



10 years long-term assessment on characterizing spatiotemporal trend and source apportionment of metal(loid)s in terrestrial soils along the west coast of South Korea



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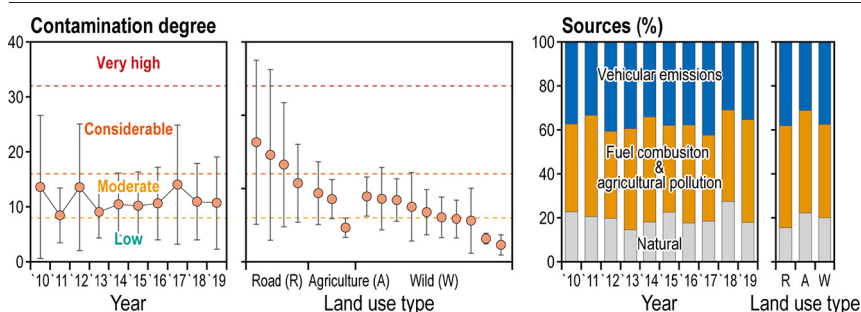
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HIGHLIGHTS

- Long-term (10 years) trends of metal(loid)s and sources in soil were investigated.
- Distribution of metal(loid)s was determined by land use type than temporal variation.
- Concentrations of metal(loid)s were great near roads than agricultural and wild land.
- Contamination factor was great in Pb, Zn, and Cr, with great potential risk for Cd.
- Vehicular emissions and agricultural pesticides were main sources of metal(loid)s.

GRAPHICAL ABSTRACT



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ABSTRACT

Long-term trends in the spatial distributions and sources of metal(loid)s in soils adjacent to the west coastal areas of South Korea have been systematically investigated for 10 years (2010–2019). Monitoring in 17 sites clearly showed site- and region-specific distributions, being associated with land use type (significant differences, as road > agriculture > wild) ($P < 0.05$), rather than temporal variation. The great concentrations of all metal(loid)s were found near Lake Shihwa (LS) and Geum River (GG), near the road, indicating that transportation activity was the main source of metal(loid)s contamination in soil. Especially, Cd (0.5 mg kg^{-1}), Hg (0.04 mg kg^{-1}), Pb (65 mg kg^{-1}), and Zn (184 mg kg^{-1}), related to the transportation activity near the road, showed twice greater than other land use types, on average. The concentration of metal(loid)s in each site and with the same land use type did not greatly vary over the years, with no significant annual difference ($P > 0.05$). The degree of metal(loid)s contamination compared to the background levels was identified in the order of Pb > Zn > Cr > Cu > As > Cd > Ni > Hg, with the contaminated hotspots mostly in LS or GG. The potential ecological risk was evidenced for Cd and Hg, but such a trend was temporally irregular over the years, indicating site-specificity. The sources of metal(loid)s were carefully determined as natural (20%), fuel combustion & agricultural pollution (43%), and vehicular emissions (37%) using the Positive Matrix Factorization model. The relative contribution of each source to contamination over the last decade was found to be similar, supporting that site-dependent lesser variation in metal(loid)s contamination in the coastal areas of South Korea. Overall, the distribution of metal(loid)s in the soil near the west coastal areas over the last decade largely depended on land use activities, and contamination degree was associated with non-point sources, such as transportation and fuel combustion.

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1. Introduction

Metal(loid)s contamination of soil, the skin of the earth, has long been a global environmental issue attracting the interest of academia and public attention. Metal(loid)s exist as parent materials in nature but also accumulated in soils through anthropogenic activities, including mining, discharge of wastewater and sewage, atmospheric depositions, use of fertilizer, fossil fuel combustion, and transportation activities (Cardarelli, 2018; Kumar and Gottesfeld, 2008; Niu et al., 2013; Pathak et al., 2013; Song and Gao, 2011; Zhang et al., 2020a). While some essential metals are necessary for the maintenance of life for living organisms, excess metal(loid)s have adverse effects. Due to the ubiquity, persistence, bioaccumulation, and toxicity of metal(loid)s, they are of considerable concern because of the risks they pose to human and animal health (Khan et al., 2013; Shi et al., 2019; Zhao et al., 2012). To improve the quality of soil for sustainable use, it is important to quantify the concentration, sources, and potential ecological risk of metal(loid)s (Yang et al., 2020).

The identification of sources and apportionment corresponding contributions of each metal(loid) in soils are important to design work plans that proactively reduce and control pollution in terrestrial and aquatic environments. In previous studies, the sources of metal(loid)s were qualitatively estimated through multivariate statistical methods, such as cluster analysis (CA), correlation analysis (CoA), principal component analysis (PCA), and geographic information systems (GIS) (Dong et al., 2018; Qu et al., 2013; Tian et al., 2020). However, the contribution of different pollutants could not be discriminated against when using these approaches because separate sources within the same region could not be quantified. In particular, the inability to discriminate the contribution of natural and anthropogenic sources within the same region could lead to large errors because metal(loid)s in soil originate from both natural and anthropogenic sources. Recently, receptor models have been applied to quantify source apportionment and to calculate the contribution of contaminants. Such models include PCA-multiple linear regressions (PCA-MLR), Positive Matrix Factorization (PMF), chemical mass balance (CMB), and edge analysis (UNMIX) (Li et al., 2003; Paatero and Tapper, 1994; Sahu et al., 2011; Shi et al., 2011). In general, PCA-MLR and PMF are primarily used because of their ability to process extensive monitoring data and no requirement for pre-measured source profiles. PMF tends to have better results in terms of interpretation and is considered to be the latest receptor model (Salim et al., 2019). In previous studies, successful classification of various sources such as agricultural, industrial, irrigation, mine, natural, road, sludge, and traffic sources using the PMF model has been reported (Cai et al., 2019; Huang et al., 2018; Liu et al., 2021; Zhang et al., 2020b).

The west coast of Korea has been subject to extensive industrialization and urbanization, with continued economic development. Rapid development has increased the emissions of contaminants originating from various sources, leading to intensive pressure on the environment and associated issues. Local environmental pollution has become a problem, resulting in many studies being conducted on various persistent toxic substances, including metal(loid)s, and associated toxicity in the soil in different regions of Korea adjoining the west coast (Hong et al., 2012; Kim et al., 2014, 2016; Naile et al., 2010, 2013; Liu et al., 2020). However, these studies only analyzed samples at a single investigation, with only one study on metal(loid). Liu et al. (2020) reported that concentrations of some metal(loid)s exceeded background levels, with moderate risk in some regions of the west coast; however, temporal variation in concentrations of metal(loid)s and major sources were not examined. In addition, studies performed in other regions of Korea were mainly conducted around mines or industrial complexes, and data on one survey or one-year survey was mainly reported (Ji et al., 2013; Kunhikrishnan et al., 2015; Kwon et al., 2013; Lee et al., 2019; Park and Choi, 2013; Yun et al., 2018). Long-term (10 years) study on metal(loid)s in soil has been very limited in South Korea.

The research hypothesis of the present study is that the concentrations of metal(loid)s in the soils of the west coast of Korea have varied over the past 10 years (2010–2019), and those are closely related to the surrounding land use activity. The specific objectives were to: (1) investigate the spatio-

temporal distribution of metal(loid)s in soils, (2) determine the distribution patterns of metal(loid)s associated with land use type, (3) assess potential ecological risk of metal(loid)s contamination, and (4) identify the sources of metal(loid)s.

2. Materials and methods

2.1. Sampling

Samples of surface soil (0–15 cm) were collected in May of 2010–2019 from different sites in Korea in the west coast region (Fig. 1). Sampling was performed at 13 sites (LS1, LS2, AS1, AS2, SG1, SG2, SD, ML, AM, GG1, GG2, YS1, and YS2) from 2010 to 2019 and 4 sites (DB, GS, HP, and JD) from 2014 to 2019. Land use types adjacent to the sampling sites were classified as a road, agriculture, and wild. Samples were packed in plastic zipper bags and were air-dried at room temperature in the laboratory. Air-dried soil samples were passed through a nylon sieve (100 mesh) after removing debris and were homogenized for subsequent analyses.

