INTRODUCTION

In Korea, chemical spill accidents are becoming more frequent as industrial and economic development progresses. Concern regarding chemical spills has increased in recent years, following several high-profile incidents, including a hydrofluoric acid spill in Gumi in 2012, a hydrochloric acid spill in Sangju during 2013, and a hydrofluoric acid spill in Cheongju in 2014 [1]. Following these accidents, the importance of effective hazardous chemical management was re-emphasized and the Chemicals Control Act (CCA) was implemented in January 2015. Based on risk-level, toxicity, and exposure probability, a total of 97 accident preparedness substances were assigned to be managed under the CCA. In the present study, we classified the substances into six categories (i.e., acid/metal-corrosive, inorganic, reactive, oxidative, organic, and flammable) based on physical hazards defined by the material safety data sheets (MSDS). The protocol to classify the substances used in this study is shown in Figure 1. The acid/metal-corrosive category includes hydrofluoric acid, sulfuric acid, hydrochloric acid, bromine, titanium tetrachloride, silicon tetrachloride, formic acid, and nitric acid.

On contact with water, acids will dissociate into protons and anions, and a major control of their toxicity is the pH decrease that occurs with increasing proton concentration. At high concentrations, acids also have strong corrosive characteristics. In the globally harmonized system (GHS) health hazard classification system, the eight acids/metal corrosive substances stated above are classified as skin corrosion/irritation and serious eye damage/irritation substances. Exposure of skin, eyes, mucous membrane, or the respiratory system to these acids can result in necrosis or burns. Hydrofluoric acid is extremely toxic and will penetrate tissue because of its highly corrosive properties [2]. Sulfuric acid is classified by the international agency for research on cancer (IARC) as a group I carcinogen (carcinogenic to humans) [3].

The toxicity of a spilled acid may vary with the physical and chemical properties of geomedia onto which it has spilled. The concentration of protons may decrease if the acid is neutralized during acid–substrate interaction with geomedia. Dissociated anions and cations may be dissolved from geomedia, causing additional toxicity concerns. It is therefore important to understand the fate, behavior, and biogeochemical reaction pathways of acids in the soil-groundwater environment to es-
In the present study, we focus on sulfuric acid and hydrofluoric acid, as these acids were designated as priority substances based on volumes produced/transported/used, past high-profile spill events, and their toxicity [4]. Existing studies on sulfuric and hydrofluoric acid spills into the subsurface environment, including soil-groundwater environments, are reviewed. The key biogeochemical reaction pathways of sulfuric and hydrofluoric acids in a variety of environmental settings are discussed, in addition to the probable environmental effects.

**CHARACTERISTICS OF SULFURIC AND HYDROFLUORIC ACIDS AS CONTAMINANTS OF SOIL AND GROUNDWATER**

**Physical and chemical properties**

The European Chemicals Agency (ECHA) database provides substance information, including physical and chemical properties, environmental fate and pathways, ecotoxicological information, and toxicological information. Similarly, the Hazardous Substances Data Bank (HSDB) is a toxicology database providing information on human exposure, industrial hygiene, emergency handling procedures, environmental fate, regulatory requirements, nanomaterials, and related areas. However, in the ECHA database, there is no information on the environmental fate of sulfuric and hydrofluoric acids, including their transformation behavior in air, water, and soil, hydrolysis, biodegradation, bioaccumulation, sorption, and desorption. In the HSDB, information on environmental fate is available for sulfuric acid, but not for hydrofluoric acid.

As the pKa value of sulfuric acid is 1.92 at 25°C [5], it is fully dissociated into protons and sulfate ions in water. Sulfuric acid is totally miscible in water. When water is present in the soil environment, the viscosity of a sulfuric acid plume decreases and its mobility increases [6,7]. As a sulfuric acid plume reaches the saturated zone, it migrates downward, as it has a higher density than groundwater, and its concentration decreases by dispersion and diffusion [7]. Henry’s law constant for sulfuric acid is $9.9 \times 10^{-15}$ atm-m$^3$/mole at 25°C [8]; therefore, it will not volatilize from a wet soil surface to the atmosphere. As the vapor pressure of sulfuric acid is $5.93 \times 10^{-5}$ mm Hg [9], it will not volatilize from dry soil surface to atmosphere.

The pKa value of hydrofluoric acid is 3.19, making it a weak acid that is partly miscible in water [10], and its mobility increases in the presence of water. The Henry’s law constant for sulfuric acid is $9.9 \times 10^{-15}$ atm-m$^3$/mole at 25°C [8]; therefore, it will not volatilize from a wet soil surface to the atmosphere. As the vapor pressure of sulfuric acid is $5.93 \times 10^{-5}$ mm Hg [9], it will not volatilize from dry soil surface to atmosphere.

