Hydrogen fluoride concentrations in ambient air of an urban area based on the emissions of a major phosphogypsum deposit (SW, Europe)

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ABSTRACT

Hydrogen fluoride (HF) is one of the most toxic gaseous compounds in air, the primary anthropogenic source of which is industrial activity, specifically fertilizer and waste. HF concentrations in an urban area (Huelva, SW Spain) related to a nearby major phosphogypsum (PG) deposit were measured by passive sampling during summer and winter months from 2014 to 2017 and high-resolution sampling during 2017 and 2017–2018 using an HF analyser. An HF geochemical anomaly was found in the PG pond with average concentrations of up to 19.1 µg/m^3, and concentrations of up to 1.6 µg/m^3 were exhibited in the nearest urban area. The concentrations were associated with the HF emissions from the PG deposit. Emission factors were calculated by field and laboratory experiments, and the brines exhibited the highest emission factor (2.7 kg/ha day). Several impacts of HF (> 0.1 µg/m^3) in the city were recorded throughout the year, occurring at noon in the summer and during fog events in the winter. Consequently, the PG system should be restored to protect the population living in Huelva from the impacts of HF emission.

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Keywords: gaseous HF, hydrogen fluoride, ambient air, phosphogypsum deposit, brines

1. Introduction

Fluorine (F) is the most electronegative element in the periodic table, and it can bind to most elements (Tressaud, 2006). F is present in the upper continental crust, seawater, and atmosphere. The global flux of F involves emissions to the atmosphere from natural sources (e.g., volcanoes, seawater, and marshlands) and anthropogenic sources (e.g., industry, mining, and coal combustion). In addition to the atmosphere, the hydrosphere and lithosphere can act as a sink for this element (Tressaud, 2006). Airborne F is present in particulate matter (cryolite (Na_3AlF_6), chiolite ($Na_5Al_3F_{14}$), CaF_2, AlF_3, and NaF) and in the gaseous phase. As a gas, F exists in the form of hydrogen fluoride (HF), carbon tetrafluoride, hexafluoroethane, and silicon tetrafluoride (Lewandowska, 2013). HF is the most important compound, accounting for the 75% of the F present in the atmosphere (Coleman et al., 2006).

In 1970, this element became important in the study of atmospheric chemistry owing to the discovery of the harmful effect of the chlorofluorocarbons (CFCs) on the ozone hole in the stratosphere and the potential effects of increased UV exposure on ecosystems and human health

(Newman et al., 2009). Although CFCs are reactive in the stratosphere, HF does not react photochemically in the troposphere. HF is inert at concentrations below 8.2 mg/m^3 (Cheng, 2017). The inert character of HF has been studied by Aiuppa et al. (2007). A decrease in the HF levels (from 900 µg/m^3 to 0.35 µg/m^3 in approximately 10 km), during short-range transport in a volcanic plume, because of atmospheric dilution. Owing to the high solubility of HF in water, rainfall could be the most important removal mechanism for HF (Lewandowska et al., 2013). However, the worldwide average wet deposition velocity for HF is 0 (US EPA, 1977). This could be because other gases, such as SO_4^{2-} or NH_4^+, compete for the water droplets (Lines, 1995). The US Environmental Protection Agency reported a residential time of 3.5 days in the troposphere for this compound (US EPA, 1977).

Regarding toxicology, HF is a highly corrosive gas and an irritant for the respiratory track at low concentrations (Bertolini, 1992). When it reaches the bloodstream, spreading across the tissues and bones, it can cause skeletal fluorosis (Ozsvath, 2009). HF intake could develop into haemorrhagic pulmonary oedema and death (Coleman et al., 2006). The exposure to low levels of HF can cause asthma-like symptoms (Bertolini et al., 1992; Lund et al., 2002). Because of its toxicity and harmful effects, the World Health Organization recommends that the concentration does not exceed 1.0 µg/m^3 to protect crops and cattle (WHO, 2000). There is no European or American legislation regarding the HF concentration in ambient air. Nonetheless, because it is difficult to achieve reliable measurements of HF, minimal studies on ambient air concentrations have been performed. Hance et al. (1997) reported a concentration of 220 ng/m^3 in California. Most studies are focused on industrial exposure through releases (Cheng, 2017). Measurements are commonly based on HF adsorption in impregnated filters to obtain an average concentration (IPCS, 1984; Jayarathne et al., 2014; Lewandowska et al., 2013; Okita et al., 1967; Sidhu S.S., 1979; Thompson et al., 2016). These methodologies cannot record concentration spikes that could last seconds to minutes (Hoke, 2002).

Among the industries that emit HF, phosphate fertilizer factories are of special interest (Semrau, 1957). The starting material for processing phosphates is phosphate rock (PR), with an average concentration of 13–14% of P and 3–4% of F (Ranjan and Ranjan, 2015). The production process generates phosphogypsum (PG) as a residue. Phosphoric acid can be produced by two different processes: heating the PR in an electric furnace (dry process) or treating the PR with sulphuric acid (wet process). The dry process is more efficient for removing F than the wet process. However, because of the high-energy cost required for PR heating, the wet process is more extensively used worldwide (Tayibi et al., 2009). For the wet process, the PG has to be defluorinated (Linero and Baker, 1978), and a large amount of PG is generated (5 tonnes of PG per tonne of PR treated). Various PG uses have been studied, including soil amendment (Abril et al., 2008; Enamorado et al., 2014) and building materials (Mazzilli and Saueia, 1999; Cuadri et al., 2004). However, only 15% of the global PG production is reprocessed, and 85% remains stockpiled (Al-Hwaiti et al., 2015). Consequently, PG management is a worldwide issue, considering that the annual production is estimated to be between 100 and 280 $\cdot 10^6$ tonnes (Parreira et al., 2003). Atmospheric pollution from a PG deposit could occur from HF emissions (Rutherford et al., 1994). However, most studies have focused on radioactivity (Köster et al., 1985; Bolivar et al., 2000; Santos et al., 2006). No studies on a real time assessment of HF in ambient air near a PG deposit have been published.

This study reports the HF concentrations in an urban area (Huelva, SW Spain) near a major PG deposit. Six sampling schemes using passive cartridges for three years and high-resolution HF measurements for two years were performed. Fugitive HF emissions from the PG deposit were assessed to achieve an emission factor for the industrial waste.

2. Methodology

2.1. The study area

Huelva (SW Spain), with a population of ca 145 000 (IEA, 2017), is located next to the estuary formed at the confluence of the Odiel and Tinto Rivers. The city has a Mediterranean climate characterised by dry and hot summers and temperate and rainy winters. The 20-year average rainfall is 490 mm. The wind direction is dominated by NW, SW, and NE winds (**Fig. 1**), owing to the breeze circulation adapted to the topography (NW-Odiel, NE-Tinto valleys) (Querol et al., 2002).

Since the 1960s, urban areas have been highly industrialized. Two industrial complexes are located near the population (**Fig. 1**). Historically, the industrial estates have focused on metallurgical processing of Pb-Zn-Cu ores north of the region. Currently, the main activities are a fertilizer company, Cu-smelter factory, and petroleum refinery. The PG deposit from the fertilizer company consists of open-air piles over a marshland on the banks of the Tinto River, and has maintained this location for nearly 40 years (**Fig. 1**). Originally, 20% of the produced PG was dumped directly into the estuary. This is still occurring in Morocco and Tunisia (El Zrelli et al., 2018). In 1986, a regional regulation for industrial wastes was promulgated, and the fertilizer company modified the disposal procedure. Various options were evaluated (e.g., transport the PG to an abandoned mine or use the PG as a soil amendment for crops or H_2SO_4 production). However, these processes were not economically advantageous. In 1997, with the support of the local government, the company created a pyramidal stack less than 25 m linked to a pond at surface level (evaporation pond) that would eliminate possible leakages into the estuary. The PG deposit is therefore a system with solid and liquid phases interconnected.