2.2. Sample analyses

Metal(loid)s in soil were analyzed following the method of Liu et al. (2020), with minor modifications. The samples were digested with an acid mixture consisting of 75% nitric acid (HNO₃, Sigma Aldrich, Saint Louis, MO) and 25% perchloric acid (HClO₄, Sigma Aldrich) on a hot plate for Cd, Pb, Cu, Zn, Cr, and Ni. Samples were evaporated, and a 7 mL acid mixture [71% hydrofluoric acid (HF, Sigma Aldrich) and 29% HClO₄] was added. The residues were then deliquesced and diluted using 1% nitric acid. Samples were determined by an Elan 6100 inductively coupled plasma with a mass spectrometer (ICP-MS) (Perkin-Elmer SCIEX, Norwalk, CT) and Optima 7300DV ICP-optical emission spectrometer (ICP-OES) (Perkin-Elmer SCIEX). For, As and Hg, samples were acidified with an acid mixture containing 5:1 v/v of 1 M hydrochloric acid (HCl, Sigma Aldrich) and 10% HNO₃. After centrifuging the residues, As was analyzed using ICP-MS, and Hg was determined by FIMS 100 mercury analysis system (Perkin-Elmer SCIEX). The certified reference material (GBW07403) was analyzed, and recovery showed a generally acceptable range from 82.3% to 115.9% (mean = 95.9%). Soil pH was determined using an Orion Star A211 pH meter (Thermo Scientific, Waltham, MA) at a soil-water ratio of 1:1, following an existing method (Eckert and Sims, 1995). Total organic carbon (TOC) was analyzed using an elemental analyzer (Flash EA1112, Thermo Scientific, Milan, Italy) after decalcification with 10% HCl (Lee et al., 2021).

2.3. Soil contamination and potential ecological risk assessment

Soil contamination was evaluated using contamination factor (C_f) and contamination degree (C_d) for single- and multi-element contamination, respectively. C_f was calculated following Eq. (1) (Håkanson, 1980):

$$C_f = \frac{C_i}{C_b} \quad (1)$$

where C_i is the concentration of each metal(loid) in soil, and C_b is the background value of each metal(loid) in natural soil. Data on C_b were obtained from previously published reports on soil in Korea (Kim and Kim, 1999; Yoon et al., 2009). C_f values were classified as: low contamination ($C_f < 1$), moderate contamination ($1 \leq C_f < 3$), considerable contamination ($3 \leq C_f < 6$), and very high contamination ($C_f \geq 6$). C_d was expressed as shown in Eq. (2) (Håkanson, 1980):

$$C_d = \sum_i^n C_f \quad (2)$$

where C_d is the sum of C_f . C_d values were separated into four classifications: low contamination ($C_d < 8$), moderate contamination ($8 \leq C_d < 16$), considerable contamination ($16 \leq C_d < 32$), and very high contamination

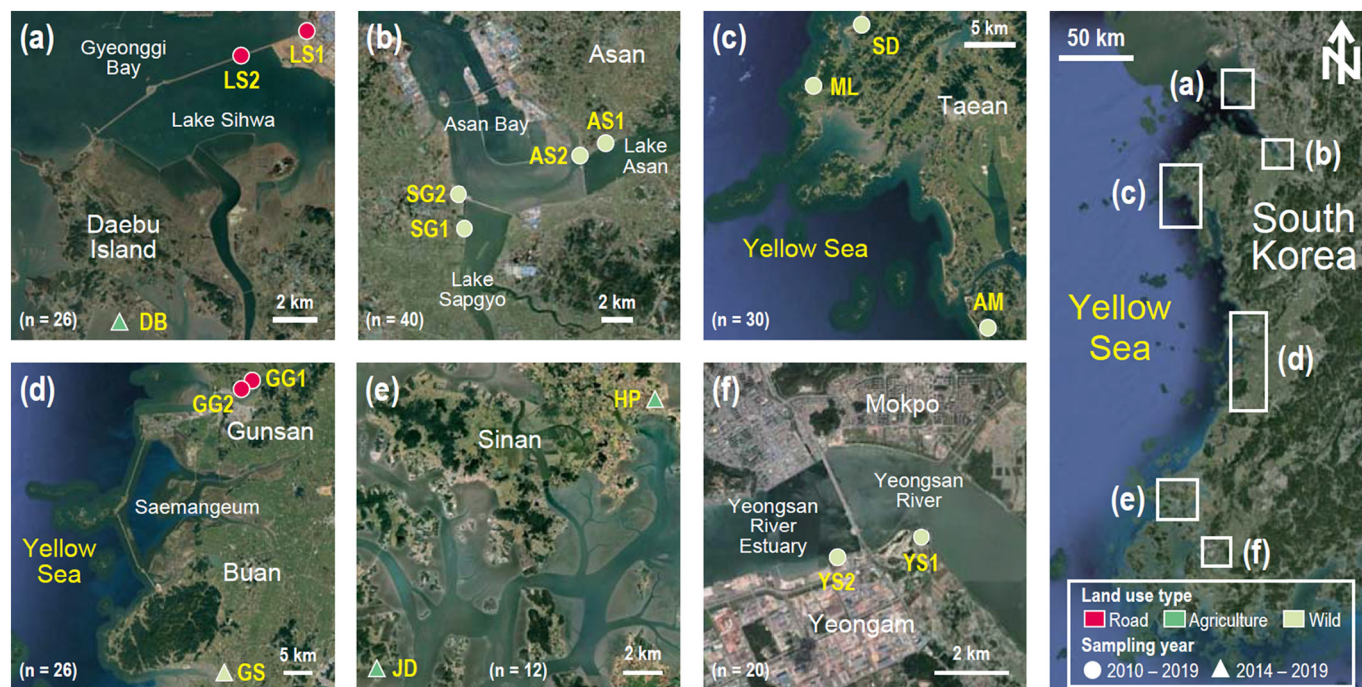


Fig. 1. Map showing the sampling sites for long-term soil monitoring (2010–2019) in the west coast region of Korea. Panels: (a) Lake Sihwa and Daebu Island, (b) Lake Sapgyo and Asan, (c) Tae'an, (d) Gunsan and Buan, (e) Sinan, and (f) Yeongsan River.

($C_d \geq 32$). The potential ecological risk was evaluated using potential ecological risk factor (E_i) and potential ecological risk index (RI) for single- and multi-element risk, respectively. E_i was calculated using Eq. (3) (Håkanson, 1980):

$$E_i = T_i \times C_f \quad (3)$$

where T_i is the toxic response factor of metals proposed by Håkanson, 1980. T_i values were allocated as 10, 30, 2, 5, 40, 5, 5, and 1 for As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn, respectively. E_i levels were classified as: low ($E_i < 40$), moderate ($40 \leq E_i < 80$), considerable ($80 \leq E_i < 160$), high ($160 \leq E_i < 320$), and very high ($E_i \geq 320$). RI was expressed as Eq. (4) (Håkanson, 1980):

$$RI = \sum_i^n E_i \quad (4)$$

where RI is the sum of E_i . RI was separated into four classifications: low ($RI < 150$), moderate ($150 \leq RI < 300$), considerable ($300 \leq RI < 600$), and very high ($RI \geq 600$).

2.4. Positive matrix factorization receptor modeling

The PMF model Ver. 5.0 of the U.S. Environmental Protection Agency model was employed to allocate the sources of the metal (loid)s (Norris et al., 2014). PMF modeling was performed following the previously described method (Yoon et al., 2020). The model was run 20 times for the best optional solution, and three factors (2, 3, and 4) were performed. The best number of factors was determined as the Q_{True}/Q_{Exp} value based on runs of 2–4 factors. The resulting slope from PMF modeling ranged from 0.54 to 1.08, with a mean R^2 value (0.72), except for Cd, indicating reliable results. Displacement (DISP) and Bootstrap (BS) were employed to test random errors and to explore rotational ambiguity. DISP outputs were 0, indicating no errors. The mapping value of BS was >80 , indicating that uncertainties could be interpreted.

2.5. Data analyses

Statistical analyses were performed using SPSS 25.0 software (SPSS INC., Chicago, IL) and SigmaPlot 13.0 (SPSS inc.). Simple linear regression analysis was used to explore the significant relationship between the concentrations of each metal(loid) and year. The Kruskal-Wallis test was used to evaluate differences in concentrations of metal(loid)s with respect to year and land use type. The Mann-Whitney test with Bonferroni correction was then applied as a post-hoc analysis. Spearman correlation analysis was performed to assess significance between metal(loid)s and environmental parameters (pH and TOC), due to the non-normality of the data.

3. Results and discussion

3.1. Spatio-temporal distribution of metal(loid)s

The spatial and temporal distributions of metal(loid)s in soil along the west coast region of Korea over the last 10 years (2010–2019) varied depending on sites and metal(loid), rather than trends in temporal distribution (Figs. 2, S1, and Table 1). The concentrations of As and Cu were greater at Geum River, whereas concentrations of Cd, Pb, and Zn were greater at Lake Sihwa. In addition, concentrations of Cr, Hg, and Ni were greater at both Geum River and Lake Sihwa. The sites with relatively high concentrations of metal(loid)s showed the same surrounding land use type (road; GG and LS). In previous studies, metals such as Zn, Cd, Cr, Cu, Ni, Pb, and Hg are known to be related to tire, brake wear, and road wear (Adachi and Yoshiaki, 2004; Hjortenkrans et al., 2007; Ozaki et al., 2004; Schauer et al., 2006). Thus, relatively high concentrations of metals in Sites GG and LS were affected by transportation activity on nearby roads, indicating that the contamination of metal(loid)s in the soil was closely associated with adjacent land use types of sampling sites. In addition, the concentrations of all metal(loid)s were significantly correlated with TOC ($P < 0.01$), while Cr, Hg, and Ni were also significantly correlated with soil pH ($P < 0.01$) (Table S1). Thus, local environmental parameters cause differences in the distribution of metal(loid)s (Ennaji et al., 2020; Yin et al., 2002). Overall, the concentrations of metal(loid)s in soil from

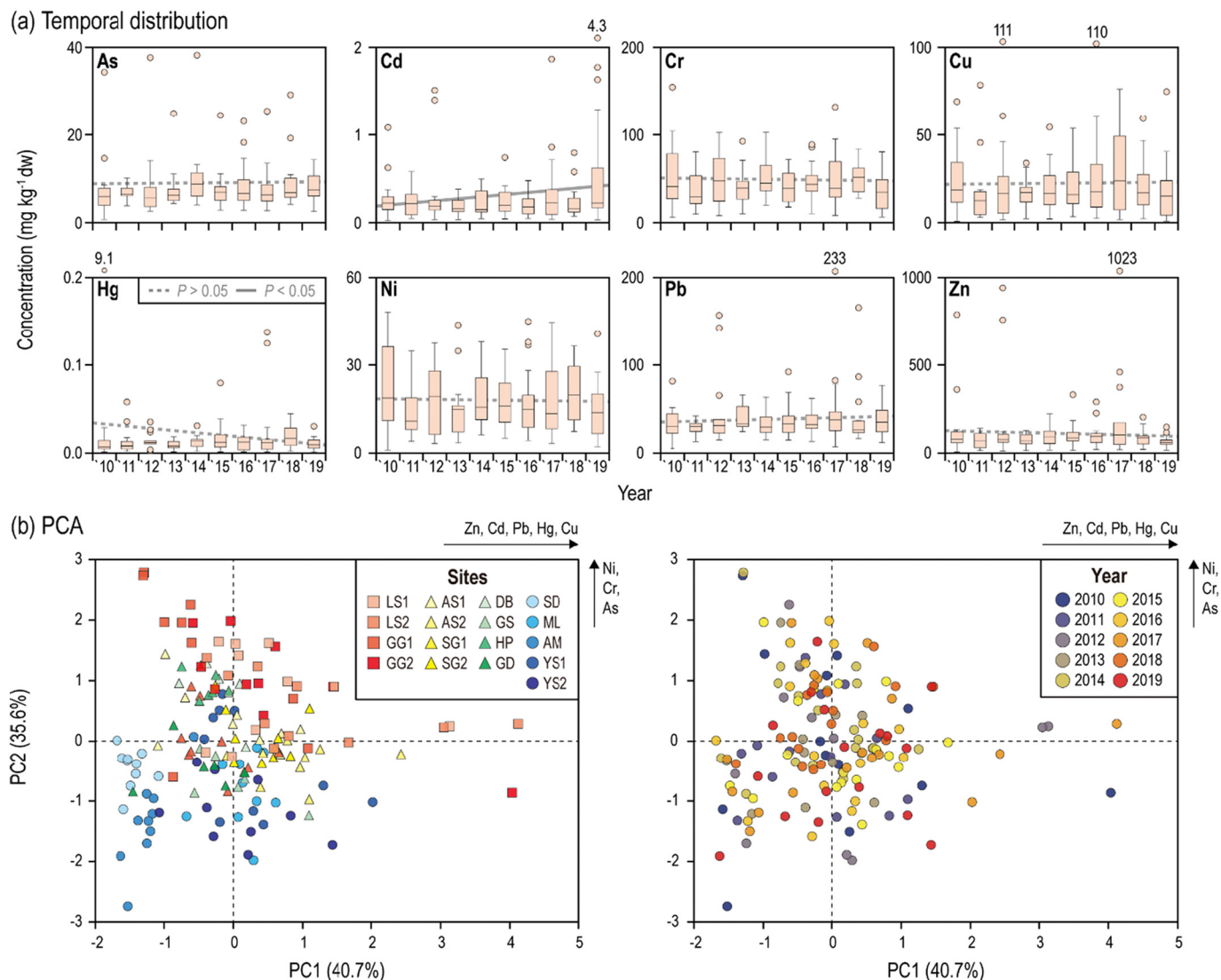


Fig. 2. (a) Temporal distribution of metal(loid)s in soil from the west coast region of Korea from 2010 to 2019. The solid line indicates a significant relationship ($P < 0.05$), and the dotted line indicates a non-significant relationship ($P > 0.05$). (b) Principal component analysis (PCA) ordination of metal(loid)s in the soil from the west coast region.

the west coast region showed differences depending on region, suggesting an association with land use type and environmental parameters.

An increasing or decreasing trend in the entire west coast region of metal(loid)s was not found over the past 10 years (2010–2019) (Figs. 2, S1, and Table 1), with no significant annual difference ($P > 0.05$) (Table S2). The significant increasing trend was only found for Cd ($P < 0.05$), whereas other metal(loid)s showed no significant differences ($P > 0.05$). However, the annual mean concentrations of Cd were similar, and the increasing trend was not significant when the highest concentration in 2019 was excluded ($P > 0.05$). These results indicated that the concentration of metal(loid)s in the soil of the west coast region minimally changed over time. Although there was no trend in the entire region, metal(loid)s showed site-specific temporal distributions over the last 10 years (2010–2019). A significant increase or decrease trend was observed for all metal(loid)s at some sites ($P < 0.05$), except for Ni. However, significant correlations ($P < 0.05$) with time (years) were only found for 7.3% of all metal(loid)s and sites, with no tendency. Thus, trends in changing the concentration of metal(loid)s over time were not constant. In the national pollutant release and transfer register system in Korea, the emission of metal(loid)s to soil was reported as zero from 2008 to 2019 (MOE, 2021). These results indicated that metal(loid)s contamination in the soil was mainly affected by non-point sources, such as transportation activity,

stormwater runoff, possibly resulting in similar concentration levels over the last decade. Consequently, concentrations of metal(loid)s in soils in the west coast region over the past 10 years were similar, and the site- and metal-specific trends were inferred to be controlled by non-point sources.

3.2. Distribution of metal(loid)s in relation to land use types

The concentrations of metal(loid)s and other persistent toxic substances have been reported to be affected by the surrounding land use type (Fig. 3) (Guan et al., 2018; Liu et al., 2020; Yoon et al., 2009). The distribution of metal(loid)s in the present study also clearly differed in relation to the three land use types (agriculture, wild, and road). All metal(loid)s in the soil near roads had higher concentrations compared to soil in the agricultural and wildland. The mean concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn in soil near roads were 14 mg kg⁻¹, 0.5 mg kg⁻¹, 69 mg kg⁻¹, 39 mg kg⁻¹, 0.04 mg kg⁻¹, 29 mg kg⁻¹, 65 mg kg⁻¹, and 184 mg kg⁻¹, respectively. These concentrations were 1.3 to 3.2 times higher (mean 2.2 times) compared to those of agricultural and wildland. The concentrations of As, Cd, Cu, Pb, and Zn near roads were significantly higher compared to those near agricultural and wildland ($P < 0.01$). Cr and Ni concentrations were significantly higher compared to wildland ($P < 0.01$)

Table 1

Concentrations of metal(loid)s and values of environmental parameters in soil on the west coast region of Korea from 2010 to 2019 [min–max (mean)].