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outlined in Table 1.

REVIEW OF ACID SPILL ACCIDENTS IN KOREA
AND THEIR IMPACTS ON THE ENVIRONMENT

A 2013 survey investigating acid spill incidents, undertaken by the Korean Ministry of Environment [15], showed that acid spill incidents account for 37% of all cases. Hydrochloric acid has the highest rate (42% of total acid spill incidents), followed by sulfuric acid (26%), hydrofluoric acid (12%), and nitric acid (7%) [15].

The Chemistry Safety Clearing-house (CSC) system (https://csc.me.go.kr) established by the Korean Ministry of Environment reports that 29 sulfuric acid spills and 8 hydrofluoric acid spills occurred between 2000 and 2018. The majority of spills were minor and contained within working areas. However, five significant spills affected the soil-groundwater environments. In 2014, one ton of sulfuric acid was spilled as a result of container damage at a construction site located in Namyang-ju, resulting in contamination of a nearby sump and soil. In 2017, 1.84 tons of sulfuric acid was spilled during a tanker truck accident in Bonghwa, Gyeongbuk Province, contaminating a nearby stream and soil. Generally, acid-contaminated soil and waste acid are removed, and residual acid in soil is neutralized by slaked lime, dry sand, or vermiculite, or is water-flushed. In 2015, a hydrofluoric-nitric acid mixture was spilled when a tank was damaged in Yeongcheon, Gyeongbuk Province, and it flowed into a nearby stream. In 2014, hydrofluoric acid was spilled from a storage tank as a result of staff error in Geumsan, Chungnam Province, entering the surrounding environment. The spilled acid was treated using slaked lime and the site was subjected to environmental monitoring of water, air, soil, and vegetation. The limited number of case studies means there is insufficient information to understand the effects of acid spills on soil-groundwater environments.

Several studies have investigated the environmental effects of a hydrofluoric acid spill in Gumi during 2012. An et al. [16] analyzed fluoride content in soil at the site and showed that fluoride distribution may represent the extent of the hydrofluoric acid spill, and that fluoride content in rice correlates with that in soil. Shin et al. [17] studied mineralogical changes in soil samples that have undergone sulfuric or hydrofluoric acid treatment by measuring pH, mineral composition, and cation dissolution. Hydrofluoric acid more effectively dissolves soil minerals than did sulfuric acid at the same normality. The dissolution of aluminosilicates was greater by hydrofluoric acid than by sulfuric acid, and the dissolution of metal (hydr)oxides and carbonates was greater by sulfuric acid. Reaction of the added acid with soil minerals occurs mainly by protonation on the surface of soil minerals and organic matter, and reactivity increased with decreasing soil particle size and higher cation exchange capacity (CEC). Lee et al. [18] treated a range of geo-media with sulfuric acid and analyzed their neutralization reactions, showing that the relative reactivity is as follows: sandstone (sedimentary rock) > granite > basalt > schist > montmorillonite > kaolinite. X-ray diffraction analyses showed the dissolution of feldspar in granite and mica in metamorphic rock. Peat (i.e., well-humidified organic matter) showed a higher acid-neutralization capacity than did humic acid. Based on these studies, it is expected that the acid consumption of soil increases with decreasing soil particle size, higher CEC, and higher quantities of aluminum minerals, feldspar, and mica. Under these conditions, acid toxicity may decrease.

Few studies have investigated acid spills in soil environments, and of those, most have focused on prolonged acid stresses caused by processes such as acid rain [19], acid mine drainage [20], and soil acidification [21]. Sulfuric acid dissolves cations (e.g., calcium, magnesium, and aluminum) from soil and carbonate minerals [7], and forms salts from the cations [14]. Small amounts of hydrofluoric acid persist in soil because of vapor pressure, and the fluoride content in soil has been used to estimate the range of influence of hydrofluoric acid spills. MacIntire et al. [22] analyzed residual fluoride content and hydrofluoric acid emissions in four different soil samples after adding hydrofluoric acid. The retention of fluoride increased with increasing quantities of aluminum in soil, because of aluminum silico-fluoride formation. Calcium and magnesium dissolution was decreased by adding hydrofluoric acid. Hydrofluoric acid can dissolve silica minerals [10,23]. Aluminum, Mg, and Fe were preferentially dissolved from mineral lattices by other inorganic acids, but in the presence of hydrofluoric acid the minerals were dissolved according to the elemental ratios in the lattices.