Currently, the PG deposit in Huelva covers ca. 1200 ha, and it is divided in four main zones. Two of them were restored in 1992 with a thin layer of natural soil and vegetation and were settled during the first 30 years of production. The two unrestored zones were established in 1997 and cover 395 ha (**Fig. 1**). They correspond to a PG pyramidal stack of 25 m covering 190 ha and an adjacent area of 204 ha, 53 ha forms the evaporation pond. In total, the PG deposit contains up to 1 Mm^3 of brines that are transported to the evaporation pond. When the brines evaporate, the evaporation pond surface is covered by layered salts that precipitate from the brines.

In 2010, the company was forbidden to continue dumping residue and was forced to restore the PG deposit. Because both zones are open-air piled, they emit gaseous pollutants as well as particles into the atmosphere.

In the past, the air quality in the city has been influenced by industrial plumes originating at the copper smelter during winding conditions (Querol et al., 2002). Several studies have found toxic elements, such as As, Se, Bi, Cu, Zn, and Pb from the copper smelter and P from the fertilizer industries (Alastuey et al., 2006; Fernández-Camacho et al., 2010). Another toxic element found in the particulate matter of the Huelva atmosphere was ^{238}U, which is related to PG (Borrego, 2007). Furthermore, the authors characterized fugitive particles derived from the PG deposit in the city of Huelva; thus, F^- in the soluble fraction is an indicator of the PG impact on air quality (Torres-Sánchez et al., 2019).

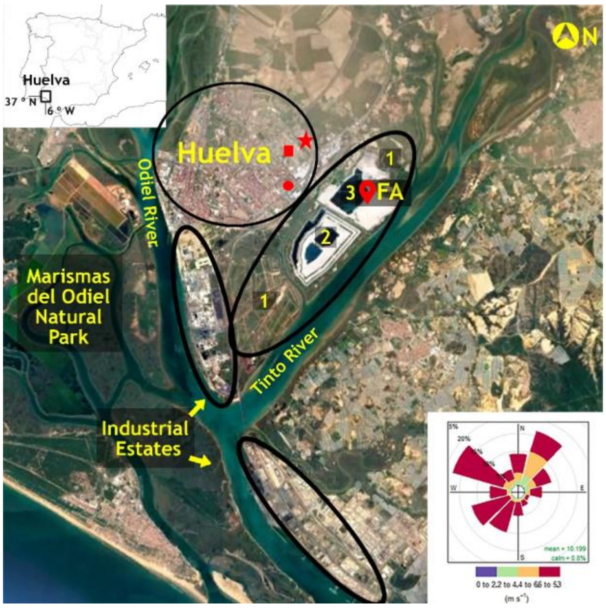

Fig. 1. Location of the city of Huelva, industrial estates and principal industrial states, and the PG deposit: (1) restored areas, (2) PG pyramidal stack, (3) PG evaporation pond, and (FA) PG sampling point. The location of the Los Rosales monitoring station is shown in the red circle. The location of the Campus monitoring station is shown in the red square. The wind rose represents the wind direction frequency (%) for the studied period with data obtained in the meteorological station (red star).

2.2. HF air concentrations

The HF concentrations in air were measured using two different methodologies: passive sampling and high resolution real-time sampling.

2.2.1. Passive sampling

Passive sampling was performed using specific Radiello® passive cartridges for HF. The study zone was divided into the PG evaporation pond and its surroundings (PG1; PG2; and PG3), the city (HU1; HU2; HU3; and HU4), and control zone (MTS), a rural monitoring station 54 km from the city (**Fig. 2**). The HU4 sampling point coincided with the location of the Campus monitoring station. Winter and summer experiments were performed from 2014 to 2017 with a total of 180 samples analysed. Each passive cartridge was sampled for two weeks. For the sample treatment, an eluent solution as added to the tube and stirred by a VORTEX for 2 minutes. Then the tube was let standing for 10 minutes. Afterwards the solution was directly analysed by IC

An ion analysis was performed using Methrom 883 Basic IC plus equipped with a column of polyvinyl alcohol with quaternary ammonium groups. An injection volume of 20 µl and mobile phase flow rate of 0.7 ml/min was stablished and calibration was performed with DIONEX standard solutions for anions and cations ranging from 0.05 to 200 mg/~~l~~L. The detection limit for F^- was 0.05 mg/~~l~~L.

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Fig. 2. Passive cartridge sampling points in the PG evaporation pond and surroundings: (1) PG1, (2) PG2, and (3) PG3; the city of Huelva: (4) HU1, (5) HU2, (6) HU3, and (7) HU4; and (8) control zone MTS.

2.2.2. High-resolution measurements

High-resolution real-time measurements were obtained using an HF on line cavity enhanced LASER absorption spectroscopy analyser (Los Gatos Research). The use of this technology has resulted in equipment that provides fast, sensitive and accurate measurements with no need of exhaustive calibration and minimal drift. Furthermore, the selectivity of the technique produces the exhibition of minimal cross-interferences owing to background gases (Gupta, 2012). The instrument was set up with a Teflon inlet of 6.35 mm diameter and a 3 l/min flow rate. Measurements were obtained every 100 s, and an hourly average was used in the data treatment in order to pair with meteorological data. The HF analyser performs a very sensitive laser measurement in the range of 0.01 µg/m^3 to 1.63 mg/m^3 with a response time of less than 20 µs.

The HF analyser ~~by~~ was located in the Campus del Carmen monitoring station of the air quality network of Andalusia (**Fig. 1**) from 01/01/2017 to 31/12/2017. From 01/05/2018 to 30/04/2019, the HF analyser was located in the Los Rosales monitoring station (**Fig. 1**), 0.5 km from the PG deposit.

2.3. Emission factor experiments

To calculate the emission rate of HF from the PG deposit, different experiments were conducted under laboratory and field conditions (Fig. 3).

Fig. 3. Emission factor experiments conducted for a) PG, b) layered salts, and c) brines.

2.3.1 PG and layered salts

The emission factors of HF from PG and layered salts were calculated under the field condition using Specific Radiello® passive cartridge samplers. The sampling was performed inside two methacrylate boxes (50 × 50 ×50 cm). One was placed on the PG surface, and the second was placed on the layered salt surface (**Fig. 3**), both in the PG evaporation pond. Six samples were collected each year, in winter and summer (two and four samples, respectively), each corresponding to a sampling time of two weeks. The sampling was performed for three years. In addition to the emission rate of HF, the emission rate of HCl was considered and studied simultaneously, as this compound is also present at a high concentration in the PG and layered salts. HF and HCl were extracted from the passive cartridges and analysed by ion chromatography.

2.3.2. Brines

To calculate the emission factors of HF and HCl from the brines, an emission experiment under laboratory conditions was conducted. An aliquot of 100 ml brine, collected in the PG pond in 2015, was heated in a Teflon sub-boiling still assembly (Savillex®) up to 70 °C with an infrared lamp for 16 h. The assembly consisted of two Teflon containers connected by a still Teflon elbow of Savillex® (Fig. 3). Five aliquots (A1, A2, A3, A4, and A5) were collected during the distillation experiment and analysed. The chemical properties (pH, ~~conductivity,~~ and redox potential) of the original sample and aliquots were measured. The anions were determined by ion chromatography

2.4. Statistical Analysis

Wind roses, polar plots, and polar frequency plots were created using the open-air R package (Carslaw and Ropkins, 2012). Meteorology data were provided by the Agencia Estatal de Meteorología of the Spanish Government. An hourly average concentration of HF and the meteorological data were employed for source assessments.

3. Results and discussion

3.1 HF air concentrations

The HF concentrations in ambient air were measured by 1) passive sampling during three years in the PG pond and nearby urban area and 2) high resolution in two sampling points of the city.

3.1.1. Passive sampling

The average concentrations in winter and summer using passive sampling are shown in **Fig. 4**. The concentrations of HF are higher in the PG evaporation pond and surroundings than those in the city of Huelva and the control zone for winter and summer.

For the PG evaporation pond and surroundings, seasonal differences in the concentrations were shown, higher values in summer than those in winter. The summer concentrations ranged from 3.1 to 20 μg/m^3 for HF. The winter concentrations, with a lower average, ranged from 0.8 to 31 μg/m^3 for HF. For HF, the highest winter concentration, 31 μg/m^3, was found in the centre of the evaporation pond (PG1).

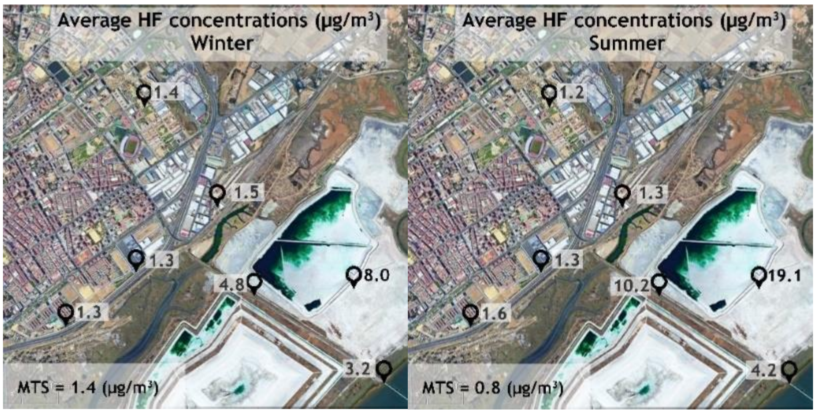

Fig. 4. Winter and summer average concentrations obtained by passive sampling in Pond 3 and the surroundings, the city of Huelva, and the rural control zone (MTS).

Compared to the PG evaporation pond and its surroundings, the concentrations in the city were lower than those at MTS. The average concentrations for HF in the winter and summer were similar (1.3 and 1.4 μg/m^3, respectively), with higher concentrations measured at the nearest point to the PG deposit (HU1). Compared to MTS, the concentrations in the city during summer were double the concentrations in the control zone. The difference in summer was owing to the evaporation of the brines from the evaporation pond in Huelva (Lieberman et al., 2019; Torres-Sánchez et al., 2020). In winter, similar average results for MTS and the city of Huelva were shown, representing the background value associated with seawater owing to the lack of PG in MTS (**Fig. 2 and 4**). High concentrations of HF were measured at sampling point HU1 (4.0 μg/m^3) and were associated with PG. Detailed maps of the passive measurements are shown in **SD Fig. 1-6**.

3.1.2 High resolution measurements

HF is chemically inert at low concentrations (Cheng et al., 2017), and the passive cartridge underestimates the high concentration excursions that last a few seconds or minutes (Hoke, 2002).

The result of the high resolution sampling during two years in the Campus monitoring station (2017) and Los Rosales monitoring station (2017 - 2018) show a background concentration of 0.04 µg/m^3, higher than the global background of 0.003 µg ~~3.0 ng~~/m^3 (Sloof et al., 1988). A threshold of 0.1 µg/m^3 was stablished to determine impacts. The impacts were recorded throughout the year. The winter season showed the highest number of days with recorded impacts (Fig. 5). Previously, in October, when the rainy season begins, rainfall dissolves the layered salts generating brines, providing higher HF availability (Lieberman et al., 2019; Torres-Sánchez et al., 2020.). The impacts recorded in the warm season in 2017 were more concentrated than those in winter (Fig. SD 7a), greater than 0.5 µg/m^3, and occasionally 1 µg/m^3. Warm season impacts are directly associated to the evaporation of brines from the PG pond coinciding with temperatures > 20 ° C and RH < 30% (Fig. 6) The cold season impacts reached 0.3 µg/m^3 in 2017 and 2018–2019 (Fig. SD 7b) and occurred mostly at night associated to temperatures < 20 ° C RH > 60% (Fig. 6). In addition, the impacts were related to the SSW-E wind directions, coinciding with the location of the PG deposit (Fig. 7). Other minor sources identified ~~was~~ were seawater (W) and the marshland at NW of the city.

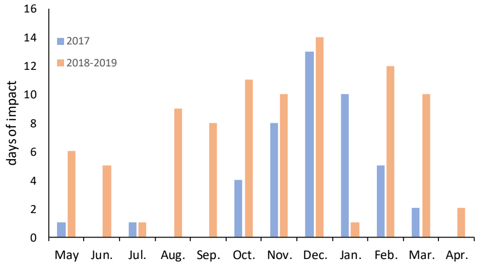

Fig. 5. Number of days with impacts per month during the sampling period.

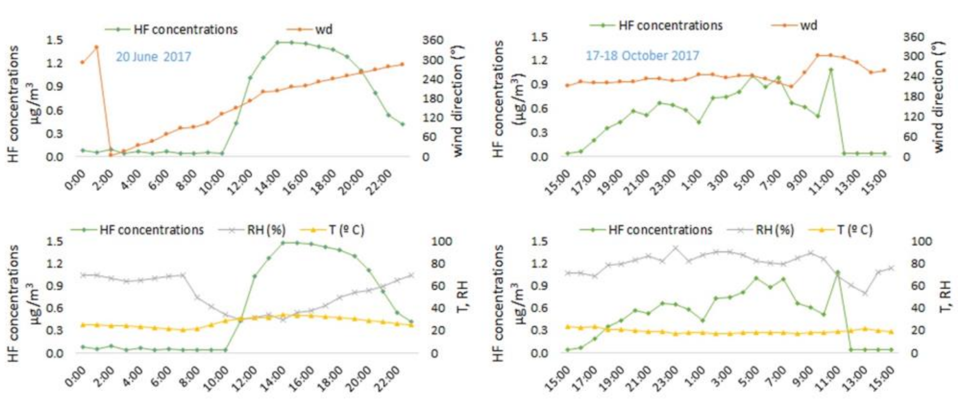

Fig. 6. Representation of typical impact days in the warm season (June 2017) and cold season (17-18 October 2017). Both impacts were recorded in the Campus monitoring station. Wd = wind direction, RH= relative humidity, T = temperature.

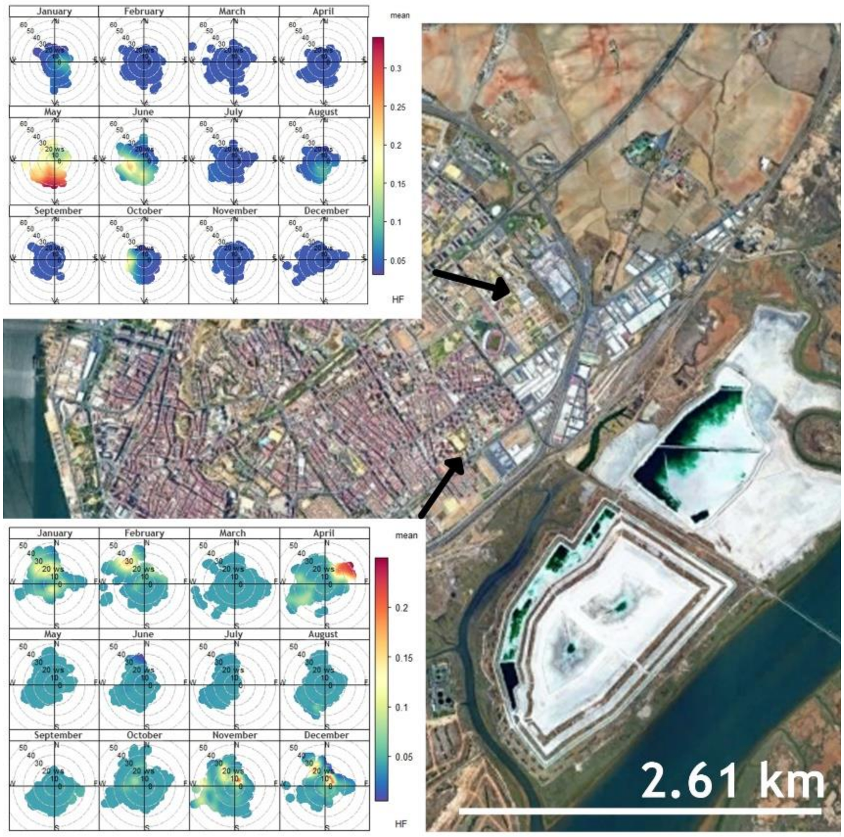

Fig. 7. Polar plots obtained from the Campus monitoring station (2017) and Los Rosales monitoring station (2018–2019).

The concentrations obtained with the HF analyser are lower than those obtained with the passive sampling (SD Fig. 8). Factors such as temperature and detection limit of the instrumentation can contribute to the difference. Detection limit for passive cartridges is 7 µg/m^3 for 24 hours' exposure, much higher than the detection limit of the HF analyser (0.01 µg/m^3). Regarding the experiments conducted in this work, results from summer experiments show a higher difference than those in winter (SD Fig. 8). Therefore, the passive sampling was performed to study the difference in concentrations regarding spatial variation of HF concentrations, while the high resolution sampling performed with the HF analyser was used to determine temporal trends and population exposure.

Considering the average volume of air inhaled by a resting adult, 0.54 m^3/h (Martins et al., 2015), an annual intake of 4.2 g and 2.2 g was recorded in the city for the 2017 and 2018–2019 sampling periods. A daily intake of 0.95 mg was recorded during the highest impact of 2017, higher than those reported for other European countries, such as the Netherlands (0.06 mg) or England (0.01–

0.04 mg) (WHO, 2000). Inhalation of low levels of hydrogen fluoride can cause irritation of the respiratory track (Bertolini, 1992) presenting symptoms that can be mistaken as asthma, such as coughing and choking (Lund et al., 2002)., Chronic exposure to the concentrations measured in this study, could be one of the environmental causes of the high asthma incidence in the city of Huelva, especially for children and teenagers, compared to the rest of the country (Pereira et al., 2007 and 2008). Therefore, the decrease on anthropogenic emissions of this pollutant should be a priority in order to protect population.

3.2. Emission factor of HF

The emission factors of HF were calculated using different experiments conducted in 1) PG and layered salts and 2) brines.

3.2.1. PG and layered salts

The average emission factors measured in methacrylate boxes in summer and winter are listed in **Table 1**. The HF emission was higher for PG in summer (190 µg/m^{3}ha day in winter) than that of the layered salt surface (160 µg/m^{3}ha day in winter). Conversely, the HCl emission was higher in the layered salt surface, especially for summer (4.3 mg/m^{3}ha day) than that of the PG surface (4.1 mg/m^{3}ha day). The HF emission was lower than the HCl emission for both sources in winter and summer (**Table 1.**).

Table 1.

Emission factors calculated by the passive sampling results for the PG and salt surfaces.

HF emission mg/m^{3}ha day	Summer			Winter		
	Average	Max	Min	Average	Max	Min
PG	0.19	0.39	0.07	0.07	0.59	0.02
Layered salt	0.16	0.28	0.03	0.05	0.09	0.01

Seasonal differences were shown. The emission factors were higher in summer than those in winter owing to the higher temperatures. During the summer, after full evaporation of the brines, the PG stack and PG evaporation pond showed an emission factor of 72 g/day of HF and 1.6 kg/day of HCl. In winter, the maximum emission by the solid phase of the PG deposit was lower, reaching 21 g/m^{3}day and 0.1 kg/m^{3}day of HF and HCl, respectively. The winter emission factor was lower than that of summer because the average temperatures were lower in winter (8 °C in winter, 24 °C in summer), and there were less PG and acid salt surfaces exposed to the atmosphere than those in summer owing the presence of brines.

3.2.2. Brines

The brine sample is acidic (pH 1.64) with a redox potential of 107.60 mV and contains high concentrations of F$^-$ (2.1 g/l). The results from the distillation experiment shows an evaporation of F^- in a 0.15% (Fig. 8). Simultaneously to the evaporation, precipitation of salts occurred. An acidic gel-like residue (pH < 0 and redox potential of 5.17 mV) remaining from the process contains 91 mg/~~l~~ L of F^-. Besides, F^- precipitates forming acid salts, which shows several minerals such as malladrite (Na_2SiF_6) (Lieberman et al., 2020).

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According to this experiment, the brines with an F^- concentration of 2.1 g/L exposed to high temperatures could emit HF to the atmosphere at a rate of 2.7 kg/ha day. Considering the evaporation of the 75% of the brines contained in the evaporation pond (1 Mm^3) during 15 days (Lieberman et al., 2020), a total emission of 2.5 tonnes of HF into the atmosphere would be expected. Owing to the fact that F^- concentrations in brines show~~s~~ a high variability depending on meteorological conditions such as evaporation and rainfall (Torres-Sánchez et al., 2020), the emission can vary from year to year.

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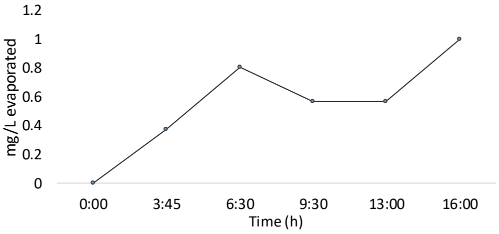

Fig 8: Mg/L~~l~~ of F^- concentration (mg(L) evaporated from the original sample regarding time of experiment

A summary scheme of the daily emission factor in the PG system of Huelva is shown in Fig. 9.

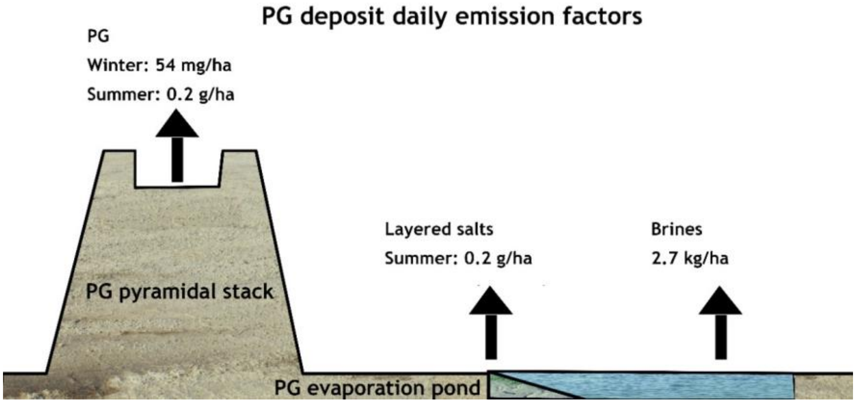

Fig. 9. Representation of the daily HF emissions factors calculated for the PG system from Huelva.

4. Conclusion

For the first time, a geochemical anomaly for HF in ambient air of an industrialized city (Huelva, SW Spain) was characterized, based on a PG deposit.

In the city, the impacts recorded during the warm season at noon were more concentrated and fewer than those recorded in winter, which were associated with fog events at night and in the early morning. The availability of F^- in brines, which is controlled by rainfall, is the main factor affecting the concentrations of HF in the city. A total ~~an~~ annual intake of fluoride through HF inhalation has been settled in 4.2 g and 2.2 g for 2017 and 2018-2019 respectively. The intake can vary depending on meteorological conditions. The chronic exposure to low concentrations of HF can be one of the environmental causes for the high incidence of asthmatic symptoms in the city of Huelva.

The PG deposit can emit HF through all its components (PG, layered salts, and brines). The highest emission factor associated with the brines, especially in summer, was 2.7 kg/ha day, which was higher than the emission factor of the PG and layered salts (0.2 kg/ha day).

The results of this study suggest that restoration of the PG deposit is required to prevent HF emissions, removing the brines and layered salts and covering the PG.

Acknowledgements

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This study was supported by the Autonomous Government of Andalusia and Ministry of Economy and Competitiveness of Spain (Project CGL2014-54637-P; BES-2015-071239).

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