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RESEARCH ARTICLE

Quantitative analysis of persistent volcanic fluoride risk reveals differential exposure pathways for adults and children downwind of Masaya Volcano, Nicaragua

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Abstract
Volcanoes in a persistent state of open-vent degassing can contaminate air, water, soil, and vegetation with fluoride. People living in their shadow are exposed to this substance via several routes and for prolonged periods of time. They incur a health risk, but the exposure pathways have not been well quantified. We assess the intakes of fluoride through air inhalation, water consumption, inadvertent soil ingestion, and dermal contact with soil for children and adults in communities located within ~ 35 km downwind of Masaya Volcano, Nicaragua. A sampling network was deployed in January 2009 in order to determine the concentrations of fluoride in the air, drinking water, and surface soil. Using relevant exposure factors, we evaluated the contribution of each exposure route to the estimated total daily intake (EDI_{tot}) of fluoride. The EDI_{tot} for children varies between 0.11 and 0.46 mg/kg body weight/day and a risk of dental fluorosis occurs across the surveyed area. For children, fluoride intake due to air inhalation and/or incidental soil ingestion is always larger than that contributed by water consumption. Overexposure to fluoride in adults is less common and water is usually the primary exposure route to fluoride, although inhalation is important and even dominates at a few sites. The exposure assessment provides a simple screening tool for rapid identification of the pathways driving the health risk. Its application may help to target effort to remediate exposure levels for the greatest effect.

Keywords Masaya Volcano · Open-vent degassing · Fluoride · Exposure and risk assessment

Introduction

Fluorine is the most electronegative chemical element and it always occurs as the fluoride ion in the environment. Excessive exposure of humans and animals to fluoride in drinking-water, or in combination with intake from other sources, can give rise to a number of adverse health effects. These range from dental mottling starting in childhood (dental fluorosis) to abnormal bone growth in any stage of life, which with prolonged and higher level of exposure may become deforming and crippling (skeletal fluorosis) (WHO 2001; IPCS 2002). The sources of fluoride contamination in the environment are various, but fluoride is commonly associated with volcanism. For example, surface and ground waters in contact with extrusive rocks in the Rift Valley of East Africa frequently contain fluoride concentrations exceeding the 1.5 mg/l permissible limit established by the World Health Organization (Kut et al. 2016). In Tanzania, Kenya and Ethiopia, a high prevalence of dental and skeletal fluorosis is recorded among communities with a long-term use of high-fluoride groundwater (Rango et al. 2012; Demelash et al. 2019 and references therein).

Volcanic activity is also a major contributor of fluoride to the atmosphere. Globally, subaerial volcanoes release at least ~ 0.6 Tg/yr of the gas hydrogen fluoride (HF) via both quiescent and explosive episodes of magma degassing

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This paper constitutes part of a topical collection:

Open-vent volcanoes

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(Fischer 2008; Pyle and Mather 2009). Hydrogen fluoride in the atmosphere has a short residence time and is rapidly transferred to the Earth's surface via dry and wet deposition processes (Cheng 2018), thereby exposing vegetation, water sources and soils to potential fluoride contamination. Tephra from explosive eruptions may also carry variable amounts of fluoride-containing compounds (e.g., Cronin et al. 2003; Witham et al. 2005; Delmelle et al. 2007, 2021; Armienta et al. 2011) that may solubilize upon exposure to water, potentially posing a health hazard to livestock and in rarer cases, humans (e.g., Georgsson and Pétursson 1972; Thorarinsson 1979; Araya et al. 1993; Cronin and Sharp 2002; Cronin et al. 2014).

Volcanoes exhibiting open-vent behavior characterized by magmatic gas emissions in the atmosphere for many years or decades may add fluoride to all environmental compartments (i.e. air, water, soil and vegetation). There is some evidence that elevated concentrations of HF in the air occur downwind of such systems (Delmelle et al. 2001; Delmelle 2003; Aiuppa et al. 2004). The sustained release of a volcanic gas plume containing HF also increases fluoride in atmospheric depositions downwind of the crater, which may then lead to contamination of rainwater, open-top water tanks, vegetation and soils (Harding and Miller 1982; Garrec et al. 1984; Cronin and Sharp 2002; Bellomo et al. 2003; Delmelle et al. 2003; Allibone et al. 2012; D'Alessandro et al. 2012). In a such situation, conditions of prolonged multi-media exposure to fluoride may develop for the local residents, possibly evolving to a long-term health hazard.

While consumption of drinking water is generally assumed to be the major route of fluoride intake in people (WHO 2001; IPCS 2002; Ayoob and Gupta 2006), the considerations above warrant that, in the context of persistent open-vent degassing, other exposure pathways that are traditionally regarded as minor, including inhalation of the gas HF in the air, inadvertent ingestion of soil that receive atmospheric depositions enriched in fluoride and consumption of locally grown food contaminated by fluoride, represent potentially significant additional fluoride sources. In other words, the cumulative fluoride intake, and thus the fluorosis risk, in residents living nearby quiescently degassing volcanoes may be substantially greater than that estimated solely from the ingestion of fluoride-contaminated drinking water.

In this study, we evaluate exposure at any one time to fluoride in air, drinking water and soil of residents near Masaya Volcano, Nicaragua, an open-vent system that has been emitting a gas plume in the atmosphere quiescently for more than 20 years. We use the results to examine the distribution and contributions of different pathways of fluoride intake and fluorosis hazard and risk in adults and children across the study site. We conclude that, beside consumption of drinking water, inhalation in adults and incidental soil ingestion in children are critical fluoride intake routes for the residents downwind of Masaya Volcano. The health risk is site and age-specific.

Methods

Masaya Volcano and its residents

Masaya is a low-elevation (635 m a.s.l.), tholeiitic basaltic shield volcanic complex (van Wyk de Vries 1993; Walker et al. 1993) in Central Nicaragua (Fig. 1). Masaya Volcano is the youngest edifice of the complex and has four pit craters, namely Nindiri, San Antonio, San Pedro and Santiago. It sits within two Pleistocene nested calderas, the Las Sierras Caldera and the Masaya Caldera (Girard and van Wyk de Vries 2005). The Masaya caldera is a 6 × 11 km east–west elongated feature which was formed by a series of basaltic plinian eruptions (Williams 1983; van Wyk de Vries 1993). The steep walls lend morphological distinction to the ~ 20 km-wide Las Sierras Caldera; the entire caldera is asymmetric in height and slanted to the east, so that the western summit is ~ 900 m a.s.l., while the east rim is only ~ 250 m a.s.l. A small plateau, informally known as Llano Pacaya, extends ~ 3 km west of this rim summit, as well as ~ 8 km north–south at 700–900 m a.s.l. and 10–15 km directly west of Masaya Volcano (Fig. 1). West of the Llano Pacaya, the land slopes gently down to the Pacific Ocean.

Masaya Volcano has been the site of frequent open vent degassing episodes since European discovery by the Conquistadors in 1525 (Rymer et al. 1998; Viramonte and Incer-Barquero 2008). A convecting lava lake occupied Nindiri crater at that time. Santiago formed in ~ 1853 and has remained in a near constant state of activity ever since with small explosive eruptions, degassing events lasting years to decades and intermittent lava lake appearance (McBirney 1956; Rymer et al. 1998). The ongoing degassing "crisis" began in June 1993 (Rymer et al. 1998; Delmelle et al. 1999) and the gas composition and emission rates of Masaya's plume have been studied during several direct sampling and remote sensing campaigns (Martin et al. 2010; Aiuppa et al. 2018; Pering et al. 2019). In the dry season (December–May), consistent northeasterly trade winds direct the volcanic plume across the Llano Pacaya area. In March 2009 (i.e., a few weeks after our field survey; see below), Martin et al. (2010) measured SO_2, HCl and HF emission rates of 690, 230 and 25 Mg/day. The mean SO_2 emission over 1996–2009 was 830 Mg/day. According to these authors, the plume's gas composition remained virtually unchanged during this period.

Masaya city (population ~ 186 000 (City Population 2021)) lies 5 km east of the volcano, while emissions from the volcano are blown mainly to the west-southwest over

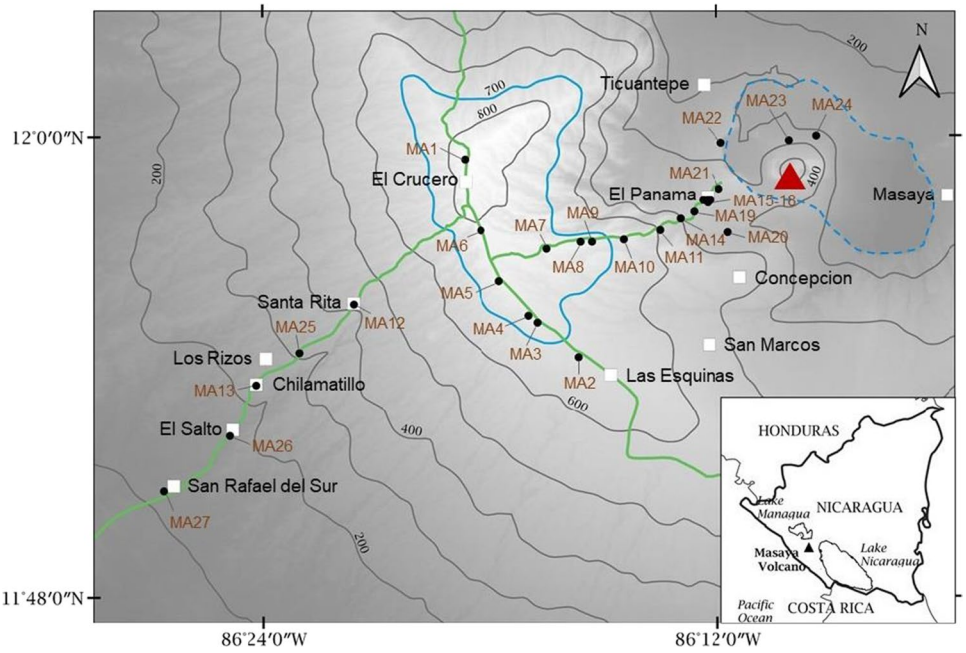

Fig. 1 Location map. Inset shows location of Masaya Volcano in Nicaragua. The plain and dashed blue lines show the approximate boundaries of the Llano Pacaya highlands and Masaya Caldera, respectively. Masaya Volcano is depicted by a red triangle. A selection of localities mentioned in the text is shown with white squares. Black circles represent sampling sites for air, water (except MA3, MA5, MA19, MA20, MA23 and MA24) and soil (except MA3, MA5, MA19, MA20, MA23, MA24) (see also Table S1). The background gas concentrations were measured at sites MA23 and MA24. The green lines are the main roads used to install the sampler network

smaller settlements. The rural inhabitants downwind of the degassing crater are scattered across the plains to the east and west of the Pan American Highway with population clusters in San Rafael del Sur (population ~ 55 000), Ticuantepe (population ~ 38 000) and El Crucero (population ~ 16 000) (City Population 2021) (Fig. 1). Thus, the estimated population potentially affected by the gas plume downwind is in excess of 100 000 residents. Previous studies have shown that the SO2-rich gas plume from Masaya Volcano influences air quality across a 1,250-km^2 area downwind (Delmelle et al. 2001; 2002), with potentially deleterious effects on human health (Van Manen 2014). Strong vegetation damages are visible within 15 km of the degassing crater due to excessive concentrations of volcanic gases in the air (McBirney 1956; Delmelle et al. 2002). Rural inhabitants depend largely on subsistence farming with supplemental cash cropping (pitaya cactus, pineapple and squash). For potable water, residents are supplied purified water which they keep in storage tanks. These are often open to air. The vulnerability of this rural population to malnutrition and food shortage is high. The local inhabitants also have low mobility and tend to occupy the same land for multiple generations.

Sample collection and analysis

In order to evaluate location-specific multimedia exposure to volcanogenic fluoride in the area downwind of Masaya Volcano, a sampling network was established in the dry season (January 2009). The network sampling sites are shown in Fig. 1 and summarized in Table S1. The sites were chosen to capture resident's exposure. Site selection was based on accessibility (e.g., road and vehicle access) and after gaining permission from the members of the local community. The number of sites was limited by the length of time spent in the field to install and retrieve sampling equipment, as well as the number of samplers available for data collection.

Twenty-five residence and school sampling sites were selected: seven sites in the El Panama area directly west of the crater, five sites in the Llano Pacaya, the grassy plain east of the Pan American Highway, with an additional site each in Ticuantepe and Concepcion, six sites along the Pan American Highway between Las Esquinas and El Crucero, and five sites installed further west along the road to San Rafael del Sur (Fig. 1). Sites were at a distance ranging from 4.2 to 34.4 km from the volcano. In addition, two sites east of Santiago crater within Masaya Caldera (sites MA23 and MA24) were used to discriminate the natural background concentration of the gases SO_2, HCl and HF. The total study area is ~ 230 km^2. Sampling consisted of time-averaged air concentrations, surface soils and drinking and non-drinking waters. It was not possible to collect all types of samples at all sites, depending on the availability of the media, or whether permission was granted (Table S1).

Diffusive (passive) samplers have been used extensively for general air quality monitoring (Ferm and Rodhe 1997; Ferm and Svanberg 1998). Delmelle et al. (2001; 2002) initiated their usage in the volcanic situation and other studies followed (Aiuppa et al. 2004; van Manen 2014). A diffusive air sampler measures time-weighted average gas concentrations in air. Gases are trapped on a sorbent (impregnated filter paper) at one end of a tube, by molecular diffusion through an internal volume of air or membrane filter. The diffusion tubes (Fig. S1) were prepared in the laboratory

and details on their construction and how to operate them are provided as Supplementary Information (SI). The sampler installation consisted of two diffusion tubes, with an exposure time of approximately 20 days. Due to a damaged installation at sites MA19 and M24, the diffusion tubes had to be replaced during the survey, resulting in a shorter sampling duration (7 days). Field duplicates were also deployed but not at all the sites. Samplers were secured mainly to trees with an average height of ~ 3 m above ground, suspended at least ~ 15 cm horizontally away from the vertical surface (Fig. S2). Care was used to locate the sampling sites upwind of residential activities, especially cooking fires. After exposure, samplers were capped, tightly sealed, transported back to the laboratory and refrigerated at 4 °C until extraction.

At Masaya, the majority of drinking water samples were sourced from community municipal wells to the tap or trucked into large, local storage tanks. Although non-potable rainwater collected in shallow cement tanks or steel drums are utilized for irrigation, clothes-cleaning and bathing, it is also presumed that this water is for occasional consumption. Water from in-house taps and storage tanks was collected from 19 residences (Table S1). In addition, two non-drinking water samples were collected from open storage tanks (sites MA18 and MA21). The water samples were filtered on site using 0.45 µm membrane filters.

Soils in the study area derive from the weathering of Quaternary basaltic tephra, with a remarkably time-invariant composition, erupted by Masaya Volcano (Walker et al. 1993). A composite sample of ~ 30 g of loose surface soil material was collected from 23 locations (Table S1) within ~ 10 m of each sampler installation site. The samples were placed in clean plastic bags, double-sealed and transported at ambient temperature. In the laboratory, the soil samples were air-dried and sieved to < 2 mm. Soil total fluoride (F_{tot}) was obtained by mixing a sub-sample of the crushed soil with lithium metaborate ($LiBO_2$). After sintering at 1050 °C, the sintrate was dissolved in concentrated nitric acid (HNO_3), and the fluoride concentration in solution was measured with an ion-selective electrode (Orion Research, Model 920) after addition of a total ionic strength adjustment buffer (Bodkin 1977). This method was tested successfully on the US Geological Survey reference basaltic rock material BHVO-2, for which a total fluoride concentration of 370 mg/kg is reported (Wilson 1997) and a concentration of 366 ± 58 mg/kg ($n = 4$) was measured.

Soil sub-samples were extracted at a solution to liquid ratio of 1:100 for two hours at room temperature in order to estimate the water-soluble fluoride (F_w). The water leachates were then centrifuged and filtered (0.45 µm) prior to measuring the dissolved fluoride concentration (F_w). In general, the soluble fraction of a contaminant in soil underestimates the oral bioaccessibility (the fraction of a compound that is soluble in the gastrointestinal tract and is available for absorption) and other analyses are needed to provide a more robust assessment of this parameter. The Unified BARGE Method (UBM) developed by the BioAccessibility Research Group of Europe (BARGE) is regarded as a valid in vitro test for measuring the oral bioaccessibility of metal contaminants in soils with a range of physicochemical properties (Wragg et al. 2011). Unfortunately, the UBM entails high costs in equipment and reagents and is also time-consuming.

Given the practical limitations of the UBM, we applied a simplified chemical extraction for the estimation of the oral bioaccessibility of fluoride in the soil samples. Pelfrêne et al. (2020) showed that the treatment of contaminated soils with a hydrochloric acid (HCl) solution at pH ~ 2 can be used as a first-tier screening to assess the oral bioaccessibility of metals (metaloids). Hydrochloric acid is the primary acid in human gut and the pH of the stomach in digestion is 1.5 to 2 (Sams et al. 2016). Similarly, we estimated the proportion of bioaccessible fluoride in the Masaya soils by measuring the concentration of fluoride in solutions (F_{HCl}) obtained by extracting the soil materials with 0.01 mol/l (pH 2) HCl solution (solution to liquid ratio of 1:100 and a 2-h extraction time at room temperature). For the sake of comparison, we also analyzed the fluoride extracted with the UBM test (F_{UBM}) on three soil samples (sites MA9, MA12 and MA21). The protocol of the BARGE method used in this study is briefly described in the SI.

The concentrations of fluoride, chloride, and sulfate in the different aqueous solutions (diffusion tube extracts, water samples, and soil extracts) were determined by suppressed ion chromatography. Additional details on these analyses are provided in the SI.

Assessment of exposure to fluoride

The populations of interest in our analysis are children (3 to < 6 years of age) and adults (> 21 years of age). These age groupings are in accordance with U.S. EPA (2011). The permanent teeth (except the third molars) are considered collectively to be susceptible to development of fluorosis during the first 6–8 years of life (e.g., Larsen et al. 1985; Bårdsen and Bjorvatn 1998). In brief, exposure to fluoride is assessed by calculating an estimated total daily intake (potential dose; i.e., the amount of agent that is actually inhaled, ingested, or applied to the skin) of fluoride (EDI_{tot}, mg/kg body weight/day) from all relevant exposure routes, i.e., inhalation (EDI_{inh}), consumption of drinking water (EDI_{wat}), incidental soil ingestion (EDI_{soil}) and dermal contact (EDI_{derm}), for children and adults (US EPA 2019):

$$EDI_{tot} = \Sigma C_n I_n = EDI_{inh} + EDI_{wat} + EDI_{soil} + EDI_{derm} \quad (1)$$

where C_n is the concentration of fluoride in a specific medium n (air, water, soil) and I is the intake rate in this

medium. Determination of fluoride intake from the different medium concentrations requires assumed values of body weight and I. The approach adopted to perform the exposure assessment, including choice of the relevant parameters, for the residents affected by Masaya Volcano's gas plume is described in the SI.

The Integrated Risk Information System (IRIS) (U.S. EPA 2003) provides the toxicity values (e.g., reference dose or *RfD*) for individual non-carcinogenic chemicals, including fluoride. The *RfD* is an estimate of the daily exposure to children and adults that is likely to be without appreciable risk of deleterious effects during a lifetime. The *RfD* for fluoride is 0.06 mg/kg body weight/day for children and adults, with uncertainty and modifying factors of unity (U.S. EPA 2003). Details on the basis and rationale of the fluoride *RfD* are provided in IRIS and is beyond the scope of this study. The EDI_{tot} obtained via the application of Eq. 1 is compared to the *RfD* to compute the hazard quotient (*HQ*):

$$HQ = \frac{EDI_{tot}}{RfD} \quad (2)$$

The *RfD* of 0.06 mg fluoride/kg body weight/day corresponds to a maximum *EDI* of ~ 1.2 mg of fluoride for children (average body weight of 18.6 kg) and ~ 4.2 mg for adults (average body weight of 70 kg). An $HQ > 1$ indicates that excessive exposure has occurred and there is a valid risk of dental fluorosis (children) or skeletal fluorosis (adults) (U.S. EPA 2003).

Results

Time-average SO_2, HCl, and HF concentrations in air

Time-averaged SO_2, HCl, and HF concentrations at sample sites are presented in Table 1, and are within the ranges 52–1266, 11–278, and 3.3–35.6 µg/m^3 respectively. The

Table 1 Concentrations of the volcanic gases SO_2, HCl and HF in the air as measured by the diffusion tube installation, concentrations of sulfate, chloride and fluoride in the water samples and concentrations of water-extractable fluoride (F_w), HCl-extractable fluoride (F_{HCl}), bioaccessible fluoride (F_{UBM}) and total fluoride (F_{tot}) in the soil samples. See text for explanations

Site	Air			Water				Soil		
	SO_2	HCl	HF	SO_4^{2-}	Cl^-	F^-	F_w	F_{HCl}	F_{UBM}	F_{tot}
	µg/m^3			mg/l				mg/kg		
MA1	89.0	12.8	3.3	22.1	12.9	1.0	17	101	-	407
MA2	52.1	11.0	3.4	16.6	12.3	0.4	73	256	-	763
MA3	112.5	24.4	3.9	-	-	-	-	-	-	-
MA4	188.8	38.7	7.0	24.3	14.3	1.2	66	283	-	834
MA5	258.4	51.2	10.9	21.5	14.1	1.1	63	308	-	891
MA6	140.0	25.4	4.0	-	-	-	-	-	-	-
MA7	251.0	43.3	10.8	17.7	14.4	1.1	59	394	-	1271
MA8	256.8	55.9	3.9	19.6	13.1	1.1	66	231	-	735
MA9	333.7	71.0	7.1	24.0	16.4	1.1	166	147	381	838
MA10	1266.2	277.7	35.6	20.3	13.5	1.2	64	146	-	494
MA11	233.3	23.4	4.1	17.0	11.3	1.2	36	110	-	458
MA12	141.8	27.4	5.2	31.2	24.2	0.5	130	210	360	1414
MA13	146.0	32.2	6.9	28.5	20.6	0.4	74	116	-	692
MA14	222.7	57.7	6.1	45.4	30.3	1.4	70	167	-	443
MA15	478.9	125.1	9.3	32.2	20.1	1.2	76	205	-	396
MA16	506.3	138.6	11.5	34.2	22.2	1.4	81	230	-	383
MA17	613.8	150.8	16.1	39.2	24.0	1.4	86	358	-	507
MA18	536.1	147.8	23.1	41.4	26.9	1.4	125	304	-	482
MA19	278.6	69.2	6.8	-	-	-	156	336	-	469
MA20	65.7	16.5	6.2	-	-	-	18	92	-	155
MA21	676.3	179.2	18.2	49.3	27.9	1.8	33	148	172	467
MA22	61.9	17.9	8.9	36.8	30.1	1.1	64	97	-	299
MA23	3.3	2.7	< d.l	-	-	-	-	-	-	-
MA24	6.4	5.3	< d.l	-	-	-	-	-	-	-
MA25	147.5	30.1	6.3	29.40	21.0	0.5	78	128	-	735
MA26	113.8	25.9	9.1	30.00	22.2	0.5	61	132	-	689
MA27	73.7	16.9	3.5	26.20	19.6	0.4	44	104	-	588

d.l. detection limit;-; no data

concentration of SO_2 is always higher (~two to four times) than that of HCl, which itself exceeds the concentration of HF by a factor varying between 1.1 and 7.9. High gas concentration values are typically encountered within 5 km downwind of the crater (El Panama area) (Fig. 2). However, additional maxima occur between 10 and 15 km (Llano Pacaya). The installation at site MA10 (Llano Pacaya) recorded the maximum average concentrations of all three gases. The lowest gas values are found at sites MA1 (fourth lowest for SO_2 and second lowest for HCl) and MA2 (second lowest for HF), which are the northern and southern boundaries of the installation area on the Pan American Highway (Fig. 1). Baseline sites located upwind of the crater (sites MA23 and MA24) have average SO_2 and HCl concentrations of 3.3 and 6.4 and 2.7 and 5.3 µg/m^3, respectively, whereas HF was not detected by the diffusion tubes.

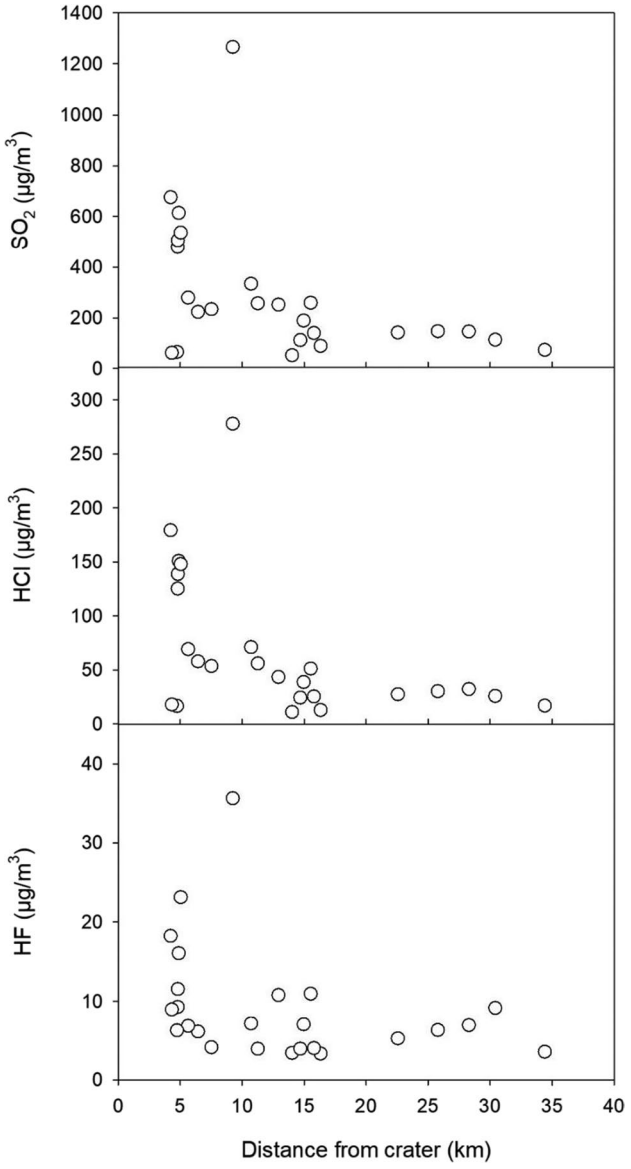

Fig. 2 Concentrations of the volcanic gases SO_2, HCl and HF in the air as measured by diffusion tubes versus distance from Masaya Volcano's degassing crater

Sulfate, chloride, and fluoride concentrations in waters

The concentrations of sulfate, chloride, and fluoride in the water samples are reported in Table 1 and are in the ranges 16.6–49.3, 11.3–30.3, and 0.4–1.8 mg/l, respectively. The maximum sulfate and fluoride concentrations (49.3 and 1.8 mg/l, respectively) correspond to site MA21 in the El Panama area, whereas the lowest values (16.6 and 0.4 mg/l, respectively) are measured in the drinking water sampled at site MA2 on the southern margin of the study area (Fig. 1). Dissolved chloride is maximum at site MA14 (30.3 mg/l) and minimum at site MA11 (11.3 mg/l). Similar to the trend inferred for the time-averaged gas concentrations, the water samples from the El Panama area have higher sulfate, chloride and fluoride concentrations (Table 1). Secondary maxima in sulfate and chloride occur at Santa Rita (MA12) and Chilematillo (MA13), along the road to San Rafael del Sur (Fig. 1). Although there are only two non-potable water samples (sites MA7 and MA9), there appears to be no marked difference in results between water for drinking (from taps and storage tanks) and water for washing.

Water- and HCl-extractable fluoride, bioaccessible fluoride, and total fluoride concentrations in soils

Soil sample extraction results are tabulated in Table 1. The concentration of F_w ranges from 17 mg/kg at site MA1 to166 mg/kg at site MA9. The HCl-extractable fluoride is comparatively higher at all but one site (MA9) and varies between 92 mg/kg (site MA20) and 394 mg/kg (site MA7). The F_{tot} values in the soils are comparatively greater, ranging from 155 mg/kg (site MA20) to 1414 mg/kg (site MA12). Figure 3 indicates that both low and high F_w and F_{HCl} concentrations are measured within 5 km of the degassing crater. In contrast, the soils richest in F_{tot} (sites MA7 and MA12) correspond to distances from the degassing crater comprised between ~ 12 and 23 km. Application of the UBM method to the soil samples collected at sites MA9, MA12 and M21 produced F_{UBM} concentrations of 381, 360 and 172 mg/kg, respectively.

Fluoride exposure assessment

The results of the exposure assessment exercise and the *HQ* values associated with fluorosis are reported in Table S2 for children and Table S3 for adults. The contributions of the different exposure pathways to *EDI* are illustrated in Fig. 4. The *EDI* for children range from 0.11 to 0.46 mg/kg body

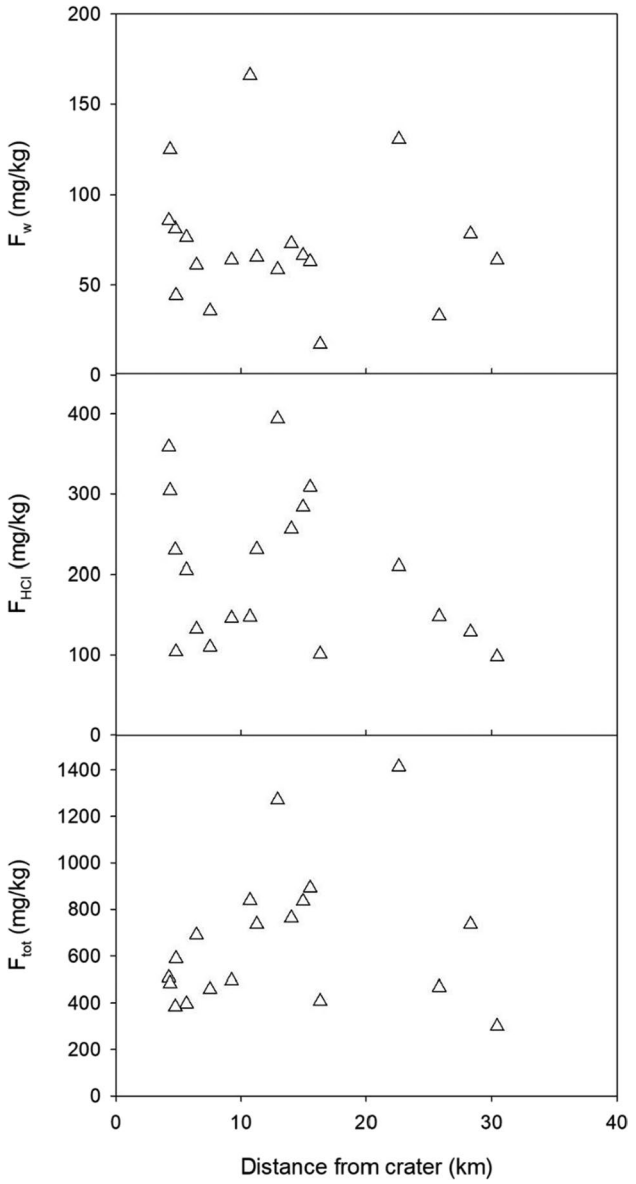

Fig. 3 Concentrations of water-extractable fluoride (F_w), HCl-extractable fluoride (F_{HCl}), and total fluoride (F_{tot}) in the soil samples *versus* distance from Masaya Volcano's degassing crater

weight/day, while adults have a *EDI* of 0.39–2.36 mg/kg body weight/day. The largest *EDI* values correspond to site MA10, which also has the highest average HF concentration in the air. For children, the contributions of air inhalation, drinking water and incidental soil ingestion to *EDI* vary in the ranges ~ 15–68, ~ 14–42, and ~ 17–71%, respectively. For adults, ~ 23–73% of the *EDI* is due to air inhalation, ~ 26–75% to drinking water and ~ 1–7% to incidental soil ingestion. Fluoride exposure via dermal contact is always negligible (≤ ~ 1% of *EDI*).

Figure 5 shows the calculated *HQ* values for children and adults. The results for all the sites in the gas plume-affected zone indicate a significant risk of dental fluorosis in children (*HQ* > 1). Site MA18 corresponds to the highest *HQ* (7.6) for children. For adults, the *HQ* clearly exceeds 1 at three sites (MA10, MA18 and MA21), suggesting some risk of developing skeletal fluorosis with chronic exposure to fluoride. Sites MA5, MA7, MA16 and MA17 (*HQ* = 1.15, 1.17, 1.30, and 1.35, respectively) may also be associated to a such risk.

Discussion

Plume dispersion and fluoride deposition

The analysis of the passive samplers deployed downwind of Masaya Volcano highlights the striking consistency of S/Cl molar ratios: all sampling sites are within the range ~ 2 to 4, with 87% of results grouped within 2.0–3.0 (mean 2.6 ± 0.5) (Fig. S4). Using open-path Fourier transform infrared spectroscopy and filter packs over 20–24 March 2009, Martin et al. (2010) measured a S/Cl molar ratio of 1.7 in the gas plume at Santiago crater, i.e. a value compatible with our measurements. A broader range of S/F molar ratio values (~ 2.2–20.6) is inferred from the passive samplers (Fig. S4), but the mean (9.5 ± 4.4) compares relatively well with the gas plume's S/F ratio (8.8; Martin et al. 2010). Noting that Masaya Volcano is the only source of atmospheric fluorine in the region, these results confirm the volcanic origin of the gas HF measured by the diffusion tubes. The impact of Masaya Volcano's emissions on HF in the air is significant: the time-averaged concentrations are ~ 7 to 70 times greater than the typical natural background value of 0.5 μg/m^3 (IPCS 2002; DEFRA 2009).

Dilution of the gas emissions during transport downwind cannot explain the spatial variability of the S/F ratio. Contrary to SO_2, chemical reactions are ineffective in the elimination of HF from the atmospheric boundary layer (Cheng 2018) and therefore, dry and wet depositions are the only removal pathways. Wet deposition probably plays a minor role during the dry season, although the intermittent formation of dew and fog in the early hours of the morning on the Llano Pacaya highlands (Delmelle et al. 2001; 2002) may allow the transfer of gaseous HF molecules to water droplets. Instead, the apparent non-conservative behavior of the S/F ratio downwind may reflect local differences in the rates at which HF gas molecules impinging on the surfaces of plant leaves, soils, rocks, etc. are retained by them. The wide range of dry deposition velocity values (0.016–0.1 m/s) reported for the gas HF (Peterson 1977; Sehmel 1980) supports the idea that its removal from the troposphere can fluctuate greatly spatially, depending on land cover and meteorological factors. This probably explains the presence of high HF

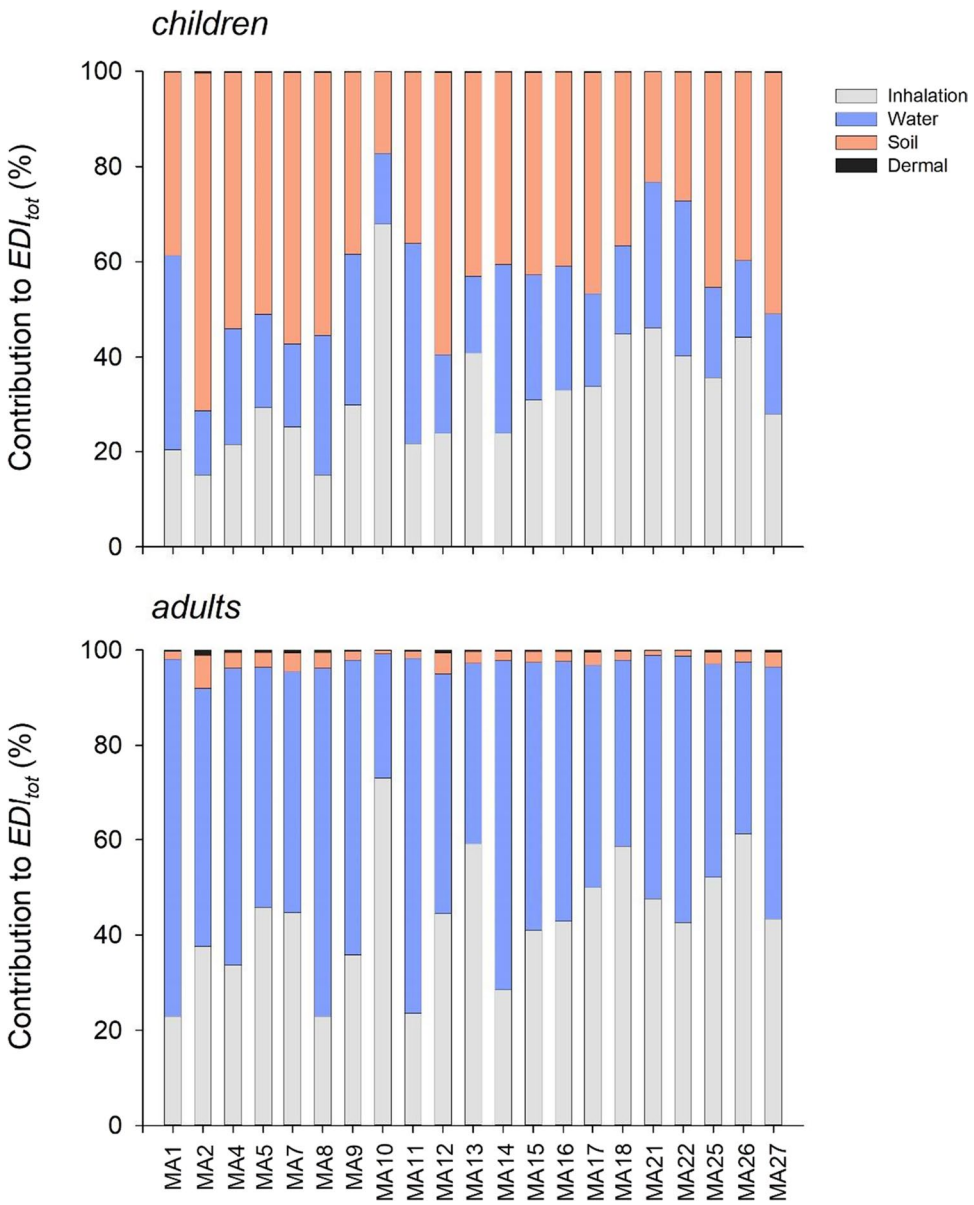

Fig. 4 Contributions of the inhalation, water consumption, incidental soil ingestion and dermal contact exposure routes to the estimated total daily intake of fluoride for children (top) and adults (bottom)

concentrations at sites relatively close (i.e. El Panama) to the volcanic degassing source, but also at greater distances from it in the Llano Pacaya area (Table 1; Fig. 2).

Delmelle et al. (2001; 2002) highlighted that the volcanic plume is forced by thermal inversion against the Llano Pacaya highlands (Fig. 1). Plume grounding is supported by the additional SO_2 and HCl concentration maxima recorded in this area, and is likely responsible for some of the high HF values (Table 1; Fig. 2). Thus, the anomalously elevated HF concentration of site MA10 (~ 36 μmol/m^3) suggests a recurrence of plume grounding and land fumigation in this location. Site MA14 (Concepcion) and site MA22 (Ticuantepe), although relatively near the volcanic crater at 6.4 and 4.3 km, respectively, have comparatively low measurements of gas concentrations (Table 1). These sites, located on the plume margin, not directly downwind, are exposed to more dilute emissions.

Arguably, the dry deposition of HF from the low-altitude volcanic plume is a major route for the addition of fluoride to vegetation, soils and water bodies in the Masaya area. Using minimum and maximum dry deposition velocities of 0.016 and 0.1 m/s (Peterson 1977; Sehmel 1980), respectively, and an average HF concentration in the air of ~ 9.3 μg/m^3 (Table 1) is predicted to produce an annual rate of fluoride deposition downwind of Masaya Volcano in the range ~ 4.7×10^{-3} to 2.9×10^{-2} Gg/km^2/yr. Over the ~ 230 km^2 study area, this corresponds to deposition of ~ 1.1–6.8 Gg of fluoride, or ~ 12–61% of the annual (in 2009) magmatic fluorine emitted by Masaya Volcano (8.9 Gg/yr; Martin et al. 2010). The upper estimate, which reflects the

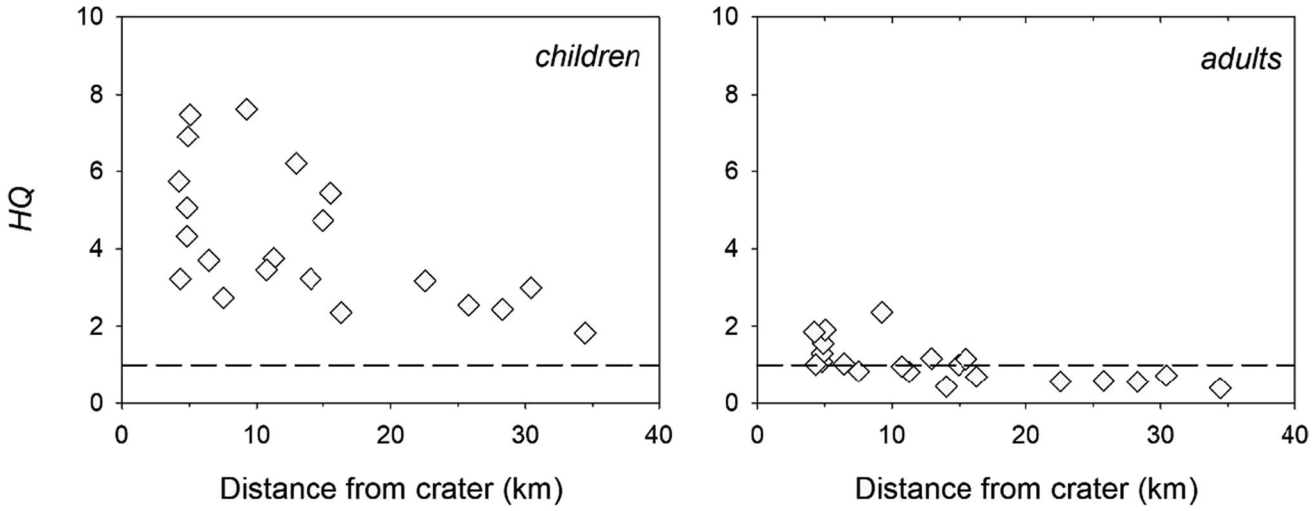

Fig. 5 Hazard quotient (*HQ*) versus distance from Masaya Volcano's degassing crater as calculated for children (left) and adults (right). The dotted line represents $HQ = 1$; i.e., the value above which the fluoride intake may be in excess of that likely to be without appreciable deleterious health effects (US EPA 2003)

highest dry deposition velocity value given for fluoride, is unrealistic. For Mt. Etna, Aiuppa et al. (2004) inferred for the period May–June 2002 a fluoride deposition flux equivalent to only ~ 3% of the volcano's HF emissions (~ 7.7 Gt/yr), i.e. well below the conservative estimate of 12% obtained for Masaya. The lower concentrations of HF generally measured in the air around Mt. Etna (i.e., ≤ 1.5 μg/m^3 at sites located between 1.7 and 25.6 km from the summit crater (Aiuppa et al. 2004)) explain the large difference with our study. Bellomo et al. (2003) estimated that no more than ~ 1% of the fluoride present in the gas plume released by Stromboli volcano, Italy, between October 2000 and October 2001 is deposited downwind via rainwater. The comparatively large fluoride deposition flux inferred at Masaya points to recurrent plume grounding and land fumigation (Delmelle et al. 2001; 2002), a phenomenon that becomes less frequent and intense when the gas emissions are released at a higher altitude in the troposphere.

Transfer of fluoride to environmental media

Fluoride concentrations in media determined in this study supply quantitative evidence of the extent to which the environment exposed to Masaya Volcano's gas emissions is contaminated by volcanogenic fluoride. Despite dilution and local air circulation patterns, the gas HF is detected at all sites. Dissolved fluoride is also measured in drinking water and the soil samples contain significant concentrations of bioaccessible fluoride.

Both the drinking and non-drinking water samples contain dissolved fluoride at concentrations above the natural background value for surface water (i.e., 0.2 mg/l (Weinstein and Davison 2004)). Only one site (MA21) exceeds the World Health Organization guideline limit for fluoride in drinking water (i.e., 1.5 mg/l (WHO 2017)). Although drinking water was purported to be from a purified source, many storage tanks in the surveyed area are open to external air. Thus, both dry and wet deposition of Masaya's plume may act as a source of fluoride for the water samples.

In Fig. 6, the relative fluoride, chloride and sulfate concentrations in the non-drinking and drinking waters form a

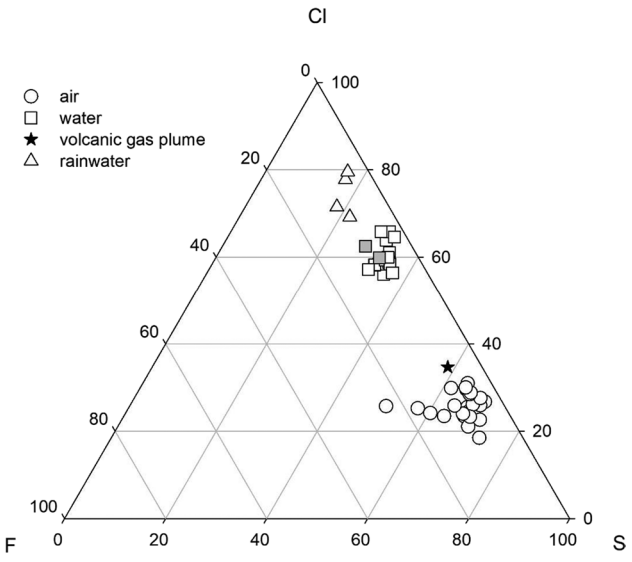

Fig. 6 Relative molar concentrations of sulfur, chlorine and fluorine in air, water, volcanic gas plume and rainwater samples. The two grey-filled squares represent the non-drinking water samples. See text for explanations

cluster, suggesting a common origin for the dissolved anions. However, all the water samples are markedly enriched in chloride (and have lower S/Cl molar ratios, i.e., ~ 0.5–0.7) relative to the air composition inferred from the diffusion tube measurements (S/Cl ~ 2.0–3.9). Assuming that the source of dissolved sulfate and chloride in the waters is the volcanic gas plume, this likely reflects the lower solubility in water of dry-deposited SO_2 compared to HCl (NIST 2021). The open water tanks also collect rain of which the composition is affected by the volcanic emissions. Delmelle et al. (2003) reported low pH values (~ 3.5–4.2) for rainwater in the El Panama and Llano Pacaya areas. Back in the 80 s, Johnson and Parnell (1986) also measured acid rain (pH 2.5–5.0) from Masaya's volcanic plume. The solubility of the gas SO_2 in aqueous solutions decreases with acidity (Hales and Slitter 1973) and accordingly, the rain samples have a much lower S/Cl ratio (~ 0.2–0.3) than that of the gas plume (~ 1.7 (Martin et al. 2010)) (Fig. 6).

The S/F molar ratio values (~ 3–11) in the drinking and non-drinking water and air samples (S/F ~ 2–15, omitting sites MA8 (S/F ~ 21) and MA11 (S/F ~ 18)), compare relatively well (Fig. 6). They also approximately match the rainwater composition measured in 2002 (Delmelle et al. 2003). This behavior contrasts with that observed for the S/Cl molar ratio. It is also at odds with the full miscibility of the gas HF in water (NCBI 2021), which should lead to lower dissolved S/F values compared to Masaya Volcano's gas emissions. This suggests that another source of soluble sulfate and fluoride affect both the rainwater and tank water compositions. We hypothesize that wind-blown soil dust plays this role.

According to Delmelle et al. (2003) and Delfosse et al. (2005), the soils exposed to Masaya's gas plume accumulate fluoride and sulfate in significant quantities but not chloride. In volcanic soils such as those found downwind of Masaya, fluoride typically binds irreversibly to the reactive surfaces represented by amorphous and poorly crystalized secondary solid phases (typically allophanes and ferrihydrite (Mizota and van Reeuwijk 1989)), whereas sulfate is less strongly adsorbed and will tend to be released upon contact of the soil with water much more readily than fluoride (Hingston et al. 1967; Gebhardt and Coleman 1974; Delmelle et al. 2003). Hence, contamination of rainwater and tank water by suspended soil dust may increase the concentrations of sulfate, whereas the effect on dissolved fluoride will be comparatively minor. Additional laboratory analyses of a new set of surface soil materials from the Masaya region would be needed to confirm this suggestion.

As documented by Delmelle et al. (2003), dry and wet depositions downwind of Masaya Volcano increase the fluoride content in the soils exposed to them. Our measurements (Table 1) indicate that the HCl solution extracts a larger fraction of the soil's total fluorine content than deionized water (15–72% compared to 5–33%). This simply reflects the strong retention of fluoride in volcanic soils. Using HCl at pH 2 leads to partial dissolution of the soil's secondary solid phases (allophanes and ferrihydrite), thereby allowing the release of fluoride adsorbed onto them.

Although they derive from compositionally identical tephra deposits, the soils affected by Masaya Volcano's gas emissions differ in their weathering degree (Delmelle et al. 2003; Delfosse et al. 2005). Soils in the vicinity of the caldera are relatively young and poorly developed; they are rich-in volcanic glass fragments and are known as Vitric Andosols (ISSS 1998; Delmelle et al. 2003; Delfosse et al. 2005). They typically occur in the El Panama area. Older soils in a more advanced stage of weathering (Eutric Andosols) are found in the Llano Pacaya and farther away towards the Pacific coast. These soils are comparatively richer in allophanes and ferrihydrite, i.e. the products of basaltic parent material weathering.

Figure 3 suggests that F_{tot} tends to be higher in the Eutric soils compared to the Vitric soils, a feature pointing to the larger capacity of the former to adsorb fluoride due to their distinctively high contents in allophanes and ferrihydrite (Saeki and Matsumoto 1993; Cronin et al. 2000; Delmelle et al. 2003). Combined with a high specific surface area (several 100 s m_2/g), the presence of reactive surface sites (aluminol and hydroxyl groups in the cases of allophanes and ferrihydrite, respectively) on these secondary solid phases explains their high affinity for fluoride. In contrast, the F_w and F_{HCl} measurements do not differ markedly between the two soil types (Table 1). In fact, the majority of the Vitric soil samples contains proportionally more water- and HCl-extractable fluoride than the Eutric soils (Fig. 3). This is interpreted in terms of a lesser capacity of the younger and less weathered soils to bind fluoride inputs strongly due to comparatively lower contents in allophanes and ferrihydrite.

Fluoride exposure and fluorosis risk

A striking result obtained for children exposure to fluoride is that incidental soil ingestion is a primary source contributing to cumulative daily fluoride intake in contaminated areas (Fig. 4). On average, the soil exposure pathway accounts for ~ 42 ± 13% of the total fluoride exposure and is even higher than that related to the presence in the air of the volcanic gas HF (~ 31 ± 12%). We also note that our estimates of the oral bioaccessibility of fluoride in the Masaya soils probably represent minimum values as the UBM method applied to three soils produced concentrations of bioaccessible fluoride which are higher (1.2 to 2.6 times) than those obtained by treating the soil material with HCl (Table 1). The intakes from HF inhalation and incidental ingestion of soil clearly rival with the drinking water pathway (~ 26 ± 9%). For adults, soil ingestion becomes a negligible source (< 2.5 ± 1.4%) of fluoride intake and ingestion of

water remains the main exposure route (~ 56 ± 13%) (Fig. 4). However, air inhalation (~ 42 ± 13%) gains in importance compared to the children scenario, reflecting the larger air volume breathed daily by an adult (U.S. EPA 2011). At sites in El Panama (MA17 and MA18) and Llano Pacaya (MA10) where particularly elevated concentrations of HF in air prevail (Table 1), the inhalation exposure route outweighs the contribution due to drinking water.

As shown in previous works (Delmelle et al. 2001; 2002), topography exerts a strong control on the dispersion of Masaya Volcano's gas plume. The steep caldera walls encircling the degassing crater to the west is a direct obstacle for the dispersion of the low-altitude volcanic plume. This topographical barrier promotes downflow of the airborne volcanogenic pollutants, generating the high HF concentrations measured by the diffusion tubes installed on the outer caldera rim slope in the El Panama area (Table 1). Similarly, a rise in the terrain associated with the Llano Pacaya ridge leads to chronic fumigation by the fluorine-rich volcanic emissions of the highlands and steep valleys farther downwind of the caldera. Overall, these peculiar conditions increase the concentration of HF in the air but also its dry deposition and thus, the transfer of the volcanogenic pollutant to water reservoirs and soils. It is the combination of open-vent degassing and low height of the degassing crater relative to the land downwind which is ultimately responsible for a multiple pathway exposure to fluoride in the Masaya area.

The results shown in Fig. 4 highlights soil ingestion as an important route of exposure to fluoride for children living in the shadow of Masaya Volcano. This is a consequence of child behavior (children spend a significant amount of time playing on the ground outdoors) and soil properties (fluoride readily binds to volcanic soils). Further, the results of the soil analyses suggest that fluoride is more bioaccessible in the Vitric soil materials in El Panama than in the more weathered Eutric soils farther away in the LLano Pacaya and beyond. However, the Eutric soils have a higher F_{tot} content (a direct result of their enrichment in allophanes and ferrihydrite; Delmelle et al. 2003; Delfosse et al. 2005) that partly compensates for the comparatively low anion mobility. Therefore, counterintuitively, the contribution of incidental soil ingestion to total fluoride intake for children living far from the volcano is as high as that for children living in proximity of it. Adults in the Masaya area are exposed only marginally to fluoride in soils because their pattern of activities differs from that of children (U.S. EPA 2011). Their intake dose is also lower due to a greater body weight.