TOXICITY OF ACIDS IN THE SUBSURFACE ENVIRONMENT

The acute toxicity of six accident preparedness substances (sulfuric acid, nitric acid, formic acid, toluene, methanol, and methyl ethyl ketone) was measured with *Einsenia fetida* [24]. However, few studies have investigated acid toxicity changes caused by environmental factors. Wilson and Hyne [25] showed that acid–sulfate soil leachate inhibited early embryonic development in the Sydney Rock oyster, *Saccostrea commercialis*, and that toxicity increased by adding aluminum. In the case of sulfuric acid, Swarts et al. [26] tested the resistance...
of brook trout to sulfuric acid solution and water polluted by acid mine drainage, and showed that the resistance time of fish was shorter in mine-polluted water than in the sulfuric acid solution at the same pH. Ecotoxicity of acid mine drainage was also analyzed [27]; however, only acute and chronic toxicity of the acidic water and heavy metals was studied, not the effect of environmental factors.

The toxicity change of acids in soil environments can be indirectly determined by analyzing microbial community dynamics. Shin et al. [17] investigated the responses of microbial communities in three different soils to sulfuric or hydrofluoric acid, and to subsequent neutralization treatment. The abundance of Gram-negative β-Proteobacteria significantly decreased by adding acid, while spore-forming Gram-positive Bacilli increased. Neutralization treatments increased the abundance of Gram-negative γ-Proteobacteria. The microbial community dynamics in the hydrofluoric-acid-exposed soil samples were similar to those observed in response to acid addition and neutralization of the sulfuric-acid-exposed samples, except for the response time to acid shock. Hydrofluoric acid might have a higher neutralizing capacity than sulfuric acid; thus, it can be expected that the toxicity of hydrofluoric acid decreases more than that of sulfuric acid. Soil samples with smaller particle size, higher surface area, and higher CEC showed less change in microbial community dynamics, possibly caused by reaction of the acids with soil components.

The Korea Institute of Geoscience and Mineral Resources provides a geological information system (http://mgeo.kigam.re.kr) that includes information on bedrock, geological age, topography, and lithofacies. Based on this information and the study of Lee et al. [18], the main bedrock types underlying industrial complexes (ICs) in Korea have been identified and are listed in Table 2. As discussed in Section 3.1, it is expected that the toxicity of spilled acid may decrease at a faster rate in the ICs which have granite or sedimentary bedrock (e.g. Donghae, Pohang, Onsan–Ulsan–Hyundai Mipo, Daejeon, and Daegu ICs), than in the Gunsan, Daesan–Sihwa, and Gwanju ICs, which have schist or gneiss bedrock. The Donghae, Onsan–Ulsan–Hyundai Mipo, Yeosu, and Daejeon ICs have a relatively high drainage capacity, whereas the Pohang, Gunsan, and Daesan–Sihwa ICs have a lower drainage capacity. The Gwangju and Daegu ICs have medium drainage capacity. Since clay-rich soil has low infiltration rates and drainage capacity [28], and the Donghae, Gwanju, and Yeosu IC soils have relatively high clay contents, it is expected that infiltration and drainage rates would be lower in these soils than in the other ICs. Low infiltration and drainage capacity indicate that once a chemical spill occurs, dispersal will be minimal. More rigorous study is needed to fully understand the relationship between soil characteristics and chemical spills; however, we believe that the characteristics outlined here are important controls on the fate of spilled chemicals in the subsurface environment.

**CONCLUSIONS**

Advanced accident-prevention systems, and human and institutional infrastructure should be established to prevent chemical spills, including major industrial accidents. In the present study, sulfuric and hydrofluoric acids were selected from the accident preparedness substances list, and their physi-
cal, chemical, biological, and toxicological properties were investigated in terms of potential soil and groundwater contamination. Soil texture, CEC, the quantities of feldspar, mica, and aluminum minerals are important factors affecting the toxicity of acids in soil and groundwater environments. For a given normality, hydrofluoric acid may show lower toxicity than sulfuric acid. The findings of this study, particularly the importance of geological properties at spill sites, can contribute to the development of Korea-specific action guidelines for acid spills.

