, 2006).

Fauna is also diverse at Popocatépetl, and jointly with Iztaccíhuatl accounts for over 10 % of the total Mexican mammalian species. A total of 52 mammal species within 37 genera and 16 families inhabit the study area. Rodents dominate, represented by 5 families and 21 species, followed by carnivores, bats and insectivores. Fir forests are very important for squirrels (*Sciurus* and *Spermophylus*), racoons (*Procyon*), and skunks (*Conepatus* and *Mephitis*), among others. Tropicalpine grasslands are a restricted habitat for the volcano mouse (*Neotomodon*), and preferential habitat for all ground-specialised genera (e.g., *Microtus, Sorex, Mustela*). About one fifth of the species are endemic, such as the mouse (*Neotomodon alstoni and Reithodontomys chrysopsis*) as well as other 24 subspecies. Five of the species are endangered like "Teporingo" or volcano's rabbit (*Romerulagus diaza*) (Velázquez, 1988; Velázquez et al., 2001).

Table 1. Sampling site locations and dates.

Sampling site	Sampling Date (day-month-year)	Site Number
Tochimilco	15-03-1996	6
Volcano slopes 4100 m a.s.l.	11-04-1996	1
Volcano slopes 4000 m a.s.l.	18-09-1996	1
Atexcac	06-03-1997	10
Tlamacas	21-06-1997	2
Santiago Xalitzintla	01-01-1998	4
Ecatzingo	24-11-1998	7
Tetela del Volcán	30-11-1998	9
Amecameca	04-09-2000	8
Tlamacas	13-12-2000	2
Tochimilco	18-12-2000	6
Km 13 Amecameca-Tlamacas Road	05-07-2001	3
Amecameca	15-08-2001	8
Tlamacas	23-01-2002	2
Tetela del volcán	18-06-2002	9
Amecameca	23-06-2003	8
Amecameca	19-07-2003	8
Cuautla	09-01-2005	11
San Pedro BJ	01-12-2005	5

Forestry (especially wood production), agriculture and cattle raising are the main economic activities in the area. Livestock includes cattle, pigs, sheep, chicken, goats and horses. Agriculture is limited to the low-lands. Main crops are maize, barley, oat, bean, wheat, forage, fruit trees, sugar cane and some vegetables (Hernández-García and Granados-Sánchez, 2006; Romero et al., 1999).

4 Analytical methods

Samples (non-exposed to rain) from various Popocatépetl volcano eruptions occurred between 1996 and 2005 were collected at different distances from the vent, in the range from about half a kilometre to 39 km (Table 1, Fig. 2). Aqueous ash leachates were obtained by agitating 1:25 ash-to-water ratio (1 g of the quartered ash added to 25 ml of deionized water) for 2 h, and then centrifuging at 3500 rpm for 15 min. The water-ash mixture was then filtered through 0.45 µm Millipore filters. Fluoride concentrations were measured in the solution by potentiometry, using an Orion EA 940 ion analyser with selective electrodes. To measure pH, 1 g of ash was agitated for 90 min with deionized water,

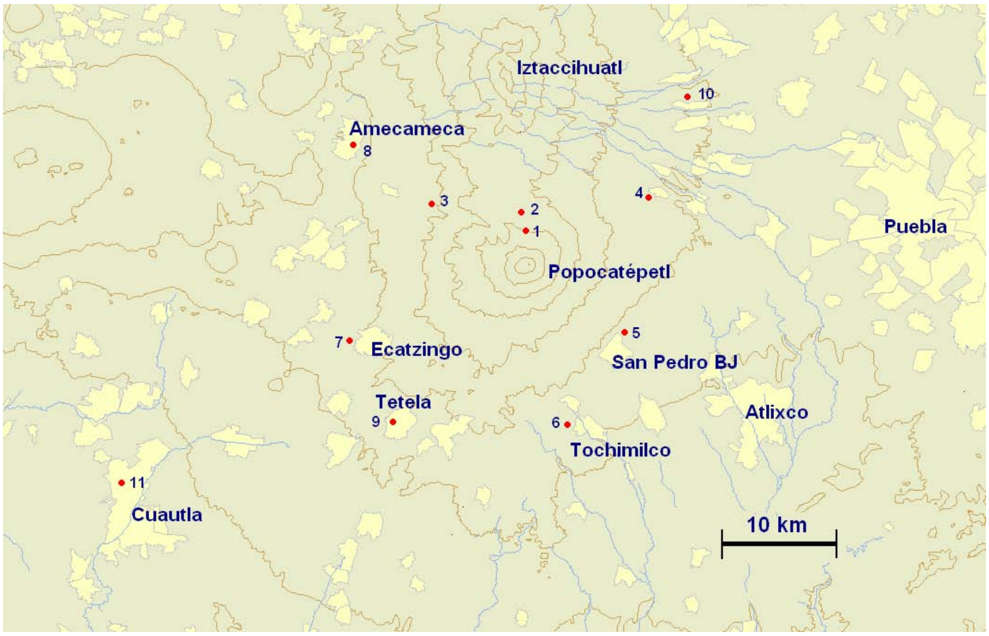

Fig. 2. Location of ash-sampling sites: 1 (4100 m a.s.l., on the volcano slope); 2 (Tlamacas); 3 (km 13 Tlamacas-Amecameca road); 4 (Santiago Xalizintla); 5 (San Pedro BJ); 6 (Tochimilco); 7 (Ecatzingo); 8 (Amecameca); 9 (Tetela del Volcán); 10 (Atexcac); 11 (Cuautla).

pH was measured in the slurry with a conductimeter PC18 calibrating with pH 4, 7 and 9 buffers at room temperature (20 °C). This methodology was developed based on the capabilities of our laboratory and the compositional range of leachates. It has been tested against the Taylor and Stoiber (1973) and Varekamp et al. (1984) methods as reported in Armienta et al. (1998), and fulfils all recommendations given by the International Volcanic Health Hazard Network IVHHN (http://www.ivhhn.org/index.php?option=com_content&view=article&id=100). In all cases, duplicate samples were analysed and results accepted when differences were less than 10 %. Calibration solutions were prepared with reagent grade salts dried overnight, deionized water, and class A volumetric material.

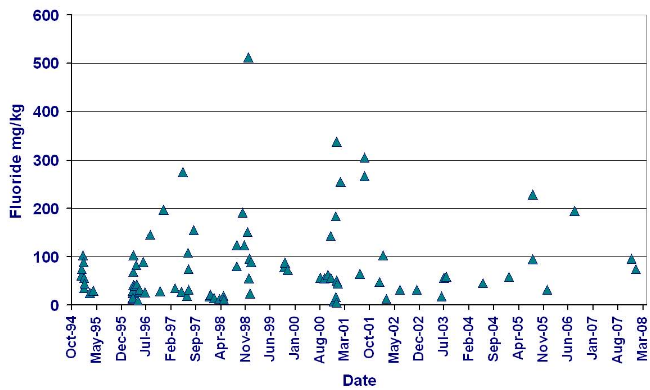

Fig. 3. Fluoride concentrations in leachates (mg kg^{-1}) of various eruption dates.

5 Results and discussion

Soluble concentrations of fluoride in ash samples of various eruptions are shown in Fig. 3. Concentrations ranged over a two-orders of magnitude, from 5 mg kg^{-1} to 513 mg kg^{-1}. The highest contents in leachates were detected on 24 November 1998 (513 mg kg^{-1}) at Ecatzingo; 20 December 2000 (338 mg kg^{-1}) at Tochimilco, 15 August 2001 (306 mg kg^{-1}) at Amecameca; and 11 May 1997 (275 mg kg^{-1}) at Santiago Xalizintla. These ash samples corresponded to episodes of new dome emplacement or to increased rates of dome growth as indicated by the monitoring data of the Mexican National Center for Disaster Prevention (CENAPRED). Such data include aerial photographs, seismic signals (VT events, tremors) and increased incandescence inside the crater, detected by the volcano video monitors (http://www.cenapred.unam.mx/popo/UltimaImagenVolcanI.html).

Although concentration variations with distance have been observed at specific eruptions (Armienta et al., 2002), a general trend cannot be unraveled from the whole dataset. However, since the amount of ash-deposited fluorine is inversely correlated with particle size, and small particles may be carried far away from the vent depending on wind velocity and column height, important amounts of fluoride may be found on soils and vegetation far away from the vent. This behaviour was observed in the eruptions of 30 April 1996

Table 2. Dietary tolerance to fluoride.

Species	F mg kg^{-1} dry weight*	Ash ingestion (g) to reach dietary tolerance levels at Popocatépetl**
Young beef	40	78
Mature beef	50	97
Feeder lamb	150	292
Horse	60	117
Finishing pig	150	292
Breeding ewe	60	117
Chicken	300	585
Hen	400	780

* National Research Council (1974); Weinstein and Davison (2004)
** considering the maximum fluoride concentration

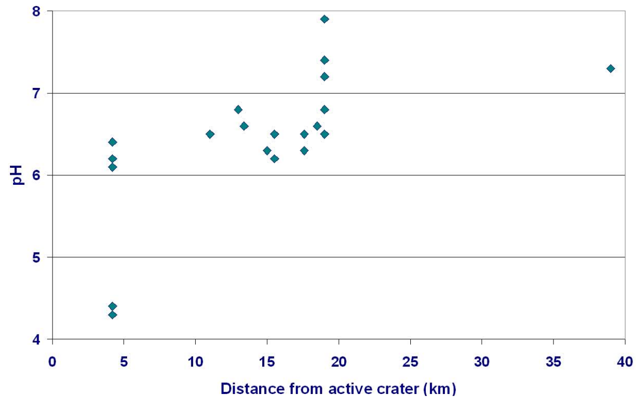

Fig. 4. pH values measured in leachates of the ash samples listed in Table 1.

and 17 October 1998 where the highest fluoride concentrations (41 mg kg^{-1} and 124.2 mg kg^{-1}, respectively) were measured at the farthest sampling locations (55.8 and 29 km respectively; Armienta et al., 2002). Both of these eruptions emitted ash clouds that produced light ashfalls on Mexico City, nearly 70 km NNW of the volcano. Moreover, a thin ash layer does not hinder grazing and sticks easily to vegetation, leading to a fluorosis hazard to humans and animals at even further distances (Thorarinsson, 1979; Armienta et al., 2002). Whether these amounts of fluoride in ash represent a serious fluorosis hazard to fauna is a question that may not be unequivocally answered from the available information. It may be argued that rain will rapidly wash the fluoride away and remove fine layers of ash so exposure would be very limited over time. As an example, we may estimate the exposure to ash fluoride during the initial stage of the current Popocatépetl activity. Martin del Pozzo et al. (2008) calculate that 1.181×10^6 m^3 of ash was emitted between 21 December 1994 to 12 March 1995, with F concentrations ranging between 20 and 100 mg kg^{-1} (Fig. 3). Those months correspond to the lowest rain precipitation, averaging about 6 mm per month. The resolution of the published isopachs (Martin del Pozzo et al., 2008) do not allow for the estimation at what distance from the emission centre such rainfall will wash the fluoride before it produces significant health damage to fauna, but the order of magnitude estimates suggest that it probably may not involve a very large area. However, between 1997 and 2003 (particularly on 30 June 1997) similar volumes (up to 1.1×10^6 m^3) of ash were emitted in a day (Martin del Pozzo et al., 2008), i.e., an emission rate about two orders of magnitude greater than in 1994. Although summer rain fall may exceed winter precipitation by a factor of about 20, it is very difficult with the available data to estimate the extent at which hazardous exposure of fauna to fluoride may occur. Furthermore, during December 2000, the volcano registered even higher magma eruption rates, forming the largest lava dome and producing frequent ash columns rising 5 km above the crater level. The ash emitted during this episode also transported high concentrations of leachable fluoride (up to 338 mg kg^{-1}). Although dwellers in the exposed zone were evacuated for over a week, animals remained in the area. Forage covered by ashes would reach dietary tolerance for herbivorous livestock according to Table 2. Due to their low fluoride tolerance, young cows would be the most sensitive farm animal group at Popocatépetl, followed by mature cows, horses and breeding ewe. Regarding wild animals, although no evidence was found of injuries caused by volcanic fluoride for the specific species living at Popocatépetl, a similar susceptibility to voles (Schroder et al., 2003) may be expected in volcano mouse and other rodents and terrestrial mammals. Volcano rabbit (one of the endangered species at Popocatépetl) might also be at risk due to their feeding habits, small size and mouth proximity to the soil. In addition, direct ingestion of sludge and soil enriched in fluoride by grazing cattle has been considered as an important source of fluoride as is herbage (Kabata-Pendias and Pendias, 2001). In fact, cotton rats exposed to petrochemical wastes presented fluorosis, and their fluoride concentrations in bones were strongly correlated with total F content in soils (Schroder et al., 2003). The main hazard to people would be related to water contamination. In many rural settlements, and even in some urban areas around Popocatépetl, drinking water is not always available from a piped water supply system. It is, thus, common that people store drinking water in large containers that may not be properly covered. In such conditions, water may have reached the Mexican drinking water standard (1.5 mg l^{-1}) by mixing 7.8 g of ashes of the Popocatépetl's eruption with the highest fluoride content in a litre of water. With regards to this, the vulnerability of people dwelling around Popocatépetl has been reduced through the persistent warning about the health problems caused by ash, and repeated recommendations about covering water deposits. However, animals (wild and livestock) may remain exposed to fluoride-polluted water.

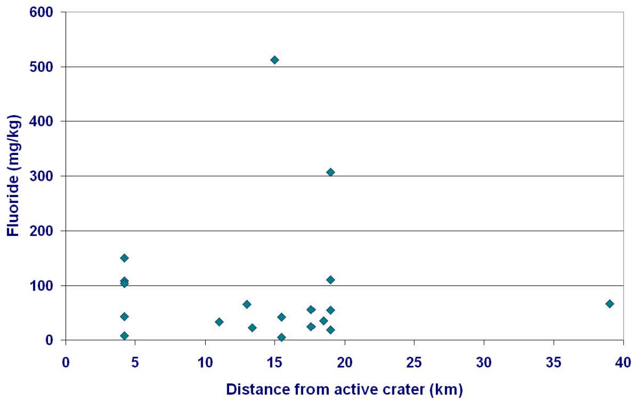

Fig. 5. Fluoride concentrations ($mg\,kg^{-1}$) in leachates of the samples listed in Table 1.

Fluoride-enriched ashes settled on soils may also affect the vegetation around Popocatépetl. However, the total fluoride contents in ash-contaminated soils may not be available for plant uptake, since fluoride absorption depends on various other factors, such as soil type, pH, organic matter, and Ca and Al contents. Concentrations of fluoride in the plant roots are proportional to the soil solution concentration (Weinstein and Davison, 2004). In addition, fluoride is most readily absorbed by plants at low pH values, at which it is more soluble. Fluoride solubility in soils of Austria showed a minimum at pH 6.0–6.5 and increased at a pH less than 6.0, and higher than 6.5 (Wenzel and Blum, 1992). It has also been found that aluminium-fluoride complexes increase plant uptake. On the other hand, fluoride adsorption on aluminium minerals decreases its lability (Longanathan et al., 2001). Formation of Al-F complexes thus explain the high solubility at low pH, and desorption from soil the solubility raise at high pH (Wenzel and Blum, 1992; Longanathan et al., 2001).

Samples from the Popocatépetl area show near neutral to slightly basic pH values, except in those collected near the vent (Fig. 4). Concentrations of fluoride in leachates in the same sites are shown in Fig. 5. On the other hand, vegetation may assimilate F in its soluble form. Hence, a close relationship between the concentration of soluble F in the soil and in the plants should be expected (Egli et al., 2004). Experimental studies with artificial soil solutions, jointly with geochemical modelling, showed that fluorine is mostly as fluoride in the soil solution (Stevens et al., 2000). Concentrations in ash-leachates may, thus, provide a good proxy to fluoride levels available to vegetation uptake from volcanic ashes.

Histological and structural effects resulting from fluorine exposure have been studied for some of the most representative plants present at Popocatépetl or for similar species. Shrinkage of chloroplasts in subnecrotic zones and fewer chloroplasts lamellae in maize were reported by Lhoste and Garrec (1975). Inhibition of H+ pumping and ATPase activity in maize roots vesicles by LiF and AlF_3 was reported by Façanha and de Meis (1995). Pinus effects identified by various studies include changes in phloem and occlusion of resin canals, dilatation of thylakoids, cell vacuolization and increase in endoplasmic reticulum (Weinstein and Davison, 2004).

Aluminium and calcium are known to be strong binders for F in soil (Rai et al., 2000). Manoharan et al. (2007), demonstrated that fluoride in soils decreased the growth of roots of barley in slightly acid soil pH values (4.25 to 5.48). This effect was due to the increase in the concentration of Al-F complex formation in the soil and was more pronounced at the lowest pH. Around Popocatépetl, slightly acid values were measured in ash samples with a pH range from 4.3 to 6.4 and highly soluble fluoride contents from 43 $mg\,kg^{-1}$ at a pH of 4.4 to 512.5 $mg\,kg^{-1}$ at a pH of 6.3 (Figs. 4 and 5). Barley crops raised in agricultural fields within that range may, thus, be affected by ash-fallout. More acid values of the ash were measured nearer to the active crater, but no agricultural activity is developed there.

6 Conclusions

Although there is no evidence that fluoride transported by volcanic ash has so far posed an acute problem to organisms exposed to the ashfall, it is clear that Popocatépetl volcano has the potential to produce larger, fluoride-rich eruptions. Therefore, soluble fluoride concentrations in ash emitted by some eruptions may pose a risk to humans, animals and vegetation around that volcano. Evaluation of such hazard is essential to design appropriate mitigation measures. Young cows would be the grazing animals most affected by fluoride-enriched ashes. Small wild mammals would also be at risk. This is particularly relevant for the volcano rabbit (*Romerulagus diaza*) and other endangered species at Popocatépetl. Effects of fluoride rich ashfall on vegetation are controlled by additional factors such as soil pH, as well as Ca and Al content.

As risk-reduction actions, fluoride must be analysed for the significant Popocatépetl eruptions, i.e., all events generating ash columns large and dense enough to produce collectable ashfall deposits, and this systematic sampling and analysis should be included in the protocols of the prevention plans. Special care has to be taken to protect cattle from eating ash-covered herbage and drinking ash-contaminated water. While evident practical difficulties exist to protect wild animals from volcanic activity, endangered mammals should be protected from other human activities that may further reduce their populations. Agricultural practices such as adding limestone to soil to decrease fluoride solubility would prevent growth problems in prone crops.

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References

Almeida, L., Cleef, A. M., Herrera, A., Velásquez, A., and Luna, I.: El zacatonal alpino del volcán Popocatépetl, México, y su posición en las montañas tropicales de América, Phytocoenologia, 22, 391–436, 1994.

Araya, O., Wittwer, F., and Villa, A.: Evolution of fluoride concentrations in cattle and grass following a volcanic eruption, Vet. Hum. Toxicol., 35, 437–440, 1993.

Armienta, M. A., Martin, A. L., Espinasa, R., Cruz, O., Ceniceros, N., Aguayo, A., and Butron, M. A.: Geochemistry of Ash Leachates During the 1994–1996 Activity of Popocatepetl Volcano, Appl. Geochem., 13, 1–10, 1998.

Armienta, M. A., De la Cruz-Reyna, S., Morton, O. Cruz, O., and Ceniceros, N.: Chemical Variations of Tephra Deposit Leachates for Three Eruptions from Popocatépetl Volcano, J. Volcanol. Geoth. Res., 113(1–2), 61–80, 2002.

Bates, M. N., Garrett, N., and Shoemak, P.: Investigation of health effects of hydrogen sulfide from a geothermal source, Arch. Environ. Health, 57, 405–411, 2002.

Baxter, P. J., Kapila, M., and Mfonfu, D.: Lake Nyos disaster, Cameroon, 1986: the medical effects of large scale emission of carbon dioxide?, Brit. Med. J., 298, 1437–1441, 1989.

Beaman, J. H.: The timberlines of Iztaccihuatl and Popocatepetl, Mexico, Ecology, 43, 377–385, 1962.

Bellomo, S., Aiuppa, A., D'Alessandro, W., and Parello, F.: Environmental impact of magmatic fluorine emission in the Mt. Etna Area, J. Volcanol. Geoth. Res., 165, 87–101, 2007.

Boulton, I. C., Cooke, J. A., and Johnson, M. S.: Fluoride accumulation and toxicity in wild small mammals, Environ. Poll., 85, 161–167, 1994.

CSLP: Hekla, Review of May–July 1970 eruption, Center for Short-Lived Phenomena Event Report, Smithsonian Institution, Card 1093–1094 (19 January 1971), CSLP, 43–70, 1971.

Cronin, S. J., Neall, V. E., Lecointre, J. A., Hedley M. J., and Loganathan, P.: Environmental hazards of fluoride in volcanic ash: a case study from Ruapehu volcano, New Zealand, J. Volcanol. Geoth. Res., 121, 271–291, 2003.

D'Alessandro, W., Bellomo, S., and Parello, F.: Fluorine speciation in topsoils of three active volcanoes of Sicily (Italy), Environ. Geol., 56, 413–423, 2008.

De la Cruz-Reyna, S. and Siebe, C.: The giant Popocatépetl stirs, Nature, 388(6639), p. 227, 1997.

De la Cruz-Reyna, S. and Tilling, R. I.: Scientific and public responses to the ongoing volcanic crisis at Popocatépetl Volcano, Mexico: Importance of an effective hazards-warning system, J. Volcanol. Geoth. Res., 170, 111–120, 2008.

DOF: MODIFICACION a la Norma Oficial Mexicana NOM-127-SSA1-1994, Salud ambiental, Agua para uso y consumo humano, Límites permisibles de calidad y tratamientos a que debe someterse el agua para su potabilización, Diario oficial de la Federación, México, D.F., 20 octubre, 2000.

Dwivedi, S. K., Dey, S., and Swarup D.: Hydrofluorosis in water buffalo (Bubalus bubalis) in India, Sci. Total Environ., 207, 105–109, 1997.

Edmunds, W. M. and Smedley, P. L.: Groundwater geochemistry and health: an overview, in: Environmental Geochemistry and Health, edited by: Appleton, J. D., Fuge, R., and McCall, G. J. H., Geological Society Special Publication, London, 113, 91–105, 1996.

Egli, M, Dürrenberger, S., and Fitze, P.: Spacio-temporal behaviour and mass balance of fluorine in forest soils near an aluminium smelting plant: short and long term aspects, Environ. Pollut., 129, 195–207, 2004.

Façanha, A. R. and de Meis, L.: Inhibition of maize root H+ -ATPase by fluoride and fluoraluminate complexes, Plant Physiol., 108, 241–246, 1995.

Fawell, J., Bailey, K., Chilton, J., Dahi, E., Fewtrell, L., and Magara, Y.: Fluoride in Drinking Water, World Health Organization, London, 134 pp., 2006.

Fulignati, P., Sbrana, A., Clocchiatti, R., and Luperini, W.: Environmental impact of the acid fumarolic plume of a passively degassing volcano (Vulcano Island, Italy), Environ. Geol., 49, 1139–1155, 2006.

Hansell, A. and Oppenhemier, C.: Health hazards from Volcanic Gases: A systematic literature review, Arch. Environ. Health, 59, 628–639, 2004.

Hernández-García, M. A. and Granados-Sánchez, D.: El parque nacional Iztaccíhuatl-Popocatépetl-Zoquiapan y el impacto ecológico-social de su deterioro, Revista Chapingo Serie Ciencias Forestales y del Ambiente, 12, 101–109, 2006.

Horwell, C. J. and Baxter, P.: The respiratory health hazards of volcanic ash: a review for volcanic risk mitigation, Bull. Volcanol., 69, 1–24, 2006.

Horwell, C. J., Sparks, R. S. J., Brewer, T. S., Llewellin, E. W., and Williamson, B. J.: Characterization of respirable volcanic ash from the Soufriere Hills volcano, Montserrat, with implications for human health hazards, Bull. Volcanol., 65, 346–362, 2003.

Kabata-Pendias, A. and Pendias H.: Trace elements in soils and plants, CRC Press, Boca Raton USA, 432 pp., 2001.

Kierdorf ,Y. and Kierdorf, H.: Temporal variation of fluoride concentration in antlers of roe deer (Capreolus capreolus) living in an area exposed to emissions from iron and steel industry, 1948–2000, Chemosphere, 52, 1677–1681, 2003.

Kierdorf, H., Kierdorf, U., and Sedlacek, F.: Monitoring regional fluoride pollution in the Saxonian ore mountains (Germany) using the biomarker dental fluorosis in roe deer (*Capreolus capreolus* L.), Sci. Total Environ., 232, 159–168, 1999.

Kling, G. W., Clark, M. A., Wagner, G. N., Compton, H. R., Humphrey, A. M., Devine, J. D., Evans, W. C., Lockwood, J. P., Tuttle, M. L., and Koenigsberg, E. J.: The 1986 Lake Nyos Gas Disaster in Cameroon, West Africa, Science, 236(4798), 169–175, 1987.

Kockum, P. C. F., Herbert, R. B., and Gislason, S. R.: A diverse ecosystem response to volcanic aerosols, Chem. Geol., 231, 57–66, 2006.

Lhoste, A. M. and Garrec, J. P.: Fluorine Effects on Chloroplast Ultrastructure of Zea-Mays Biometrical Study, Journal de Microscopie et de Biologie Cellulaire, 24, 351–364, 1975.

Loganathan, P., Hedley, M. J., Wallace, G. C., and Roberts, A. H. C.: Fluoride accumulation in pasture forages and soils following long-term applications of phosphorous fertilizers, Environ. Pollut., 115, 275–282, 2001.

Manoharan, V., Loganathan, P., Tillman, R. W., and Parfitt, R. L.: Interactive effects of soil acidity and fluoride on soil solution aluminium chemistry and barley (*Hordeum vulgare* L.) root growth, Environ. Pollut., 145, 778–786, 2007.

Martin-Del Pozzo, A. L., González-Morán, T., Espinasa-Pereña, R., Butrón, M. A., and Reyes, M.: Characterization of the recent ash emissions at Popocatepetl Volcano, Mexico, J. Volcanol. Geotherm. Res., 170, 61–75, 2008.

Michaud, J. P., Grove, J. S., and Krupitsky, D.: Emergency department visits and "vog" related air quality in Hilo, Hawai'i, Environ. Res., 95, 11–19, 2004.

National Research Council: Effects of fluorides in animals/Subcommittee on Fluorosis, Committee on Animal Nutrition, Board of Agriculture and Renewable Resources, National Research Council, National Academy of Sciences, Washington, USA, 1974.

Patra, R. C., Dwivedi, S. K., Bhardwaj, B., and Swarup, D.: Industrial fluorosis in cattle and buffalo around Udaipur, India, Sci. Total Environ., 253, 145–150, 2000.

Rai, K., Agarwal, M., Dass S., Shrivastaqv, R.: Fluoride: Diffusive mobility in soil and some remedial measures to control its plant uptake, Current Science, 79, 1370–1373, 2000.

Romero, F. J., Rangel-Cordero, H., Estévez-Ramírez, A., Escamilla, M., and Cabrera-García, L.: Aspectos sociodemográficos y actividades productivas rurales del sur de la Cuenca de México, in: Bodiversidad de la Región de Montaña del Sur de la Cuenca de México, Universidad Autónoma Metropolitana, México D.F., 229–262, 1999.

Rzedowski, J.: Principales comunidades vegetales, in: Flora fanerogámica del Valle de México, edited by: Rzedowski, J. and Rzedowski, G. C., CECSA, México, D.F., 47–54, 1979.

SEAN: Lonquimay, Continued tephra emission; cattle sickened by ash, Scientific Event Alert Network Bull., Smithsonian Institution, 14(4), 2–3, 1989a.

SEAN: Lonquimay, Continued tephra emission and lava flow; fluorine data, Scientific Event Alert Network Bull., Smithsonian Institution, 14(9), 3–4, 1989b.

SEAN: Lonquimay, Strong fluorine emission; one person and many animals killed, Scientific Event Alert Network Bull., Smithsonian Institution, 14(6), 11–13, 1989c.

Sánchez-González, A. and López-Mata, L.: Clasificación y ordenación de la vegetación del norte de la Sierra Nevada, a lo largo de un gradiente altitudinal, Anales del Instituto de Biología, Universidad Nacional Autónoma de México, Serie Botánica, 74, 47–71, 2003.

Schroder, J. L., Basta, N. T., Payton, M., Wilson, J. A., Carlson, R. E., Janz, D. M., and Lochmiller, L.: Ecotoxicological risks associated with land treatment of petrochemical wastes, I. Residual soil contamination and bioaccumulation by cotton rats (*Sigmodon hispidus*), J. Toxicol. Environ. Health A, 66, 305–325, 2003.

Stevens, D. P., McLaughlin, M. J., Randall, P. J., and Keerthisinghe, G.,: Effect of fluoride supply on fluoride concentrations in five pasture species: Levels required to reach phytotoxic or potentially zootoxic concentrations in plant tissue, Plant Soil, 227, 223–233, 2000.

Taylor, P. S. and Stoiber, R. E.: Soluble material on ash from active central American volcanoes, Geol. Soc. Am. Bull., 84, 1031–1042, 1973.

Thorarinsson, S.: On the damage caused by volcanic eruptions with special reference to tephra and gases, in: Volcanic Actitivy and Human Ecology, edited by: Sheets, P. D. and Grayson, D. K., Academic Press, NY, 125–159, 1979.

Varekamp, J. C., Luhr, J. F., and Prestegaard, K. L.: The 1982 eruptions of El Chichón volcano (Chiapas, México): Character of the eruptions, ash-fall deposits and gasphase, J. Volcanol. Geotherm. Res., 23, 39–68, 1984.

Velázquez, M. A.: Especies y habitats en peligro de extinción. El caso del conejo de los volcanes, ICYT, Información Científica y tecnológica, 10, 45–49, 1988.

Velázquez, A., Romero, F. J., Rangel-Cordero, H., and Heil, G. W.: Effects of landscape changes on mammalian assemblages at Izta-Popo volcanoes Mexico, Biodivers. Conserv., 10, 1059–1075, 2001.

Weinstein, L. H. and Davison, A.: Fluorides in the Environment, CABI Publishing, Wallingford, 287 pp., 2004.

Wenzel, W. W. and Blum, W. E. H.: Fluorine speciation and mobility in F-contaminated soils, Soil Sci., 153, 357–364, 1992.

WHO, World Health Organization: Fluoride in drinking-water, Background document for development of WHO Guidelines for Drinking-water Quality, WHO, 9 pp., 2004.

Zemek, F., Heøman, M., Kierdorf, H., Kierdorf, U., and Sedláèek, F.: Spatial distribution of dental fluorosis in roe deer (Capreolus capreolus) from North Bohemia (Czech Republic) and its relationships with environmental factors, Sci. Total Environ., 370, 491–505, 2006.