



# Fluorine distribution in soil in the vicinity of an accidental spillage of hydrofluoric acid in Korea



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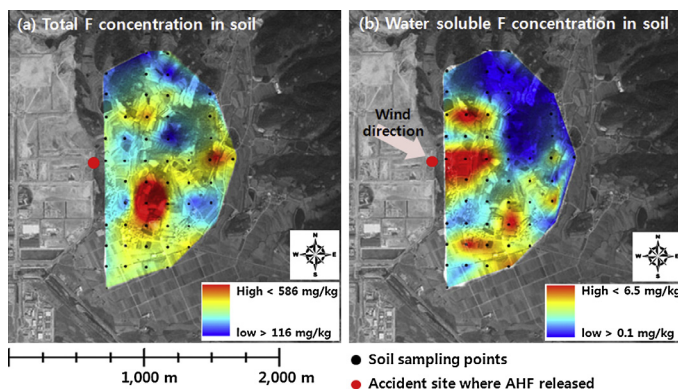
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## HIGHLIGHTS

- The status of F in soil in the vicinity of a spillage of HF in Korea was assessed.
- Soil was not considered to be contaminated with F based on its total concentration.
- Soluble F concentration in soil was significantly affected by the HF spillage.
- F content in rice was affected substantially due to soluble F concentration in soil.
- Soluble F concentration should be assessed when dealing with similar accidents.

## GRAPHICAL ABSTRACT



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## ABSTRACT

This study assessed the status of fluorine (F) in soil in the vicinity of a spillage of anhydrous hydrofluoric acid in Korea. Gaseous hydrogen fluoride dispersed was suspected to have contaminated the surrounding soil environment. Total and water soluble F concentrations in soil within a 1 km radius of the spillage were determined. Total F concentrations (mean =  $222 \pm 70.1 \text{ mg kg}^{-1}$ ) were lower than the Korean limit value (i.e.,  $400 \text{ mg kg}^{-1}$ ) and several reported measurements of background F concentrations in soils except for a single outlying case. Soluble F concentrations ranged from 0.111 to  $6.40 \text{ mg kg}^{-1}$  (mean =  $2.20 \pm 1.80 \text{ mg kg}^{-1}$ ). A negative correlation between the soluble F concentration of soil and distance from the spillage was observed. This indicates that the soluble F concentration has a crucial role in fractionating the F concentration arising from a 'non natural input' i.e., the spillage. The F content of rice samples seemed to be significantly influenced by the soluble F concentrations of soils. Rice samples collected from the control and affected areas contained  $41 \text{ mg kg}^{-1}$  and  $578 \text{ mg kg}^{-1}$  of total F, respectively.

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## 1. Introduction

Highly toxic anhydrous hydrofluoric acid (AHF) was accidentally released to the environment from a chemical plant located in Gumi City, Korea on September 27, 2012 (Lim and Lee, 2012;

Na et al., 2013). Approximately 8 tons of AHF was released during transfer from a transporting vehicle to a storage tank (Na et al., 2013). Hydrogen fluoride (HF) in the gas phase was transformed from the AHF at temperatures above  $19.5 \text{ }^\circ\text{C}$  and was rapidly dispersed into the atmosphere. HF gas can cause permanent damage to the eyes, skin, nose, throat, and bones. Once HF gas is inhaled or contact to the skin, it can induce calcium metabolic disorders via interaction with the calcium in tissues, causing cardiac arrest.

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Because of its high toxicity, five people directly exposed to HF gas died at the accident site and thousands of local citizens suffered from respiratory irritation problems (Park, 2013). In addition, HF gas dissolved in airborne moisture resulting in the formation of a corrosive hydrofluoric acid mist, which consequently killed plants in Bongsan-ri, the village closest to the accident site. The national government declared the area a 'special disaster zone', and collected and burned about 9100 tons of crops and other plants damaged by the HF gas and the hydrofluoric acid mist. About US \$33.4 million was paid in compensation for losses to citizens and local businesses (Park, 2013).

A number of similar accidents relating to HF or AHF release have occurred for last decades. For some examples, leakage of HF vapor (about 13–24 tons) into the atmosphere occurred in Marathon's petroleum refinery in Texas, US on October 30, 1987. Sixty-six people suffered from serious injuries and crops grown in a radius of 1.6 km were severely damaged. In CITGO Corpus Christi refinery located in Texas, a highly flammable hydrocarbon vapor spilled from the alkylation unit and it caused an explosion and a spillage of about 21 tons of HF gas on July 10, 2009. As increasing the use of chemical substances including HF and AHF rapidly, the possibility of an industrial accident has increased. The transferring amount of HF in Korea reaches 6776 tons per year (17th of 267 substances) according to the toxic release inventory (TRI) reported on 2011.

Although most of the HF gas transformed from the spilled AHF was dispersed into the atmosphere immediately after the accident, some may be remained and interacted with soil and groundwater (WHO, 2002). High vaporization property of HF makes its impact on the surrounding environment overlooked because people mainly pay attention to an immediate damage to human in the case of such industrial accident. However, the continuous exposure to residents through environmental media contaminated with fluorine (F) may induce health problems. Numerous local citizens have expressed anxiety regarding the chronic health effects (e.g., dental and skeletal fluorosis) associated with the accumulation of F in the environment (Cronin et al., 2000; An et al., 2012b). To meet with this requirement, Korean government recently revised the Toxic Chemicals Control Act (TCCA) and it goes into effect on January 1, 2015. Under the influence of this law, environmental impact assessment should be planned and performed when an industrial accident occurs on the basis of multimedia modeling and statistical analysis.

The objectives of this study were primarily to investigate the current status of F contamination in surrounding soils and the spatial distribution of soil F concentrations in the vicinity of the accident site. Specifically, the water soluble F concentration of soil was determined to assess the mobility and bioavailability of F. In addition, the possible effects of F contamination during the crop growing period were investigated. Crops were sampled at locations that were suspected to be affected by the accident and in a control area to confirm the effect of the accidental release of F. The investigation has provided information that can be used to assess the influence of the industrial accident on the accumulation of F in soil and the potential risk to human health and ecosystems.

## 2. Materials and methods

### 2.1. Site description and sample collection

Gumi City is located in southern Korea (latitude 36°; longitude 128°). The industrial complex is situated in the western part of the accident site, whereas agricultural activity (i.e., paddy and upland farming) is undertaken in the eastern part of the site. According to the Korea Meteorological Administration, a north western wind

(1.6 m s<sup>-1</sup>) was blowing when the accident occurred. Hence, soil samples were collected in the eastern part of the accident site within a radius of 1 km as shown in Fig. 1. Fifty-two top soil samples (i.e., from 0 to 30 cm depth) were taken from the affected area. To investigate the effect of the accident on the F content in rice (i.e., the crop mainly cultivated in the affected area), two rice samples were also collected. One was suspected to be contaminated due to its location close to the accident site, whereas the other was grown in the control area (Fig. 1).

### 2.2. Soil characterization

All soil samples were air-dried, disaggregated, and passed through a 2 mm nylon mesh sieve. Physicochemical properties including organic matter (OM) content, total phosphorus (T-P), cation exchange capacity (CEC), soil texture, pH, and the contents of 10 major elements (i.e., Si, Al, Fe, Ca, Na, K, Mg, Mn, Ti, and P) were analyzed in selected soil samples ( $n = 15$ ). The CEC was measured by using the ammonium acetate procedure (USEPA, 1986). Soil pH was measured in a water suspension using a solid liquid ratio of 1:5 (g:mL) (Sparks, 1996). The Walkley–Black procedure (Walkley and Black, 1934) was used to determine the OM content. The T-P was determined by a H<sub>2</sub>SO<sub>4</sub>–HClO<sub>4</sub> digestion method (Sparks, 1996). Three textural fractions (i.e., clay (0–2 μm), silt (2–50 μm), and sand (50–2000 μm)) were identified based on the soil texture triangle established by the U.S. Department of Agriculture (USDA). The total content of 10 major elements in soil were analyzed using a wavelength dispersive X-ray fluorescence spectrometer (PW2404, Phillips, Netherlands) after preparing a glass bead of 1:10 (sample to Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> weight ratio). The patterns of distribution of the physicochemical properties of the soil are presented in Table 1.

### 2.3. Certified reference materials

A variety of certified reference materials (CRMs) were used to assess the accuracy of the analytical procedures used in this study. Phosphate rock (NIST 694) containing 3.2% F and two types of slag (JK S10 (F content = 34.4%), BR 8flux (F content = 0.51%)) provided by the Brammer Standard Company were used as representatives of sample matrices with higher F concentrations. Granodiotite (GSP-2), mica schist (SDC-1), and green river shale (SGR-1) obtained from the U.S. Geological Survey (USGS) containing 3000, 600 ± 30, and 1960 ± 240 mg kg<sup>-1</sup> of F, respectively were also used.

### 2.4. F concentrations in soil

An analysis of total and water soluble F concentrations was undertaken for 52 soil samples. The total F concentration in soil was assessed by following the standard method of the Ministry of Korea (KMOE) (KMOE, 2009). In brief, 1 g soil and 5 g CaO was placed into a nickel pot and heated in a furnace at 500 °C for 5 h and then the temperature was increased to 800 °C. F ions were extracted from the residuals recovered in the previous ashing step by 50 mL HClO<sub>4</sub> + 25 mL deionized (DI) water with the aid of silver perchlorate (as an additive). F ions were separated from the complex matrix containing high concentrations of Al and Fe, which can hamper the F analysis, by a distillation process operated at 135 ± 2 °C. Fifty milliliters of distilled sample was mixed with 10 mL Zr-SPADNS solution (sodium-2-(parasulfophenylazo)-dihydroxy-3,6-naphthalene disulfonate with zirconyl acid) and analyzed using the spectrophotometer at 570 nm. Prior to sample preparation for the determination of the water soluble F concentration 2 g soil was shaken with 10 mL DI water for 2 h at room temperature. The suspension was centrifuged at approximately 4500g for 30 min and then filtered through a 0.45 μm GHP syringe filter (Pall,

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