Target analytes	Sampling year									
	2010 (n = 13)	2011 (n = 13)	2012 (n = 13)	2013 (n = 13)	2014 (n = 17)	2015 (n = 17)	2016 (n = 17)	2017 (n = 17)	2018 (n = 16)	2019 (n = 17)
Metal(loid)s										
As (mg kg ⁻¹)	0.7–34 (8.2)	3.8–10 (7.0)	2.6–38 (8.4)	4.4–25 (8.0)	4.0–38.2 (10.1)	2.9–24 (7.6)	2.8–23 (8.8)	2.7–25 (7.9)	4.2–29.2 (9.3)	2.6–14 (8.0)
Cd (mg kg ⁻¹)	0.02–1.1 (0.3)	0.05–0.6 (0.2)	0.03–1.5 (0.4)	0.03–0.4 (0.2)	0.05–0.5 (0.2)	0.04–0.7 (0.2)	0.05–0.5 (0.2)	0.04–1.9 (0.4)	0.07–0.8 (0.2)	0.03–4.3 (0.7)
Cr (mg kg ⁻¹)	5.9–155 (54)	9.7–81 (37)	8.0–102 (47)	10–93 (41)	20–103 (51)	18–72 (41)	10.4–89 (46)	8.3–132 (49)	28–84 (50)	6.5–81 (36)
Cu (mg kg ⁻¹)	1.1–69 (25)	3.3–78 (18)	2.0–111 (27)	2.6–33 (16)	2.5–54 (20)	3.8–54 (20)	2.8–110 (26)	2.1–76 (32)	2.7–59 (21)	1.2–75 (19)
Hg (mg kg ⁻¹)	1.3–910 (79)	1.8–58 (14)	2.1–35 (14)	1.1–18 (8.9)	1.7–31 (13)	1.1–80 (18)	1.2–31 (13)	1.1–138 (24)	1.9–45 (20)	0.9–30 (11)
Ni (mg kg ⁻¹)	1.0–48 (22)	4.0–35 (15)	3.3–38 (18)	3.5–44 (16)	6.2–38 (19)	5.0–35 (18)	4.2–45 (18)	3.3–45 (19)	7.4–37 (21)	2.2–41 (15)
Pb (mg kg ⁻¹)	5.3–82 (34)	13–42 (29)	15–157 (49)	24–66 (40)	15–63 (34)	15–92 (38)	13–62 (35)	7.0–233 (50)	16–166 (40)	12–77 (40)
Zn (mg kg ⁻¹)	4.6–788 (147)	13–139 (71)	11–941 (188)	13–127 (71)	17–221 (95)	15–331 (101)	19–290 (101)	18–1023 (180)	19–203 (85)	5.9–147 (63)
Environmental parameter										
pH	4.6–7.9 (6.7)	4.1–8.1 (6.6)	4.6–8.2 (6.4)	5.4–9.0 (7.4)	4.8–8.7 (6.7)	4.4–8.6 (6.5)	5.4–8.0 (7.3)	5.5–8.6 (7.2)	5.1–7.9 (6.6)	5.1–8.0 (6.8)
TOC (%)	0.1–1.5 (1.0)	0.1–3.4 (1.0)	0.1–6.8 (1.4)	0.1–5.1 (1.0)	0.1–3.2 (1.1)	5.4–8.0 (2.1)	0.1–6.0 (1.3)	0.1–6.2 (1.9)	0.4–4.4 (1.7)	0.1–5.7 (1.4)

(Table S3). A significant difference in concentration of Hg was confirmed in the three groups ($P < 0.05$), but no significant difference was found in individual comparisons ($P > 0.05$) (Table S3). Previous studies have reported that metals occurred at greater concentrations in the soil near roads, particularly when compared to metal(loid)s in paddy fields, orchards, and forests (Azeez et al., 2014; Hjortenkrans et al., 2006; Li et al., 2019; Zhang et al., 2012). Thus, the distributions of metal(loid)s were mainly affected by human transportation activity.

The concentrations of metal(loid)s were generally higher in agricultural land compared to wildland. The concentrations of As, Cr, Cu, Hg, Ni, and Pb were 1.1 to 1.7 times higher in agricultural land (mean 1.4 times) compared to wildland, with Cr and Ni concentrations being significantly higher ($P < 0.01$) (Table S3). A similar result has been reported in previous studies. The concentrations of As, Cr, Cd, Hg, Ni, and Zn were higher in agricultural land compared to forest, orchard, and fallow soil (Li et al., 2019; Liu et al., 2020). Cr and Ni pollution have been previously associated with

agricultural activities, including untreated water irrigation, chemical fertilizer, and manure (Alloway, 2013; Lv et al., 2015; Guan et al., 2018). The concentrations of Cd and Zn were higher in wildland; however, concentrations were not significantly different from those in agricultural land ($P > 0.05$). Hg concentrations were similar in all land use types, as most concentrations (96%) in our study were below background concentrations (Table S4). The annual concentrations of metal(loid)s were similar in all land use types and were consistent with results for the entire region and individual sites. These results indicated that concentrations of metal(loid)s were most affected by surrounding land use type, with the impact remaining at a similar level. In addition, metal(loid) concentrations in each land use type did not exceed the warning criteria of Korea (Table S5), indicating that current contamination levels in the soil in the west coast region would not affect human health or the growth of animals and plants. Overall, the concentration of metal(loid)s in the soil along the west coast region were dependent on land use type, with low temporal differences and risk.

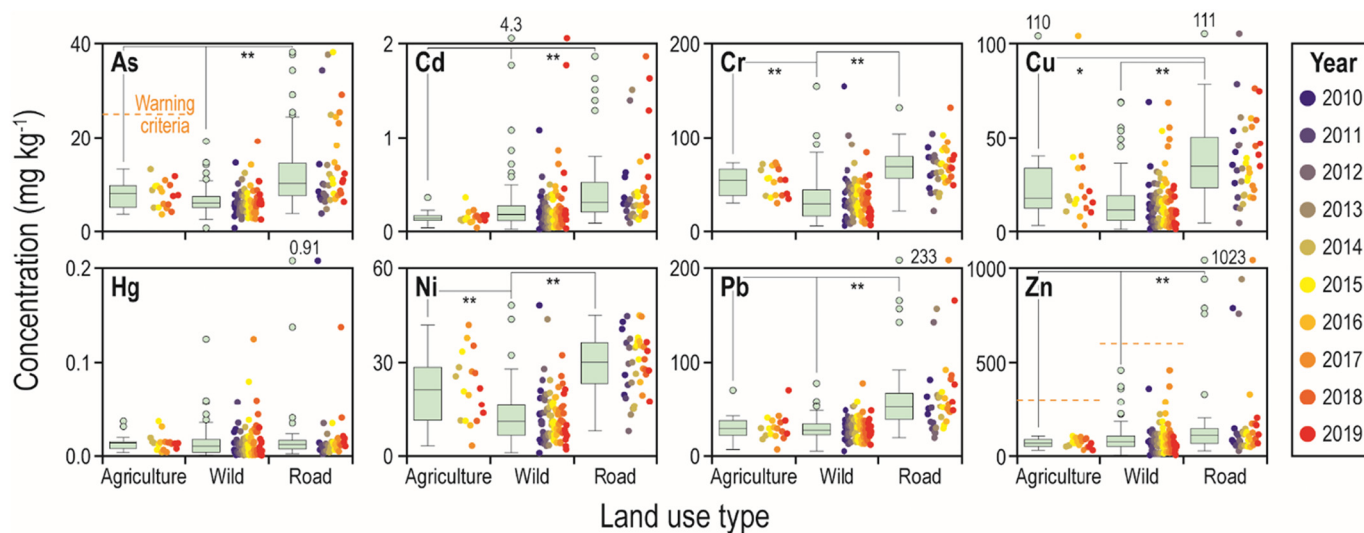


Fig. 3. Box plot of metal(loid)s relative to three land-use types (agriculture, wild, and road) from 2010 to 2019. Values for each year are represented by the color in circles. Dotted lines indicate warning criteria of metal(loid)s in the soil in Korea.

3.3. Soil quality assessment and potential ecological risk

The contamination factor (C_f) and contamination degree (C_d) varied depending on sites and metal(loid)s (Fig. 4). The mean C_f of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn in the whole region was 1.2, 1.1, 1.8, 1.5, 0.5, 1.0, 2.1, and 2.0, respectively (Pb > Zn > Cr > Cu > As > Cd > Ni > Hg). The mean C_f values of metal(loid)s, except Hg, exceeded 1, indicating moderate contamination in the soil of the west coast region. Considerable contamination was only found at sites GG1 (As), GG2 (Cu and Zn), LS1 (Pb and Zn), and LS2 (Pb and Zn), and the highest mean C_f of metal(loid)s was also found at sites GG and LS. Mean C_d was greater in the order of LS2 (21.7), GG2 (19.4), LS1 (17.6), and GG1 (14.3). Only LS2, GG2, and LS1 had very high contamination states. Although there were clear differences in contamination levels between sites, it showed irregular differences across years. Thus, soil quality in areas adjoining the west coast has not been constant over the last decade but is controlled within sites. Overall, a very high contamination state was found in some regions even recently, suggesting that continued monitoring is necessary.

The potential ecological risk factor (E_i) and potential ecological risk index (RI) in soil from the west coast region were generally low (Fig. 4). Mean E_i of metal(loid)s in the whole region ranged from 2.0 to 32.7, and were ordered as Cd > Hg > As > Pb > Cu > Ni > Cr > Zn. The range in mean E_i indicated that all metal(loid)s present low risk. In particular, the E_i of Cr, Cu, Ni, and Zn was below 40 for all sites and periods, indicating low risk in the west coast region over the last 10 years. Moderate risk was found for As, Cd, Hg, and Pb, and considerable-, high-, and very high-risk were only found for Cd and Hg. This trend was the result of differences in toxic response factor values (Håkanson, 1980) and, unlike the contamination index, the risk of Cd and Hg was evaluated as high. The potential ecological risks of each site differed across regions for metal(loid)s. Moderate risk of As and Pb was only confirmed for sites GG and LS, respectively. In contrast, Hg had moderate-, considerable-, and very high-risk at LS4, AS2, GG2, and YS2. Cd had moderate-, considerable-, high-, and very high-risk at the 10 sites (59% of total). Thus, As and Pb presented regional risks, whereas Cd and Hg may cause health risks over a wide area. In the temporal distribution, the risk of individual metals showed an irregular trend, suggesting that the risk has more regional influence over the past decade

than temporal change. The mean RI values were ordered from highest to lowest as GG2 (206), LS2 (164), LS1 (128), and AS2 (113), with only GG2 and LS2 presenting moderate risk. GG2 had a very high risk in 2010 only, while LS2 (2016) and YS1 (2019) presented a considerable risk. Nguyen et al. (2020) reported that residents in very high potential ecological risk areas had a respiratory disease, neurological disease, and skin disease due to direct/indirect effects of metal contamination. Thus, while the overall risk has been generally low and irregular over the last 10 years, continued monitoring is required, especially for Cd and Hg, which showed relatively high risk.

3.4. Sources of metal(loid)s

The results on the run of the PMF model showed that the Q_{True}/Q_{Exp} were 1.40, 1.19, and 0.78 in 2, 3, and 4 factors, respectively (Fig. S2). The Q_{True}/Q_{Exp} strongly declined for three factors, and Q_{True}/Q_{Exp} of factor 4 was less than 1. These results indicated that the three factors were suitable for model interpretation, while the four factors had large errors to interpret the model (Brown et al., 2015; Isokääntä et al., 2020); thus, three factors were selected. Factor 1 was characterized by Hg (91%). Previous studies associated Hg dominance with the use of agricultural pesticides (Song and Gao, 2011) and industrial activity, such as coal combustion, industrial discharge, and production of polyvinyl chloride (mercury chloride), when forming a group like Cd (Bhuiyan et al., 2015; Chen et al., 2016; Wang et al., 2020). However, in the current study, 96% of Hg concentration was below background levels, indicating that sources were of natural origin, influenced by pedogenic & geogenic processes, as a soil parent material. The second source was dominated by As (92%), Cr (84%), and Ni (78%). As, Cr, and Ni were 53%, 23%, and 58% below background levels, respectively, indicating that Cr was the main factor. The high proportion of Cr indicates that sources were the metal plating industry or fuel combustion. Because Cr concentrations were higher than background levels at most sites, including areas not affected by industrial activities, fuel combustion was likely the main source (Cardarelli, 2018; Pathak et al., 2013). As and Ni were mainly recorded in agricultural areas using phosphate fertilizers, herbicides, and pesticides (Liang et al., 2017). These elements are also associated with consumption and mining activity (Niu et al., 2013; Zhang et al.,

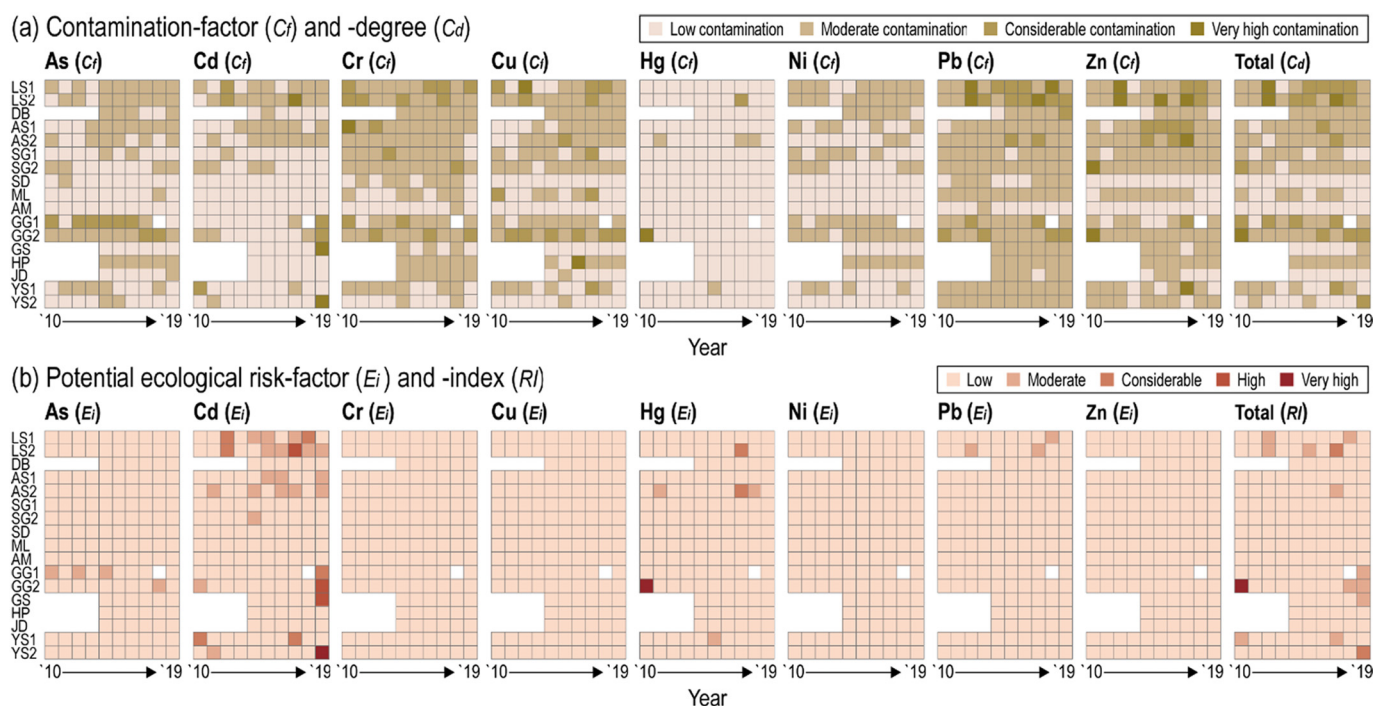


Fig. 4. Spatio-temporal distribution of (a) Contamination-factor (C_f) and -degree (C_d) and (b) Potential ecological risk-factor (E_i) and -index (RI) of metal(loid)s in soil from the west coast region of Korea from 2010 to 2019.

2020b). In our study area, As and Ni concentrations were higher than background levels near agricultural areas, and no mining activity was observed in the vicinity. Thus, factor 2 was attributed to fuel combustion and agricultural pollution. The third source contained Cu (78%), Zn (73%), Cd (72%), and Pb (52%), which are linked to vehicular emissions. Cu, Zn, Cd, and Pb were found from burnt parts of electrical equipment (Yadav and Rajamani, 2003), brakes, tire wear, and vehicle bodies (Chen et al., 2012; Monaci et al., 2000; Zhang et al., 2016), as well as in areas with dense human populations and operational vehicles (Kumar and Gottesfeld, 2008). These metal(loid)s were found at the highest concentration near the road and showed higher concentrations than the background concentrations in most regions. Thus, factor 3 was characterized as vehicular emissions.

The contribution of the three sources over the last 10 years showed a similar trend across the entire study area (Fig. 5). Fuel combustion and agricultural pollution contributed the most (44% of total), with 2012 and 2017 alone contributing the highest to vehicular emissions (42% of total). Natural sources had the lowest contribution (mean: 20%) during the entire study period. Both fuel combustion and vehicular emissions exhibited similar distributions in relation to transport activity, indicating that transport activity was the main source of metal(loid)s in soil from the west coast region. This trend was similar across land use types. Fuel combustion and agricultural pollution accounted for a mean 47%, 42%, and 48% pollution in agriculture, wildland, and roads, respectively. These results are expected as a result of the predominant use of agricultural pesticides in agricultural areas and fuel combustion near roads. Vehicle emissions were the second dominant emission source in all regions, with the highest contribution in the order of road, wild, and agriculture. Natural sources of metals were higher in agriculture (22%) and wildland (20%) compared to roads (mean 14%), indicating that roads were more strongly affected by anthropogenic activity compared to the other two land use types (Cai et al., 2019). Contributions of sources over time for the three land-use types remained similar, indicating a similar impact by sources over the last decade. Overall, metal(loid)s in the soil of the west coast region mainly originated from transportation activity, such as fuel combustion and vehicular emissions, with low temporal variation in sources over time.

3.5. Comparison with previous studies

The concentrations of metal(loid)s in the soil of the present study and previous studies around the world were compared (Fig. 6 and Table 2). Compared with previous studies of metal(loid)s in soil from Korea, metal(loid)s concentrations were moderate at our study sites in the west coast region. The metal(loid)s concentrations in agriculture and wildland of the present study were relatively higher than those that reported in agricultural soil (Ji et al., 2013; Kunhikrishnan et al., 2015; Yun et al., 2018), and were lower than those that were reported around industrial areas and mines (Kwon et al., 2013; Lee et al., 2019; Park and Choi, 2013). Compared with background concentrations in soils around Korea (Table S4), mean concentrations of metal(loid)s in the present study were about 0.46 to 2.1 times higher (mean 1.4 times), indicating both nature and anthropogenic influence. Especially, concentrations higher than the background concentration were found in Pb, Zn, Cr, and Cu (1.5 to 2.1 times). Since these metals originated from vehicular emissions and fuel combustion, indicating that metals in the west coast region were mainly accumulated by transportation activity.

Compared with the data reported in other countries, there was a difference in concentration depending on the source, even in the same land use type (Fig. 6 and Table 2). In agriculture, fallowness, forest, and park, the concentrations of metal(loid)s were similar to those of the Yellow Sea (Liu et al., 2020), the Yangtze River Delta (Liu et al., 2021), and Sydney (Zhao et al., 2018). The concentration in this study was lower than Zhongwei (Zhang et al., 2020b), Kermanshah (Doabi et al., 2018), Ranchi (Raj et al., 2019), Sukinda (Naz et al., 2018), Tadla plain (Ennaji et al., 2020), Kangal (Turhan et al., 2020), Poços de Caldas (Galhardi et al., 2020), and Taltal (Reyes et al., 2021). Relatively high concentrations were reported in areas where mining and industrial emissions were identified as sources, indicating that the level of pollution is determined depending on the source, even in the same land use type. In the road, the concentration of metals(loid)s was higher than in Melbourne (De Silva et al., 2016) and lower than in Ranchi (Raj et al., 2019) and Sukinda (Naz et al., 2018). This result could be explained by the difference in the intensity

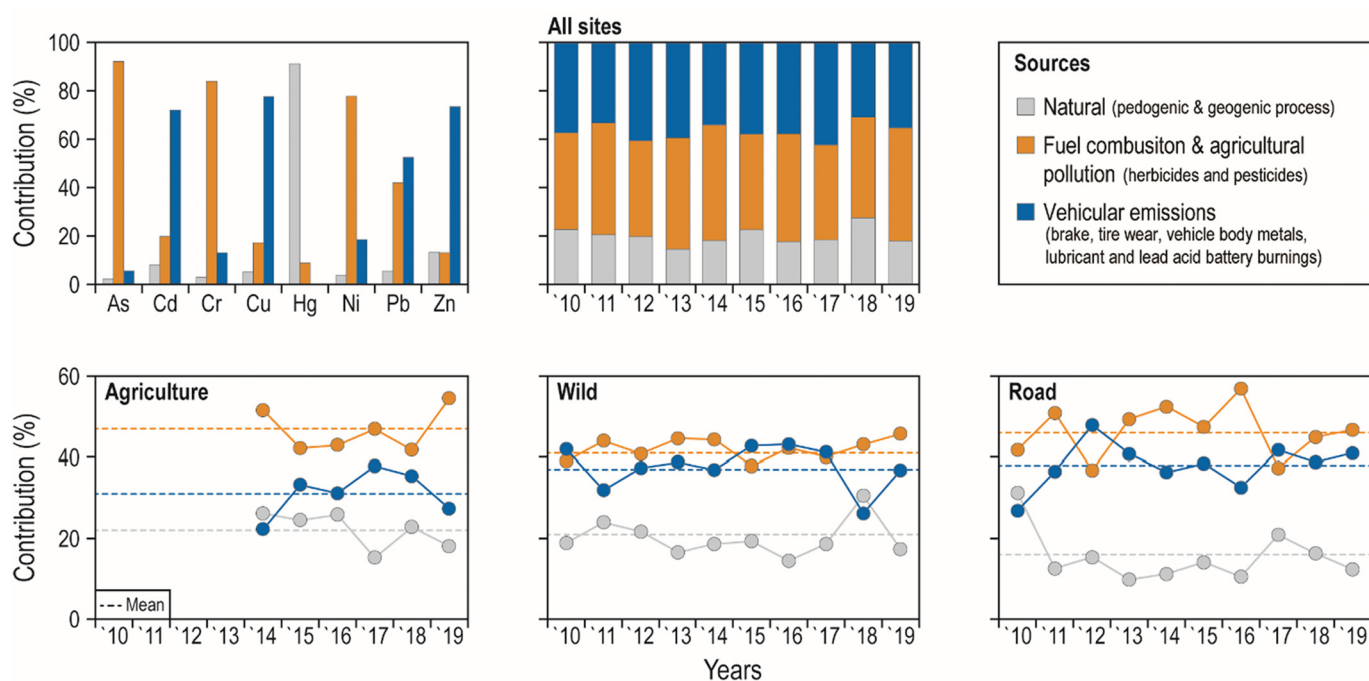


Fig. 5. Temporal variation of sources of metal(loid)s determined by a PMF receptor model. The contribution of the three sources for each metal(loid) and the contribution according to the total regions and land use type are presented.

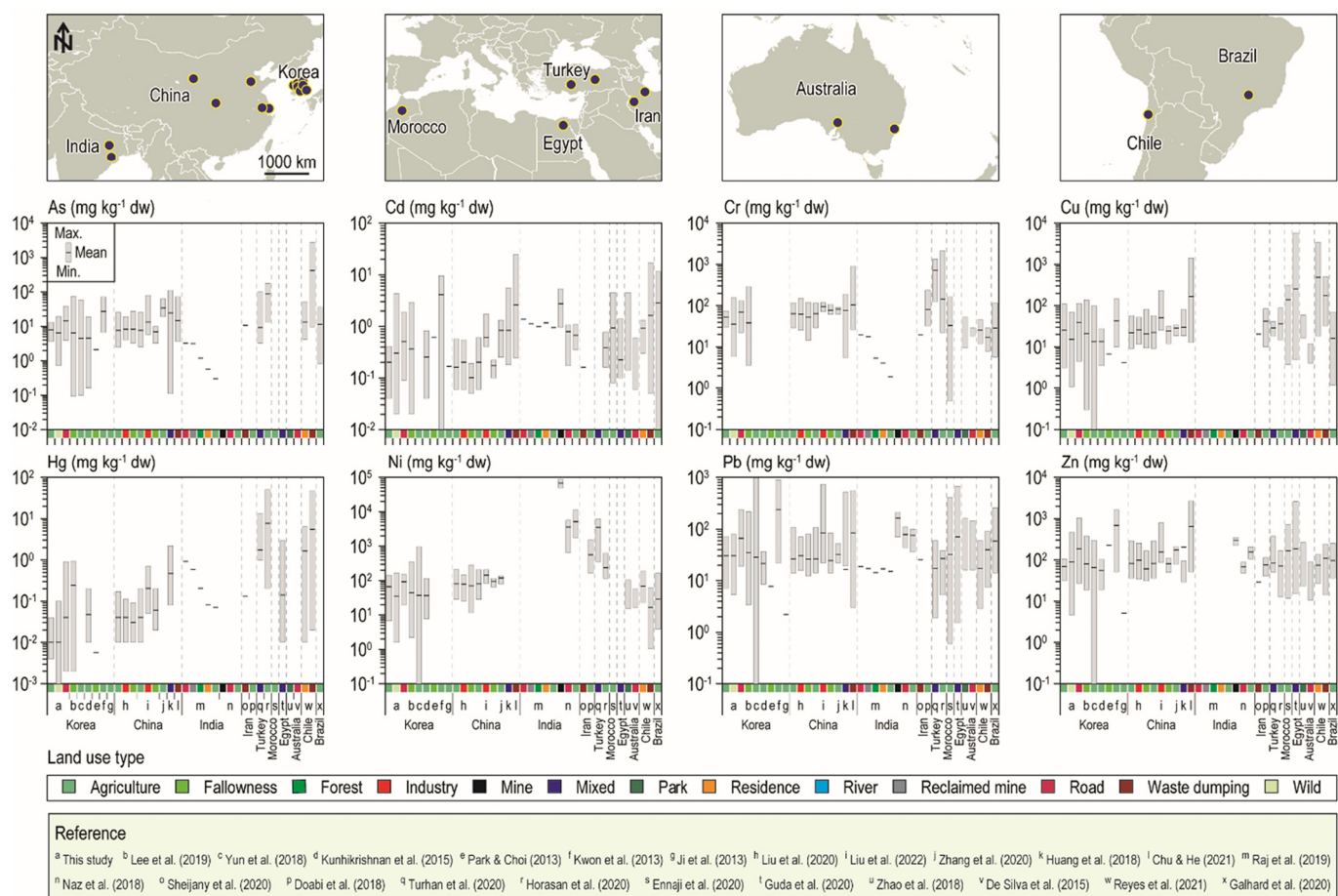


Fig. 6. Comparisons of concentration of metal(loid)s in soils from the 10 countries. The detailed land use types and sources in the study area are provided in Table 2.

of transport activity between the relatively high population of India and the low population of Australia. In addition, relatively high concentrations of metal(loid)s in all over the world have been reported in the industry, waste dumping, reclaimed mines, and mine, suggesting that the soil environment is the most accumulating source of metal(loid)s (Chu and He, 2021; Guda et al., 2020; Horasan, 2020; Huang et al., 2018; Reyes et al., 2021; Shejany et al., 2020). Overall, the concentrations of metal(loid)s in the soil of the west coast region of Korea over the last decade were not high compared to other regions in Korea and the world, but pollution management would be necessary to control the influx of anthropogenic contaminants.

The identification of changes in sources of metal(loid)s in soils in Korea was difficult due to the limitation of data (Table 2). In the same region, natural and industrial activities were suggested as major sources of metals, and Cd, Pb, and Zn have enriched that originated from industrial activity (Liu et al., 2020). This is similar to the present study. In addition, we suggested that transportation activity, fuel combustion, and agricultural pollution are the additional sources of Cd, Pb, and Zn. The sources of metal(loid)s in the soils of the west coast regions of Korea showed similar trends to previous studies conducted in various countries. Results of previous studies indicated that the sources of metal(loid)s contamination in the soils were found in the following order: mining activity, industrial activity, transportation activity, natural, agricultural, and sewage based on statistical analysis (Table 2). However, most of the studies were conducted in the mid-to-late 2010s, and some studies did not provide a sample year, so it was difficult to ascertain the changes in the sources of metals in soils over time. Overall, the sources of metal(loid)s in this study were similar to the sources in other regions of various countries; continuous monitoring is necessary to determine the temporal changes of the sources.

3.6. Metal pollution management

Korea and other countries have continued to develop policies for metal pollution management over the past 20 years. Before the 2010s, the soil pollution source management system in Korea was fragmentary management of oil and underground storage facilities, with the insufficient management system of metal pollution. To compensate for this limitation, the 1st Soil Conservation Master Plan in 2010 established a management system for human health protection, including metal(loid)s, thereby establishing a soil management foundation (MOE, 2009). After that, in 2020, the 2nd Soil Conservation Master Plan has announced the systemized monitoring and management system with warning criteria for each land use type and selected priority management areas (MOE, 2020). In China, metal soil pollution remediation projects, strengthening soil pollution prevention, and soil pollution prevention & control action plans have been announced to control soil pollution by metals (State Council, 2016). Similarly, Europe adopted the Thematic Strategy for Soil Protection in the Environmental Implementation Program in 2002, and is implementing step-by-step investigation, identification, and management of contaminated sites (EC, 2002). Focused on responsibilities among stakeholders, soil contamination monitoring for industrial complexes and soil management standards have been strengthened, and the law has been amended in Taiwan (EPA, 2010).

In addition to responding to pollution, policies for ecosystem recovery are being implemented. Japan has been managed the soil environment of cities and agricultural land separately, and policies are being pursued in the direction of increasing the productivity of the soil by focusing on the enhancement of biodiversity in recent years (MOE, 1999, 2007). In the United States, policies to improve soil health from a soil ecosystem perspective and restore contaminated sites are in progress to consider re-use after

Table 2

Comparison of the land use type, source identification methods, and sources of metal(loid)s in soils from this study and previous studies.

Country	Region	Sampling year	Land use ^a	Methods ^b	Sources	References
Korea	National area	2018	Fa	Geographic information	Industrial activity	Lee et al., 2019
Korea		2017	Ag	Geographic information	Industrial activity	Yun et al., 2018
Korea		2012	Ag	Geographic information	Pedogenic	Kunhikrishnan et al., 2015
Korea	Muju	2008	Fa	Geographic information	Mine	Park and Choi, 2013
Korea	Jangsu	2013	Ag	Geographic information	Mine	Kwon et al., 2013
Korea	Goseong	2004	Ag	Geographic information	Mine	Ji et al., 2013
China	Yellow & Bohai Sea	2018	Ag In Fa	PCA	Natural, industrial activity	Liu et al., 2020
China	Yangtze River Delta	2019	Ag In Fa	PMF	Natural, agriculture, industrial activity	Liu et al., 2021
China	Zhongwei	2017	Ag	PCA	Natural, agriculture, atmospheric, metal industry	Zhang et al., 2020b
China	Chang Zhou	2014–2015	Mixed	APCA-MLR, PMF, PCA-MLRD	Industrial hub, mine, road, fluorescent factory, dyeing mill	Huang et al., 2018
China	National area	2006–2017	Wa	PCA	Sewage sludge	Chu and He, 2021
Iran	Rasht	–	Wa	PCA	Natural, dumpsite activity	Sheijany et al., 2020
Iran	Kermanshah	–	Ag	Geo-accumulation index	Transport, industrial activity	Doabi et al., 2018
India	Ranchi	–	Ro Rm Fo Re Ag	Cluster analysis	Coal mines Pedogenic	Raj et al., 2019
India	Sukinda	–	Mi Ro Ag	PCA	Mining, transport activity	Naz et al., 2018
Australia	Sydney	–	Pa	Pb isotopic ratio	Transport activity	Zhao et al., 2018
Australia	Melbourne	–	Ro	Geographic information	Transport activity	De Silva et al., 2016
Morocco	Tadla plain	–	Ag	PCA	Anthropogenic activity, pedogenic	Ennaji et al., 2020
Egypt	Qalubia Governorate	2017–2018	Mixed	Geographic information	Natural, industrial activity	Guda et al., 2020
Turkey	Konya	2015–2016	Mixed	Cluster analysis	Mine	Horasan, 2020
Turkey	Kangal	–	Ag	Geographic information	Coal-fired thermal power plant	Turhan et al., 2020
Chile	Taltal	–	Re Wa	PCA	Mining waste	Reyes et al., 2021
Brazil	Poços de Caldas	–	Ag	PCA, Factor analysis	Mining waste	Galhardi et al., 2020
Korea	west coast	2010–2019	Ag Wi Ro	PMF	Agriculture, natural, transport activity, wild	This study

Rm; Reclaimed mine, Ro; Road, Wa; Waste dumping, Wi; Wild.

^a Ag; Agriculture, Fa; Fallowness, Fo; Forest, In; Industry, Mi; Mine, Pa; Park, Re; Residence, Ri; River,^b APCA-MLR; Absolute principal component analysis-multiple linear regression, PCA-MLRD; Principal component analysis-multiple linear regression with distance.

purification (EPA, 1976, 1996). Overall, soil pollution management policies in Korea, including metal pollution, have been focused mainly on the assessment of contamination degree and cleanup of contaminated soils. In the future, it is required to establish an eco-friendly management policy and preemptive countermeasures, including soil re-use plan after purification and identification and management of pollution sources of metal(loid)s.