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REFERENCES

1. Korea Industrial Safety Association. Annual repetition of ‘tragedies from insensitivity toward safety’ Summary of major chemical spill cases in 2013 - a day after the fair again, requiring precaution. Saf. Technol. 2013; 192:8-12. (Korean)
2. World Health Organization/International Programme on Chemical Safety. Poisons Information Monograph 268. 1990: 1-25.
3. International Agency for Research on Cancer. Monographs on the evaluation of the carcinogenic risk of chemicals to man. Geneva: World Health Organization, International Agency for Research on Cancer. 1992-present: 54-206.
4. Shin D, Moon HS, Yoon YY, Yun U, Lee Y, Ha K, et al. The current status of strong acids production, consumption, and spill cases in Korea. J Soil Groundw Environ 2014; 19 (6): 6-12.
5. Organization for Economic Co-operation and Development. SIDS Initial assessment report for 11th SIAM (Jan 2001), Sulfuric Acid (CAS 7664-93-9). [cited 2016 Jul 20 ] Available from: http://www.inchem.org/documents/sids/sids/7664939.pdf.
6. Doucette WJ. Soil and sediment sorption coefficients. In: Handbook of Property Estimation Methods for Chemicals: Environmental and Health Sciences. Boca Raton : CRC Press LLC. 2000. p. 141-188.
7. Canada E. Tech Info for Problem Spills: Sulphuric acid & Oleum. 1984:
8. National Institute of Standards and Technology. NIST Chemistry WebBook. Sulfuric Acid (7664-93-9). NIST Standard Reference Database No. 69, Feb 2015 Release. [cited 2016 Jul 21]. Available from: http://webbook.nist.gov.
9. Daubert TE, Danner RP. Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation. New York: Hemisphere Pub Corp., c1989–2000
10. O’Neil MJ. The Merck Index - An Encyclopedia of Chemicals, Drugs, and Biologicals (13th ed.). Whitehouse Station: Merck and Co., Inc. 2001:
11. Brimblecombe P, Clegg SL. The solubility and behaviour of acid gases in the marine aerosol. J Atmos Chem 1988; 7 (1): 1-18.
12. US Department of Transportation. Emergency response guidebook. Washington, D.C. 2012.
13. World Health Organization. Fluorides (Environmental health criteria 227). Available from: http://www.inchem.org/documents/ehc/ehc/ehc227.htm
14. Agency for Toxic Substances and Disease Registry. Toxicological Profile for Sulfur Trioxide and Sulfuric Acid. [cited 2016 Jul 21] Available from: http://www.atsdr.cdc.gov/toxprofiles/index.asp.
15. National Institute of Environmental Research. A study on the method of environmental impact investigation by accident of acidic chemicals. 2013 (Korean)
16. An I, Lee HA, Lee J, Yoon HO. Fluorine distribution in soil in the vicinity of an accidental spillage of hydrofluoric acid in Korea. Chemosphere 2015; 119: 577-582.
17. Shin D, Lee Y, Park J, Moon HS, Hyun SP. Soil microbial community responses to acid exposure and neutralization treatment. J Environ Manage 2017; 204(Pr 1): 383-393.
18. Lee YH, Hyun SP, Moon HS, Shin DY, Lee EH, Yoo JY. Reaction characteristics of sulfuric acid from a chemical accident with geomedia from Korea, submitted. J Soil Groundw Environ 2018:
19. Pennanen T, Fritze H, Vanhala P, Kikkilä O, Neuvonen S, Bååth E. Structure of a microbial community in soil after prolonged addition of low levels of simulated acid rain. Appl Environ Microbiol 1998; 64 (6): 2173-2180.
20. Mills A, Mallory L. The community structure of sessile heterotrophic bacteria stressed by acid mine drainage. Microb Ecol 1987; 14 (3): 219-232.
21. Blagodatskaya EV, Anderson TH. Adaptive responses of soil microbial communities under experimental acid stress in controlled laboratory studies. Appl Soil Ecol 1999; 11 (2–3): 207-216.
22. Machnire WH, Sterges AJ, Shaw WM. Fate and effects of hydrofluoric acid added to four tennessee soils in 4-year lysimeter study. J Agric Food Chem 1955; 3 (9): 777-782.
23. Kline WE, Fogler HS. Dissolution of silicate minerals by hydrofluoric acid. Ind Eng Chem Fundamen 1981; 20 (2): 155-161.
24. Nam TH, Yun I, Choi J, Lee SE. Acute Toxicity on Eisenia fetida of Six Major Chemicals Accidentally Spilled into the Environment. Korean J Environ Biol 2017; 35 (2): 123-127.
25. Wilson SP, Hyne RV. Toxicity of acid-sulfate soil leachate and aluminum to embryos of the Sydney rock oyster. Ecotoxicol Environ Saf 1997; 37 (1): 30-36.
26. Swarts FA, Dunson WA, Wright JE. Genetic and environmental factors involved in increased resistance of brook trout to sulfuric acid solutions and mine acid polluted waters. Trans Am Fish Soc 1978; 107 (5): 651-677.
27. Jun TS, Park PJH, Choi HI, Yeon IJ. Acidic mine drainage analysis based on bioassay. J Korean Soc Environ Anal 2008; 11 (1): 29-38.
28. Groenendyk DG, Ferré TPA, Thorp KR, Rice AK. Hydrologic-process-based soil texture classifications for improved visualization of landscape function. PLoS One 2015; 10 (6): e0131299.
29. National Institute of Agricultural Science. Korean Soil Information System, Available from: http://soil.rda.go.kr/; 2018: