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Reconciling Environmental Safety and Economic Feasibility: A Review of Soil Fluorine Management Strategies in the Republic of Korea

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Abstract: Fluorine naturally occurs in soil and rocks; however, concerns arise when human activities or specific compounds increase its levels or bioavailability. South Korea faces challenges in managing soil fluorine contamination even though existing regulations based on total fluorine content are stricter than those in many developed countries. However, these regulations can be economically impractical because of Korea's naturally high background levels of fluorine in the soil. This study examined the international landscape of soil fluorine management and explored potential solutions that balance environmental protection with economic considerations. We propose a shift towards regulating specific and harmful fluorine compounds and prioritizing remediation based on bioavailability assessments. This approach can guide Korea towards a more effective and sustainable strategy for managing soil fluorine contamination.

Keywords: fluorine; contamination; bioavailability; soil quality standards

1. Introduction

Fluorine is the 13th most abundant element in the Earth's crust and has high reactivity and electronegativity [1,2]. The main minerals containing fluorine include fluorite (CaF_2), cryolite (Na_3ALF_6), apatite ($Ca_5(PO_4)_3(OH,F,Cl)$), topaz ($AL_2(SO_4)F_2$), amphibole species, and mica species. There is also a mineral called Griceite that is extremely rare but contains 73 % fluorine [3].

Natural fluorine, contained in minerals, is mostly insoluble in water, very stable with little chemical reactivity and virtually no effect on the human body or ecosystems. Fluorine in soil can enter the atmosphere or water bodies through natural pathways, such as weathering, volcanic activity, marine aerosol emissions, and anthropogenic pathways, including the production and application of phosphate fertilizers, brickmaking, coal combustion, and aluminum smelting [4].

Fluorine plays an important role in teeth and gum health when used in trace amounts. It prevents tooth dissolution and inhibits bacterial growth in the oral cavity, thereby preventing periodontal diseases or cavities, supplementing minerals in teeth, and promoting re-mineralization processes [5]. However, if water contaminated with fluorine is continuously and repeatedly consumed over a long period, white spots may occur on the teeth or the skeleton may become deformed. The fluorine limit for human consumption in drinking water is 1.5 ppm [6]; therefore, a water quality test for fluorine is necessary before groundwater can be used as drinking water.

In September 2023, the Korean government proposed revising soil fluorine management standards to the Ministry of Environment. The goal was to align these standards with international practices while ensuring the protection of public health and ecosystems. This revision could potentially lead to stricter regulations compared to some developed countries. The Ministry of Environment, in collaboration with the National Institute of Environmental Research, is currently conducting research to assess the need to adjust soil fluorine remediation standards and address any potential inconsistencies. However, this proposal has sparked debate among academics and soil

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remediation companies and raises concerns about relaxing regulations without a thorough scientific understanding of the specific risks posed by naturally occurring soil-bound fluorine in Korea. Their question—"Is easing soil fluorine contamination standards truly in the best interests of the Korean people?" serves as the core motivation of this study.

To address this question, we first reviewed the existing literature to explore the sources and behavior of fluorine in the soil. Subsequently, we summarized the current challenges surrounding soil fluorine management in Korea. Next, we examined the approaches adopted by various countries to regulate soil fluorine content. Finally, by drawing on this comprehensive analysis, we offer a perspective on an optional path for managing soil fluorine contamination in Korea.

2. Origin and Sources of Fluorine

2.1. Natural Sources

Although present in some rock-forming minerals such as fluorite and apatite, the most prevalent occurrence of fluorine within the Earth's lithosphere is in hydroxysilicate minerals. In these minerals, flourine replaces hydroxyl (OH) sites within the crystal lattice structure [4]. Fluorine is naturally derived from rock-forming minerals through weathering processes, wind-blown dust, marine-derived components, natural biomass burning, and volcanic activity.

2.1.1. Weathering

Weathering is a major natural pathway for fluorine in soil profiles [7,8]. Weathering is very complicated as it is controlled by a series of intricate processes, such as adsorption-desorption and dissolution–precipitation. As granite massifs break down, fluorine is readily released at the start of the weathering process [9]; however, in the uppermost layer of the weathered profile, there is a slight increase in fluorine content. While the fluorine in apatite remains stable, the fluorine originating from mica swiftly leaches out. If present, fluorite slowly dissolves due to the movement of water. Soil profiles typically exhibit a decrease in fluorine content as the distance from the original rock increases [10], with the majority of the fluorine in clastic sedimentary rocks found in their micaceous components [11]. Specifically, argillic limestone has an average fluorine content of 200 ppm, whereas its micaceous residue averages 800 ppm [11].

Fluorine-to-OH exchange in clay minerals depends on interactions with various factors, including the fluorine concentration, circulating water pH, and specific clay minerals [12]. For example, dioctahedral and trioctahedral illite can adsorb fluorine via OH–to–F replacements. Fluorine is readily adsorbed onto clay structures in acidic environments, whereas it readily desorbs in alkaline environments [12]. Rock weathering releases fluorine, some of which is adsorbed by clay in the surrounding water [13]. The overall soil fluorine content varies depending on the composition and fluorine levels of the parent rocks, with the average fluorine content ranging from 90 to 980 mg/kg [14]. Recent studies have reported fluorine content in soils worldwide of 321 mg/kg and 557 mg/kg in the continental crust [15,16].

Organic matter decomposition is a key source of fluorine in warm and humid climate soils. In acidic soils, fluorine can easily leach away, whereas in organic matter, it may accumulate and prevent leaching. Similarly, in permafrost regions, decomposing plants release fluorine into the water, exhibiting comparable behavior. Climate also plays an important role in fluorine mobility. The higher calcium content in arid regions restricts the movement of fluorine, while in semi-arid areas, such as India, surface and groundwater chemistry dictates fluorine migration. The dry season limits fluorine movement owing to high calcium and low dissolved solids. In contrast, the post-monsoon season has increased mobility owing to lower calcium and higher ionic strength in the water [17,18].

2.1.2. Volcanic Activity

Volcanic activity releases considerable amounts of fluorine into the environment, primarily as hydrogen fluoride (HF) gas [15,19]. Most fluorine release (>90 %) occurs during inactive periods (degassing) rather than during eruptions [20]. Volcanic ash traps and transports fluorine, impacting areas beyond the immediate eruption zone. The effect of fluorine-rich volcanic emissions on drinking water and food sources is a major concern. Fluorine dissolves from ash in water and soil, potentially exceeding safe limits for human and animal consumption [21,22]. Animals grazing on fluorine-contaminated vegetation can develop chronic fluorosis, a debilitating condition affecting the bones and teeth [23,24].

Historical accounts also detail the devastating impact of volcanic fluorine on livestock populations, such as the mass die-off following the 1783 to 1784 Laki eruption in Iceland which released an estimated 7 million tons of HF, causing widespread fluorosis and crop failure due to HF phytotoxicity [25]. Volcanic fluorine enrichment has also been documented in surface and groundwater sources [26] where volcanic ash leachate can contain high levels of soluble fluorine and contaminate water supplies. Human populations living near volcanoes often rely on fluorine-enriched water sources, leading to dental fluorosis [27].

Volcanoes have been suggested as the primary source of atmospheric fluorine, with estimates ranging from 0.06 to 8.6 million tons annually [2]. However, recent studies have questioned these estimates, suggesting that they may have been overestimated. Although volcanic fluorine emissions are considerable, they may not be as high as previously thought. In addition, although several researchers have suggested that we need to prepare for possible volcanic eruptions around the Mount Baekdu region in the near future [28], almost no marked volcanic activity has occurred on the Korean Peninsula during the last 1000 years.

2.1.3. Marine-Derived Components

Marine aerosol and spray contirbutions to atmospheric fluorine and its geochemical cycle have been debated. Friend [29] proposed a considerable marine flux of fluorine to the atmosphere, estimated at 0.4 to 1 Mt annually and second only to volcanic emissions. Taverner and Clark [2] suggested values between 1 and 2 Mt, while other authors proposed a lower flux of 20,000 t. The mean seawater fluorine content is 1.3 mg/L, with marine-derived fluorine considered crucial in the hydrogeochemical fluorine cycle. Sugawara [30] and Carpenter [31] suggested seawater is a major source of fluorine in global precipitation. Fluorine emissions from seawater include gaseous HF, with F/Cl ratios in precipitation being 10–1000 times higher than those in seawater [31,32]. However, Wilkniss and Bressan [33] found no preferential fluorine enrichment in marine aerosols and attributed elevated fluorine levels to dust content. Barnard and Nordstrom [34] found no marked difference in fluorine content between coastal and inland rainfall, suggesting anthropogenic fluorine sources in rainwater. De Angelis and Legrand [35] and Saether et al. [36] reported minimal marine-derived fluorine in ice and precipitation samples, respectively.

In contrast, Linder and Frysinger [37] and Lewandowska et al. [38] suggested that coastal rainfall and marine-derived aerosols are enriched in F-, correlating with the Na content. Some areas—such as in mid-Wales and coastal soils in Victoria, Australia—show fluorine enrichment, possibly from marine sources [39]. Overall, despite conflicting evidence, marine-derived fluorine contributions to the atmosphere appear to be relatively small compared to those of volcanic and anthropogenic sources. Although it may influence coastal rainfall, runoff, and soil chemistry, its impact is likely limited to areas within 10–20 km inland.

2.1.4. Other Minor Sources

Fluorine release into the atmosphere is not solely attributed to major natural sources, such as volcanic eruptions and marine-derived components; minor sources also play an important role. Wind-blown soil, as proposed by Weinstein [3], contributes substantially to atmospheric fluorine content. Approximately 6,000 tons of fluorine are added to the atmosphere annually in the USA owing to the wind-induced removal of ~30 million tons of soil. Analytical data from ice cores in Greenland[35] and the Alps[40] indicate that wind-blown dust originating from soil was the primary source of atmospherically deposited fluorine before 1930. Despite anthropogenic activities dominating fluorine sources from the 1930s to 1980, wind-blown dust still accounted for 18 ± 2 % of the fluorine in ice cores from the Alps between 1980 and 2000.

Biomass burning, whether from natural processes or human actions such as agricultural practices and accidental fires, also contributes to atmospheric fluorine release. Although most biomass fires are anthropogenic, natural fires—although less frequent—can destroy large areas of vegetation. De Angelis and Legrand [35] found elevated fluorine concentrations from biomass burning at high latitudes such as the Greenland ice caps, whereas Lewandowska et al. [38] identified biomass burning as a fluorine source in PM10 aerosols in the Baltic Sea area of Poland. Jayarathne et al. [41] investigated the extent of fluorine emissions from biomass burning and found considerable amounts of fine particulates (PM2.5) containing fluorine; however, the degree of fluorine release varied with plant type and geographic distribution. Additionally, these authors estimated an annual release of 76,000 tons of fluorine from biomass burning, which is comparable to that from coal combustion. These minor sources, although individually smaller than major sources, collectively contribute substantially to atmospheric fluorine levels, highlighting the diverse nature of fluorine emission sources and their environmental impacts.

2.2. Anthropogenic Sources

Fluorine is also derived from anthropogenic sources. Emissions from industries—such as semiconductor manufacturing, steel production, aluminum smelting, and the production of glass, bricks, phosphate fertilizers, and items through electroplating processes—are important anthropogenic contributors to soil fluorine contamination [42].

2.2.1. Coal Combustion

Coal combustion has long been recognized as a marked source of anthropogenic fluorine emissions [3]. Fluorine is considered one of the most hazardous substances released during coal combustion [43]. The average global fluorine content of coal is ~88 mg/kg [44], a substantial portion of which is released into the atmosphere during combustion. Chen et al. [45] suggest that nearly 80 % of the fluorine present in coal is released in both gaseous and particulate forms at temperatures around 800 °C, with complete release occurring at even higher temperatures of 1100–1200 °C [46].

Numerous studies have highlighted the environmental consequences of fluorine emissions from coal combustion, including pollution, plant damage, and fluorosis in animals and humans. For instance, emissions from coal-fired power stations have been identified as the largest individual source of atmospheric fluorine in Australia, resulting in documented impacts on vegetation [47,48]. Similarly, fluorosis has been observed in grazing animals near coal-fired power stations in the UK [48], and sheep near the Yatağan coal-fired power station in Turkey [49]. In Europe, studies have shown instances of fluorosis in wildlife, attributable to emissions from coal-fired power stations, particularly in regions such as the northwest Czech Republic [50,51]

As a major producer and consumer of coal, China faces acute challenges related to the fluorine emissions from coal combustion. Chinese coal contains an average fluorine content of 130 mg/kg, with certain regions such as Guizhou Province exhibiting notably higher concentrations [52,53]. The health effects of fluorine emissions are pronounced in China, where cases of fluorosis resulting from indoor coal combustion have been reported [52]. Dental and skeletal fluorosis have been documented in several Chinese provinces, affecting millions of people [54–56]. Exposure to fluorine is attributed to various sources, including burning coal in open stoves for food preservation and direct inhalation [52,54].

In addition to direct combustion emissions, coal waste is a considerable source of environmental fluorine contamination. Gao et al. [57] found high concentrations of fluorine in coal waste in China, with soils near waste sites exhibiting elevated levels compared with background levels. The spontaneous combustion of coal spoil heaps further contributes to atmospheric fluorine pollution, potentially accounting for a substantial portion of fluorine emissions in China [57]. While most fluorine is released into the atmosphere during combustion, some is retained in the fly ash collected from power plant emissions. Although fly ash typically contains relatively low fluorine concentrations, its disposal in lagoons raises concerns regarding potential groundwater contamination [58].

Overall, coal combustion has emerged as a major anthropogenic source of atmospheric fluorine with considerable environmental and health implications. Despite efforts to mitigate these emissions, the scale of fluorine release underscores the importance of continued research and regulatory measures to address this global challenge. In South Korea, currently 58 coal-fired power plants (36,868.7 MW) operate at 14 sites. As of 2022, coal-fired power generation will account for 39.7 % of the total power generation, making it the most notable source of electricity generation [59].

2.2.2. Brick and Ceramic Manufacturing

The production of bricks and ceramics, essential building materials, has a hidden environmental cost associated with fluorine emissions [3,60]. Both brick and ceramic manufacturing involve high-temperature roasting of clays and clay-rich rocks, typically exceeding 900 °C [61]. These clays naturally contain fluorine housed in minerals such as micas [62]. During the roasting process, a considerable portion of fluorine is released into the atmosphere, primarily as HF and silicon tetrafluoride (SiF_4) [60]. Studies by Bonvicini et al. [62] and Xie et al. [63] suggest that 80 % or more of the fluorine present in the initial clay can be volatilized during firing.

Fluorine emissions have become particularly concerning in developing countries experiencing rapid urbanization. The surge in demand for bricks often leads to the expansion of poorly regulated artisanal brickmaking practices [64,65]. These facilities, frequently located near urban areas [66], contribute notably to atmospheric fluorine pollution. Ahmed et al. [66] exemplified this problem in Peshawar, Pakistan, highlighting the presence of hundreds of brick kilns operating near the city. The resulting fluorine emissions were linked to the damage observed in fruit trees and substantial reductions in bean and maize crop yields [66,67].

Estimating the global impact of fluorine emissions from brickmaking requires consideration of the production volume and clay composition. Based on industry estimates [68], manufacturing 1,000 bricks requires ~3 tons of clay. Global brick production in 2010—concentrated in Asia with China, India, Pakistan, and Bangladesh leading the way—was estimated at 1,500 billion bricks, [69]. Assuming an average clay fluorine content of 500 mg/kg (a range of 450–800 mg/kg;[70],[63]), and considering the 80 % emission rate suggested by previous studies, we can estimate an annual release of ~1.8 million tons of fluorine from brick production alone. This figure indicates the contribution of coal combustion, traditionally considered a major source of anthropogenic atmospheric fluorine [70].

The ceramic industry, which also relies on high-temperature clay firing to produce tiles and other products, faces similar challenges regarding fluorine emissions. Research by Bonvicini et al. [62] in Italy suggests considerable fluorine emissions from ceramic tile production, although it likely represents only a portion of the impact of the global ceramic industry due to a lack of data on other ceramic products, such as sanitary ware. The information compiled from these references indicates that brick and ceramic manufacturing, particularly in developing countries, poses a considerable threat of fluorine air pollution which can have detrimental effects on vegetation and crop yields, as evidenced by a study in Pakistan [66]. The adoption of cleaner technologies in these industries is crucial for mitigating environmental impacts and protecting public health.

2.2.3. Fluorine Emissions from Aluminum Smelting

Aluminum production relies on the Hall–Héroult process, which releases fluorine into the atmosphere, and although there has been much progress in reducing fluorine emissions, continued monitoring and technological advancements are crucial for minimizing environmental and ecological impacts. This summary explores the challenges and advancements in the management of fluorine emissions from the aluminum smelting industry [71–74].

During the electrolytic process that produces aluminum from aluminum oxide, fluorine is released in both gaseous (mainly HF) and particulate forms [74]. In the mid-20th century, the rapid growth in aluminum production led to severe fluorine pollution near smelters, resulting in ecological damage and health issues in livestock and wildlife [75–77]. The industry has responded by adopting cleaner technologies, particularly wet scrubbing systems, which have considerably reduced emissions [78,79]. Estimates suggest that modern smelters can emit as little as 15–30 kg of fluorine per ton of aluminum produced, with scrubbing further reducing this to <300 g per ton [71].

Despite these advances, fluorine emissions from aluminum smelters can still impact surrounding ecosystems. Rodriguez et al. [80,81] and Talovskaya et al. [81] documented elevated fluorine concentrations in vegetation and snowmelt water near smelters, highlighting their potential for long-distance transport. Hufschmidt et al. [82] and Kierdorf et al. [83] identified skeletal and dental fluorosis in kangaroos near an Australian smelter, indicating the potential health risks to wildlife. Global aluminum production is expected to reached 70.6 million tons by 2023 [74], and assuming most smelters limit fluorine emissions to 0.5–0.6 kg/ton of aluminum [71], an estimated release of 35,300–42,400 tons of fluorine annually is expected. However, data from World Aluminum [74] suggest a slightly higher emission intensity, potentially leading to an annual release >45,000 tons [41].

2.2.4. Fluoride Release during Phosphate Fertilizer Production

This section discusses the environmental impact of fluoride released during the production of phosphoric acid—a key ingredient in fertilizers—which poses a potential environmental threat due to fluoride emissions.

Phosphoric acid is primarily manufactured from phosphate rock—a mineral rich in apatite—using wet and thermal processes [3,84]. The dominant method, accounting for 90 % of global fertilizer production, is the wet process, which utilizes sulfuric acid to extract the phosphoric acid from rock [85]. Phosphate rocks naturally contain large amounts of fluoride, typically between 2–4 % [86]. During the wet process, a large portion of this fluoride is converted to gaseous HF and SiF_4 [3]. Although modern plants have implemented scrubbing systems to capture >99 % of these fluoride-containing compounds [86], some emissions still occur. Studies on fertilizer plants in Brazil and Tunisia have highlighted this issue, with elevated fluoride concentrations reported in rainwater, groundwater, and nearby vegetation [87,88].

Another concern is the production of waste phosphogypsum, a byproduct of the wet process that contains calcium sulfate. Large quantities of phosphogypsum are stored in ponds, which can also contribute to fluoride contamination [84,86] as phosphogypsum contains fluoride, and the water in these ponds has high fluoride concentrations [3,85]. Leakage from ponds or windblown particles can further contribute to the dispersion of fluoride in the environment. Fluoride released from fertilizer production can travel through the air and contaminate the soil in surrounding areas. For example, studies in Turkey have identified elevated fluoride levels in soils near fertilizer production facilities, likely due to atmospheric transport from phosphogypsum storage [89].

Appropriate levels of fluoride are beneficial to dental health; however, excessive intake can lead to dental fluorosis, a condition that causes tooth discoloration and weakening. Tanouayi et al. [90] reported endemic dental fluorosis in a community near a phosphate mine in Togo, highlighting the potential health risks associated with fluoride contamination from mining activities. The global demand for phosphate rock for fertilizer production is considerable, with an estimated 263 million tons extracted in 2017 [91]. Assuming an average fluoride content of 3 % in the rock and 10–15 % volatilization during wet processing, a potential release of 0.694–1.04 million tons of fluoride could occur. However, these estimates only consider gaseous emissions from the acidification stage and do not account for particulates or releases from phosphogypsum storage. The existing literature suggests higher release figures, with Jayarthne et al. [41] estimating combined gaseous and particulate fluoride emissions of 28,000 tons annually.

Although modern scrubbing systems have markedly reduced gaseous emissions, concerns remain regarding particulate matter, phosphogypsum storage, and the overall impact on local ecosystems and human health. Further research and stricter regulations are required to ensure sustainable practices in the fertilizer industry, minimize fluoride release, and safeguard the environment and public health.

2.2.5. Fluorde Contamination by Various Industrial Sources

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In this section, various industrial activities that contribute to fluoride contamination of the environment are discussed.

Mining and waste management

Past and present fluorite mining activities pose a considerable threat in terms of fluoride contamination. Studies in the United Kingdom have documented extremely high soil and vegetation fluoride levels near abandoned fluorite mines and waste piles. Fuge and Andrews [92] reported soil fluoride concentrations >2 % near mines in northern England and Wales. Vegetation growing at these sites also accumulates high fluoride levels, with Cooke et al. [93] finding concentrations up to 1 % in plants from the Peak District of England. Elevated fluoride levels have been linked to dental fluorosis in grazing animals [94]. Similar environmental concerns exist around china-clay extraction sites in Cornwall, where fluoride-rich tailings contaminate nearby soils, plants, and waterways [92].

Fluoride in steel production

Fluorite is used as a flux in steelmaking, and during this process, fluoride is released as HF and SiF_4 gases [95]. Although a large portion of fluoride remains trapped in the slag by-product [96], historical accounts mention instances of fluoride-related environmental problems near steel plants, including animal fluorosis [97]. However, modern steelmaking practices are likely to result in minimal atmospheric fluoride emissions, owing to advancements in pollution control technologies [3].

Glass and other industries

While glass and enamel industries have historically contributed to environmental fluoride contamination through HF emissions during production [95], the implementation of efficient scrubbing systems in developed countries has notably reduced this [3]. Additionally, the relatively small amount of fluorite used in these industries—compared to steelmaking—minimizes the overall impact [98].

Fluorocarbons and emerging sources

Hydrofluoric acid is used in various industries including the production of fluorocarbons and semiconductors. Weinstein and Davidson [3] estimated that the semiconductor industry in the USA released ~32 tons of hydrofluoric acid annually during the 1990s. Furthermore, it is used as a catalyst in the petroleum industry, and Lewandowska et al. [38] suggested that fluoride(F<- will be deleted on our final manuscript) may be emitted from vehicle exhaust fumes because of its presence in fuels.

2.2.6. Agricultural Sources

Agricultural practices—such as fertilizer application, sewage sludge disposal, and the use of certain agrochemicals—contribute to environmental fluoride contamination. Although fluoride from fertilizers is generally not readily absorbed by plants, it can pose a threat to grazing animals and potentially contaminate groundwater. Stricter regulations and monitoring of fluoride levels in agricultural inputs and practices are crucial for minimizing environmental fluoride contamination and protecting animal and human health.

Fluoride in phosphate fertilizers

As discussed in the previous section, phosphate fertilizers—a major source of phosphorus for plants—are manufactured from phosphate rock that naturally contains fluoride. During fertilizer production, some fluoride is lost as gas, whereas others remain in the final product [86]. Studies in India suggest that between 3 and 75 % of the original fluoride in phosphate rock remains in fertilizers [99]. Furthermore, practices such as adding scrubbed HF gas back into the fertilizer during processing can further increase the fluoride content [42].

When applied to the soil, fluoride from fertilizers is strongly bound to clay minerals and oxides, thereby limiting its uptake by plants. However, long-term application of phosphate fertilizers can lead to soil fluoride accumulation [100,101], raising concerns about the potential fluoride intake by grazing animals through the ingestion of contaminated soil [42,101,102]. Considering the large amounts of phosphate rock used for fertilizer production [91] and the range of fluoride content in fertilizers (0.14–3.8 wt%), estimates suggest an annual addition of at least 2.3 million tons of fluoride to agricultural soils globally. Although fertilizer-derived fluoride is largely unavailable for plant uptake, it poses a potential threat to grazing animals through soil ingestion.

Groundwater contamination risks

In some cases, fluoride from fertilizers can migrate from soil into groundwater, particularly under alkaline conditions [103]. Studies in India and Pakistan have reported elevated fluoride levels in groundwater from areas with extensive use of phosphate fertilizers [104,105].

Other agricultural fluoride sources

The application of sewage sludge to agricultural land is another fluoride source. Sewage sludge can contain fluoride from various sources, including industrial wastewater, fluoridated drinking water, toothpaste, and medications [16]. Regulations typically limit the fluoride content of sludge applied to land (e.g., 200 mg/kg in the United Kingdom), but fluoride from sludge is likely to be more bioavailable than that from fertilizers [106].

Organofluorine-based agrochemicals, including insecticides, fungicides, and herbicides, are widely used in agriculture [107]. These compounds are persistent and resistant to degradation, raising concerns regarding their potential accumulation in soil and water resources [108]. Irrigation with fluorine-rich groundwater can also contribute to fluoride accumulation in plants, particularly via foliar uptake during overhead irrigation [109]. In animals, Botha et al. [110] suggested that fluoride-rich irrigation water may be partly responsible for livestock fluorosis in South Africa.

2.2.7. Urban Fluoride Emissions and Concerns

Many industrial activities that emit fluoride can considerably affect nearby urban areas. For example, artisanal brick production in Southeast Asia and aluminum smelting in Siberia are major sources of urban air pollution [65]. Coal and fuel combustion for domestic heating can also contribute to elevated fluoride levels in urban areas [38]. Vehicle emissions, potentially from fluoride-containing fuels and components, may also contribute [38]. The incineration of municipal solid waste releases considerable amounts of fluoride, primarily as HF. Although modern incinerators have emission control systems, the uncontrolled burning of waste can be a substantial source of HF and other fluoride-containing compounds in urban environments [3,111].

2.2.8. Ubiquity and Persistence of Fluorinated Organic Compounds

Many fluorinated organic compounds exist in the environment, most of which are not naturally produced [3]. These compounds are used in various applications including agriculture, pharmaceuticals, and manufacturing. However, a major concern is the presence of perfluorinated compounds (PFCs), particularly those with long carbon chains. PFCs are resistant to degradation and can accumulate in the environment and the biosphere [112]. Studies have shown their presence in humans and wildlife, with potential bioaccumulation and biomagnification effects [113]. PFC exposure has been linked to various health problems in humans including cancer, thyroid disorders, and immune system dysfunction [114,115]. Some long-chain PFCs are classified as persistent organic pollutants owing to their environmental persistence and harmful effects.

Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are a class of PFCs that are of major concern because of their potential toxicity [116,117]. While data are limited, estimates suggest that their environmental impact on overall fluoride levels may be negligible compared to that of natural sources [116,118]. This is likely because the strong carbon-fluorine bonds in PFAS make them resistant to degradation; however, their presence in the environment and potential health effects warrant continued research and regulation.

Chlorofluorocarbons and their replacements

Once widely used in refrigeration, air conditioning, fire extinguishers, and aerosol propellants, chlorofluorocarbons (CFCs) have been discovered to be a major cause of ozone depletion [119,120]. Their production was phased out and replaced with hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs), which do not harm the ozone layer [3]. HFCs, HCFCs, and other fluoride-containing gases—such as sulfur hexafluoride and nitrogen trifluoride—are potent greenhouse gases that contribute ~2 % to global greenhouse gas emissions [121,122].

Trifluoroacetic acid: A persistent byproduct

The degradation of certain fluoride-containing compounds, including HFCs and HCFCs, generates trifluoroacetic acid (TFA). TFA is also released from industrial production processes, the burning of fluoropolymers, and household waste incineration [3,119,123]. TFA is highly stable in the environment and readily forms salts. Although low in remote areas, TFA concentrations are elevated in urban and industrial areas [3,123]. TFA is not strongly bound to soil and may move into groundwater [124]. TFA accumulates in water bodies, such as salt lakes and oceans, due to evaporation; however, its presence in seawater at levels higher than those expected from recent sources suggests a potential natural source, possibly from hydrothermal vents [124].

2.2.9. Fluoride in Petroleum

Fluoride can occur in petroleum products because of its natural presence in crude oil or additives introduced during refining. This section explores the two main pathways for fluoride mobilization from petroleum sources—combustion and produced water [15]. Only the natural fluoride content of crude oil contributes to the additional anthropogenic mobilization of fluoride as that added during refining originates from phosphate rock or mined fluoride and is already accounted for in environmental budgets. These estimates suggest that the average fluoride content of crude oil is very low (0.01 mg/kg) [125]. Considering global oil consumption data, the annual release of fluorine from petroleum combustion is estimated to be 0.000058 Tg [126]. Therefore, petroleum combustion appears to have minimal impact on the overall atmospheric fluoride budget.

Oil and gas production often involve the extraction of large volumes of water and hydrocarbons. These "produced waters" can contain large amounts of fluoride, with concentrations ranging from undetectable levels to over 190 mg/L [127,128]. Global oil production has increased steadily, leading to a corresponding increase in the amount of water produced with estimates suggesting that the water-to-oil ratio is ~3:1 globally [129]. Based on this ratio and the average fluoride concentration of 4 mg/L in produced water, these calculations indicate a small but increasing flux of fluoride associated with oil production. This flux is estimated to have grown from 0.04 Tg/yr in the early 1980s to 0.07 Tg/yr in 2018 [130]. While both petroleum combustion and produced water contribute to fluoride mobilization, their combined impact appears to be relatively small compared to that of natural sources. However, proper management and treatment of produced water remains important to minimize potential environmental contamination from this source of fluoride.

3. Balancing Soil Fluorine Standards in Korea

The Soil Environment Conservation Act of 1995 is the primary legislation governing the management of soil pollution in Korea [131] and recognizes 24 soil pollutant types to preserve the soil environment. Fluorine was newly identified as a soil pollutant in 2002, along with organic pollutants, including trichloroethylene, tetrachloroethylene, and inorganic nickel. At that time, the Korean Ministry of Environment established selection criteria named Soil Worrisome Levels(SWL) considering that soil contamination mainly occurs as secondary pollution from air, water, or various waste materials[132].

Currently, SWL for for Fluorine in Korea are designated as 400 mg/kg for region I (croplands, rice paddies, residential areas, and schools) and region II (forests and playgrounds), and 800 mg/kg for region III (factories, gas stations, and roads) based on varying land uses (Table 1). If a larger amount of total fluorine than SWL is detected in the soil collected from a construction site, construction must be stopped and resumed only after thorough soil purification.

Table 1. Soil Worrisome Levels for fluorine in Korea (unit: mg/kg).

Region	Fluorine content	Site description
I	400	Croplands, rice paddies, orchards, residences, and schools.
II	400	Forests, salt farms, playgrounds, and religious sites.

III	800	Factories, gas stations, roads, and military sites.

The geology of Korea poses a major challenge as much of the bedrock is granite [133]—a type of igneous rock naturally abundant in fluorine-containing minerals, including feldspars and micas—leading to widespread fluoride occurrence. Lim et al. [134] evaluated fluoride distribution in soil samples collected from 82 nationwide locations in Korea. They found an aveage fluoride concentration of 204.5 mg/kg (ranging from 15.3 to 504.8 mg/kg), below the global average of 321 mg/kg. Regionally, they observed average concentrations of 229.6, 195.7, and 273.4 mg/kg in regions I, II, and III, respectively. Also, a nationwide soil survey conducted by the Korea Environment Corporation between 2012 and 2021 revealed widespread fluorine contamination exceeding SWL, even in areas with naturally occurring fluorine. The survey found that 1,337 (15.2%) of the 8,768 sampling points across Korea exceeded the SWL for Region I (400 mg/kg) (Table 1). The high soil remediation costs associated with fluoride pose a major financial burden, especially for housing development projects. The cost of fluoride-related soil purification from 2018 to 2022 amounted to 585.3 billion won (~427 million U.S. dollars) in the metropolitan area of the capital Seoul alone and is estimated to be larger nationwide. These excessive costs raise concerns about the economic feasibility of the current regulations.

While some experts argue that the current standards (400 mg/kg) are crucial for protecting public health and ecosystems by citing potential health risks associated with fluoride exposure, others argue for a more nuanced approach. They highlight that, under natural conditions, most fluorine in soil minerals is insoluble and exists in a very stable state. Research directly linking health problems to stabilized soil-based fluorine compounds is limited. Additionally, while the presence of fluorine can help identify its source in the soil, the total amount of fluorine does not necessarily reflect its bioavailability [135]. Nevertheless, research on the risks posed by fluoride to air and water quality is well documented [92,136,137], raising the question of whether it is appropriate to relax SWL for fluorine. Examining how other countries manage soil fluorine contamination can provide valuable insights into the establishment of effective and practical regulations in Korea. This may involve adjusting current standards or implementing targeted remediation strategies based on factors such as bioavailability and land use.

4. Global Variations in Soil Fluorine Regulations

Table 2 summarizes soil quality guidelines for fluorine management from various sources. Before directly comparing Korean soil fluorine contamination standards with those of other countries, it is crucial to consider the prominent variations in climatic conditions and geological characteristics across different regions. Our research indicates that only a limited number of countries (at least 12) in North America, Europe, and Asia currently regulate soil fluorine as a potential contaminant (Table 2). These countries have established diverse soil fluorine management standards based on factors such as climate, geology, and intended land use.

Soil quality guidelines for fluorine exhibit a wide range, with values varying from a minimum of 45 mg/kg for special areas with high biological value in Belgium to a maximum of 4,690 mg/kg for industrial areas in the same country (Table 2). This vast discrepancy highlights the influence of land use considerations when establishing soil fluorine management standards. Stricter limits are typically implemented for areas with potentially higher human exposure, such as residential or high ecological value areas.

Table 2. Global soil quality guidelines.

No.	Country	Soil quality guidelines		References
		Land use	Concentration (mg/kg)	
1	**Canada**	Agriculture	200	CCME [138]
		Agriculture / Residential (Alberta)	200	
		Residential / Parkland	400	

		Commercial / Industrial	2000	
2	Australia	Industrial waste (Victoria)	450	EPA, Victoria [139]
3	Switzerland	All regions	400	Slooff et al. [140]
4	The Netherlands	Regions with high clay content (>25 %)	500	
		Regions with very little or no clay content	175	
5	Austria	Agricultural / Residential (trigger value)	200	Carlon et al. [141]
		Agricultural / Residential (intervention value)	1000	
6	Belgium	Special areas with high biological value	45	
		Residential	3950	
		Industrial	4690	
7	The Czech Republic	Agricultural	500	
8	Italy	Residential / Public	100	
		Agricultural	2000	
9	Lithuania	Residential/ Recreational/ Agricultural	200	
10	Slovakia	Maximum allowable limits	1000	
		Value for decontamination measures	2000	
11	The United States (US)	Residential	469	USEPA [142]
12	Japan	All regions except agricultural	4000	Noh [132]

Canada—a country with a land area nearly 100 times larger than South Korea—enforces a stricter standard (200 mg/kg) for agricultural land compared to Korea's current regulations[138]. However, Canada demonstrates flexibility by allowing a higher limit (2,000 mg/kg) for industrial and commercial lands. Similarly, Japan has a seemingly lenient standard of 4,000 mg/kg for soil fluorine[132]. However, it is important to consider that Japan enforces stricter regulations (0.8 mg/L) for fluoride in drinking water, more stringent than that recommended by the World Health Organization (1.5 mg/L)[143]. This example emphasizes how countries might prioritize regulations based on their specific environmental conditions and potential exposure pathways. Beyond the total amount of soil fluorine, the key factor influencing its mobility, plant uptake, potential toxicity, and risk of groundwater contamination is the amount of water-soluble fluoride present [8]. This bioavailable fraction of soil fluorine is a more reliable indicator of potential environmental and human health risks.

The global trend in soil fluorine management reflects a shift towards regulating specific fluoride compounds with well-defined risks. This approach prioritizes managing artificially created or naturally occurring fluoride compounds that directly impact human health or ecosystems. The focus is on regulating these specific compounds, rather than the total soil fluorine content. The United States exemplifies this trend—with 50 states possessing diverse climatic and geological characteristics, each region has established independent soil pollution standards. However, a common theme across these various standards is regulating the content of specific fluorine compounds, such as PFAS, which are harmful to human health and ecosystems even at very low concentrations (section 2.2.8). Regulatory action is then taken through risk assessments when the concentration of these specific compounds exceeds established thresholds.

To summarize, soil fluorine management standards vary considerably across different countries due to diverse climatic conditions, geological makeup, and land-use considerations. While some countries might seem to have lenient total soil fluorine limits, they might compensate with stricter regulations for specific bioavailable fractions, water quality, or individual high-risk fluoride compounds. Understanding these nuances and the global shift towards regulating specific high-risk fluoride compounds is crucial for establishing effective soil fluorine management strategies in South Korea.

5. Conclusions

An analysis of Korean soil fluorine regulations highlights the complexities of balancing environmental protection with economic considerations. While some argue for maintaining strict standards for total soil fluorine content, international practices and geological realities suggest the need for a more nuanced approach. First, the naturally high background levels of fluorine in Korean soil, due to the abundance of granite, make adherence to rigid total content standards economically impractical. The considerable financial burden associated with remediating soil that exceeds these standards, even if naturally occurring, hinders development projects and raises concerns about the overall feasibility of these regulations. Second, global trends in soil fluorine management emphasize the regulation of specific fluorine compounds with proven risks. These typically involve artificially created compounds or those exhibiting high bioavailability—such as PFAS—which have detrimental health and ecosystem effects even at low concentrations. Considering the above, a potential solution for South Korea is to adopt a two-pronged strategy.

1. Refine Standards: Revise soil quality standards for fluorine to focus on regulating specific, well-defined fluorine compounds with documented environmental and health risks, similar to the approach taken for PFAS in the United States. This shift would prioritize managing these harmful compounds.

2. Bioavailability Assessments: Implementing assessments to determine the bioavailability of soil-bound fluoride. This prioritizes remediation efforts in areas with high levels of bioavailable fluoride, which pose a greater risk of plant uptake, groundwater contamination, and potential health effects.

These approaches would allow South Korea to manage soil fluorine contamination more effectively, balancing the need to safeguard public health and the environment from an economic perspective. This would prioritize resources to address the most important concerns while minimizing unnecessary economic burdens associated with naturally occurring, stable forms of fluorine in the soil.

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