For children, the *HQ*, which integrates all exposure pathways and toxicity information, is > 1 at all sites (Fig. 5). Thus, it is very likely that some children in the surveyed area receive fluoride levels in excess of those "likely to be without appreciable deleterious effects" (US EPA 2003) and are at risk of fluorosis. While we did not collect information on teeth staining in the children, Van Manen (2014) mention that residents leaving in areas close to Masaya Volcano have this condition, possibly pointing to dental fluorosis. A similar qualitative observation was also made during a previous field campaign in 2000 (Dr. P. Baxter, pers. communication). High *HQ* values occur beyond El Panama and up to ~ 15 km from Masaya Volcano. This reflects the significant contribution from the incidental soil ingestion exposure route to EDI_{tot} for children in the Llano Pacaya area (Fig. 4; Table S2). Assuming water ingestion as the only fluoride exposure route reduces to 12 the number of sites for which *HQ* is > 1, with only one value exceeding 1.5 (MA21). This result emphasizes again the importance of air inhalation and incidental soil ingestion as major fluoride intake routes for children. Adults may incur a risk of developing adverse health effects ($HQ > 1$) due to overexposure to fluoride at sites MA5, MA7, MA10, MA15, MA16, MA17, MA18, and MA21 (Fig. 5). Although the daily intake associated with the ingestion of drinking water does not exceed the *RfD* at these sites, the cumulative intake surpasses it when the air inhalation pathway is considered.

Based on our study, we anticipate that populations in the vicinity of open-vent degassing volcanoes elsewhere are similarly exposed to fluoride via multiple media. For example, on the volcanic island of Ambrym, Vanuatu, the semi-continuous degassing at Marum and Benbow summit craters enriches the atmospheric wet deposition in fluoride. Allibone et al. (2012) concluded that the ingestion of fluoride-contaminated rainwater is the main cause of dental fluorosis in Ambrym's children. The communities on Ambrym live a traditional lifestyle of subsistence farming and gardening, taking advantage of the fertile volcanic soils and favorable subtropical climate. Similar to the Masaya situation, the conditions are probably met for Ambrym's children to be exposed to fluoride via incidental soil ingestion, and this pathway is likely to increase further the total daily intake, thus intensifying the fluorosis risk highlighted by Allibone et al. (2012). Nyiragongo volcano, in eastern Democratic Republic of Congo, is another case where multi-media exposure of inhabitants to fluoride may occur in relation to open-vent degassing (Cuoco et al. 2013).

Limitations of the study

Analysis of uncertainty is a critical component of risk assessment. The fluoride exposure assessment in the residential area affected by the gas emissions from Masaya Volcano was performed once over a brief period and thus, represents a snap-shot of the exposure profile. In the wet season (mid-May to mid-November), the prevalent wind direction shifts toward the south-east, possibly leading to less inputs of fluoride to the sites surveyed in this study. Specifically, this may

affect the concentration levels of HF in the air as well that of fluoride in open-top water tanks. In contrast, fluoride intake via inadvertent soil ingestion should not fluctuate much over the months, because fluoride is strongly bound to the soil and it would take many years of volcanic activity repose before noticing the effect of slow desorption processes on the bioaccessible fraction. Hence, single point measurements are regarded as representative of fluoride bioaccessibility in the Vitric and Eutric soils from Masaya, although we surmise that the HCl test represents minimum estimates and that application of the UBM would produce higher values.

For estimating fluoride exposure via water consumption in children and adults, we rely on the water consumption rates (l/day) recommended by US EPA for people living in a temperate climate (U.S. EPA 2011). However, it is known that significantly more water is consumed in hot tropical regions such as Nicaragua (Fawell et al. 2006). Because the daily fluoride dose determines the likely health outcomes, additional information on daily water consumption in the area surveyed should be obtained in order to refine the fluoride exposure assessment.

Fluoride exposure due to food consumption was not considered in our study but could constitute an additional source of fluoride intake. Fluoride uptake in food crops grown in fluoride-contaminated soils is not well documented, but some studies suggest it is favored in acidic conditions (Arnesen 1997; Stevens et al. 2000; Weinstein and Davison 2004). People in the rural area of Masaya live on a diet consisting of the basic staples rice, cassava and taro. Fawell et al. (2006) indicate that rice may contain up to ~ 2 mg/kg of fluoride, whereas Heikens et al. (2005) measured < 2 mg/kg of fluoride in rice cultivated in the Asembagus plain, East Java, Indonesia, an area contaminated with fluoride-rich hydrothermal waters. Rao and Mahajan (1990) report greater concentrations (~ 9 mg/kg) for rice in an arid region of South India with a high incidence of dental fluorosis in children. According to the World Health Organization (Fawell et al. 2006), roots and tubers such as cassava, taro, yam and sweet potato tend to accumulate fluoride, but the information is scarce; Kjellevold Malde et al. (1997) found concentrations in the range 1–2.5 mg/kg for cassava in East Africa. In general, bioavailability of fluoride in foods is less than that of equivalent fluoride in water (Rao 1984). Assuming a conservative fluoride bioaccessibility value of 1 mg/kg dry food and based on estimates of daily consumption of rice and cassava by children and adults in rural Indonesia (Heikens et al. 2005), we surmise that food ingestion may contribute ~ 4 and 6%, respectively, to the *EDI* of fluoride in the Masaya area impacted by the volcanic gas emissions. While this evaluation should be regarded as preliminary, it suggests food as a missing component in our fluoride exposure assessment.

Finally, inhalation of soil dust particles in suspension in the air may act as an additional source of bioaccessible fluoride. We did not measure the concentration of soil dust particles in the air and this exposure pathway was not included in our analysis. We anticipate that resuspended soil dust in the air will vary spatially depending on wind speed and direction, soil texture, vegetation cover, proximity to roads, etc. Due to their smaller size, children will be more exposed than adults. A dusty environment could also increase daily fluoride intake via food consumption as locally-grown crops will retain soil dust particles (containing fluoride) deposited on foliage and fruits via wet and dry deposition processes.

Conclusions

In contrast to many volcanic environments where (over) exposure to fluoride relates to the use of groundwater containing fluoride leached from the host rock, the emission and dispersion of the low-altitude gas plume from Masaya Volcano ultimately shapes people's exposure to fluoride in the downwind area. In the Masaya case study, air inhalation, drinking water and soil ingestion are all integral to the *HQ*, whereas dermal contact is an insignificant exposure route. The study findings further strongly suggest that all child residents in the surveyed zone (up to 35 km from the degassing crater) are overexposed to volcanic fluoride and thus, a potential risk of dental fluorosis occurs. Our case study shows that contaminated drinking water is only one part of total daily intake in children, and often not the main fluoride exposure pathway. For this population category, incidental ingestion of fluoride-contaminated soil and inhalation of HF present in the air both increase markedly total fluoride intake. For adults, inadvertent soil ingestion becomes negligible and water consumption dominates total fluoride intake, although for some sites exposure via inhalation can rival or even outweigh the drinking water pathway. A risk of skeletal fluorosis in adults is inferred for a few localities within 10 km from Masaya Volcano.

Media concentration values represent a snap-shot of the actual exposure profile given that sampling in the Masaya area was performed once over a brief period. A routine monitoring of air, drinking water and soils would yield a more reliable result. The exposure assessment would also have been improved by results of local food analysis, a refined determination of fluoride bioaccessibility from soil ingestion, and a repeated or extended sampling period to evaluate the seasonal dependence and the influence of changing volcanic activity on exposure. The contribution of soil dust inhalation to daily fluoride intake, particularly for children, and its spatial variability, also requires further attention. Lastly, a teeth examination in children and adults from Masaya by a dental specialist would allow the severity and

prevalence of dental fluorosis to be assessed and linked to the results of the health risk analysis.

Overall, for inhabited areas affected by volcanoes exhibiting open-vent degassing accompanied by fluoride-rich gas emissions, our results highlight the necessity of examining all potentially relevant exposure pathways in order to evaluate correctly cumulative daily fluoride dose, and hence health risk, in children and adults. As a simple screening tool, a such assessment allows for quick identification of sites with $HQ > 1$, indicating excessive fluoride exposure. The tool also identifies the sensitivity of the HQ to each exposure pathway; it is site and age-specific. Thus, a hierarchy of media routes emerges and this could be used to guide optimization of effort to remediate exposure levels for the greatest effect.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s00445-021-01504-w.

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Author contribution All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Julie Calkins and Pierre Delmelle. The first draft of the manuscript was written by Julie Calkins and Pierre Delmelle and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Code availability Not applicable

Declarations

Conflict of interest The authors declare no competing interests.

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