4. Conclusions

This study provides long-term trends on the distribution, potential ecological risks, and sources of metal(loid)s in the terrestrial soil from regions of South Korea adjoining the west coast. Over the last 10 years (2010–2019), temporal variation in the degree of contamination, potential ecological risks, and sources of metal(loid)s in the soil of the study area remained considerably low, with clear differences in regional basis. The degree of contamination, risk, and sources was dependent on the land use type of soil, and high contamination degree and risk were evidenced near the road exposed by fuel combustion and vehicular emissions. Although previous studies reported the distributions and potential risks of metal(loid)s in the soil around Korea, long-term trends and major sources remained unclear. This first 10 years long-term monitoring assessment on metal(loid)s contamination associated with the soil environment is important for identifying major sources, establishing activities to a reduction of pollution levels, and enhancement of soil management. Overall, the present study provided baseline historical information on soil pollution and future monitoring directions towards improving soil quality in Korea.

CRediT authorship contribution statement

Seo Joon Yoon: Conceptualization, Investigation, Formal analysis, Statistical analyses, Visualization, Writing – original draft. **Seongjin Hong:** Conceptualization, Investigation, Writing – review & editing. **Changkeun Lee:** Investigation, Formal analysis. **Junghyun Lee:** Investigation, Visualization. **Taewoo Kim:** Investigation, Formal analysis. **Jongmin Lee:** Investigation, Formal analysis. **Beomgi Kim:** Investigation. Formal analysis. **Junsung Noh:** Investigation, Formal analysis. **Bong-Oh Kwon:** Investigation, Project administration. **Jong Seong Khim:** Conceptualization, Investigation, Writing – review & editing, Project administration, Funding acquisition, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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10 years long-term assessment on characterizing spatiotemporal trend and source apportionment of metal(loid)s in terrestrial soils along the west coast of South Korea

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Supplementary Tables

Table S1. Spearman correlation analysis between the metal(loid)s and environmental parameters in soil. Values in bold indicate that the correlation was significant at $p < 0.05$.

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
pH	-0.148	-0.056	-0.261**	-0.057	-0.488**	-0.488**	-0.011	-0.038
TOC	0.319**	0.555**	0.334**	0.449**	0.787**	0.370**	0.430**	0.576**

Table S2. Statistical relationships of temporal differences among years from 2010 to 2019.

PTSs	Kruskal-Wallis test	
	F-value	P value
As	8.13	0.533
Cd	5.70	0.769
Cr	7.32	0.604
Cu	5.51	0.788
Hg	7.33	0.600
Ni	5.43	0.795
Pb	5.24	0.813
Zn	8.03	0.531

Table S3. Statistical relationships of land-use types on metal(loid)s. Bold text represents statistically significant relationships.

PTSs	Kruskal-Wallis test		<i>Post hoc</i> Mann-Whitney (<i>P</i> -values) ^a		
	F-value	P value	Road vs Agriculture	Road vs Wild	Agriculture vs Wild
As	39.8	<0.001	0.043	<0.001	0.116
Cd	26.4	<0.001	<0.001	<0.001	0.602
Cr	51.4	<0.001	0.121	<0.001	0.006
Cu	38.1	<0.001	0.023	<0.001	0.246
Hg	6.58	<0.05	1.000	0.102	0.165
Ni	52.5	<0.001	0.126	<0.001	0.005
Pb	40.1	<0.001	<0.001	<0.001	1.000
Zn	12.5	<0.001	0.019	0.004	1.000

Table S4. Background concentrations of metal(loid)s in soil from Korea (Kim and Kim, 1999; Yoon et al., 2009).

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
	(mg kg ⁻¹)							
Background concentration	6.8	0.29	25.4	15.3	0.045	17.7	18.4	54.3

Table S5. Warning criteria of soil pollution in Korea by land use types.

	As	Cd	Cr*	Cu	Hg	Ni	Pb	Zn
	(mg kg ⁻¹)							
Zone 1 ^a	25	4	5	150	4	100	200	300
Zone 2 ^b	50	10	15	500	10	200	400	600
Zone 3 ^c	200	60	40	2000	20	500	700	2000

* Cr was analyzed ion chromatography-UV/VIS Spectrometry.

^a Zone 1 includes paddy fields, farm, orchards, pasture, well, parks, historic sites, and cemeteries.

^b Zone 2 includes forest, salt fields, rivers, amusement parks, barren, wild and hybrid land.

^c Zone 3 includes factories, parking lots, gas stations, roads, railways, embankments, military facilities.

Supplementary Figures

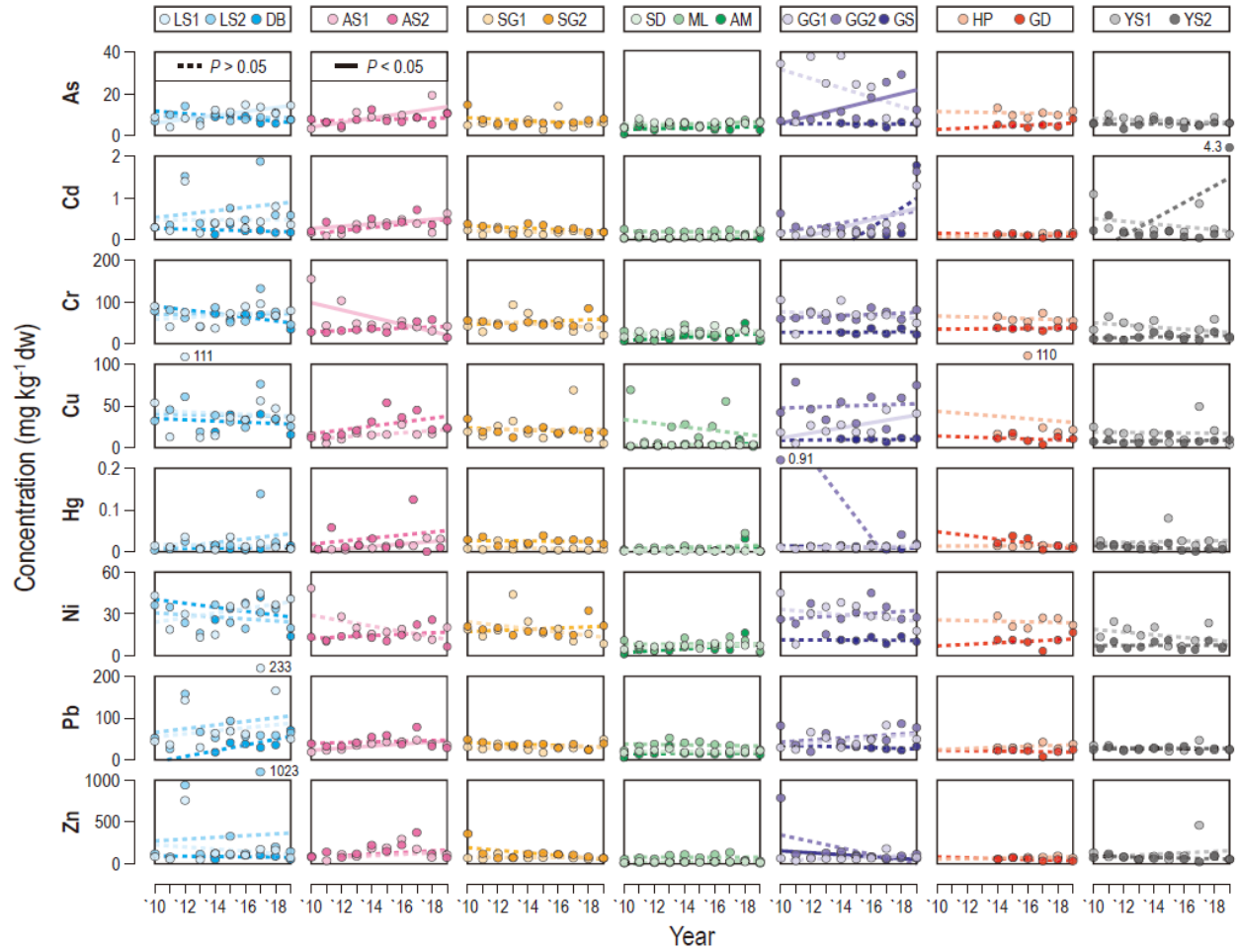


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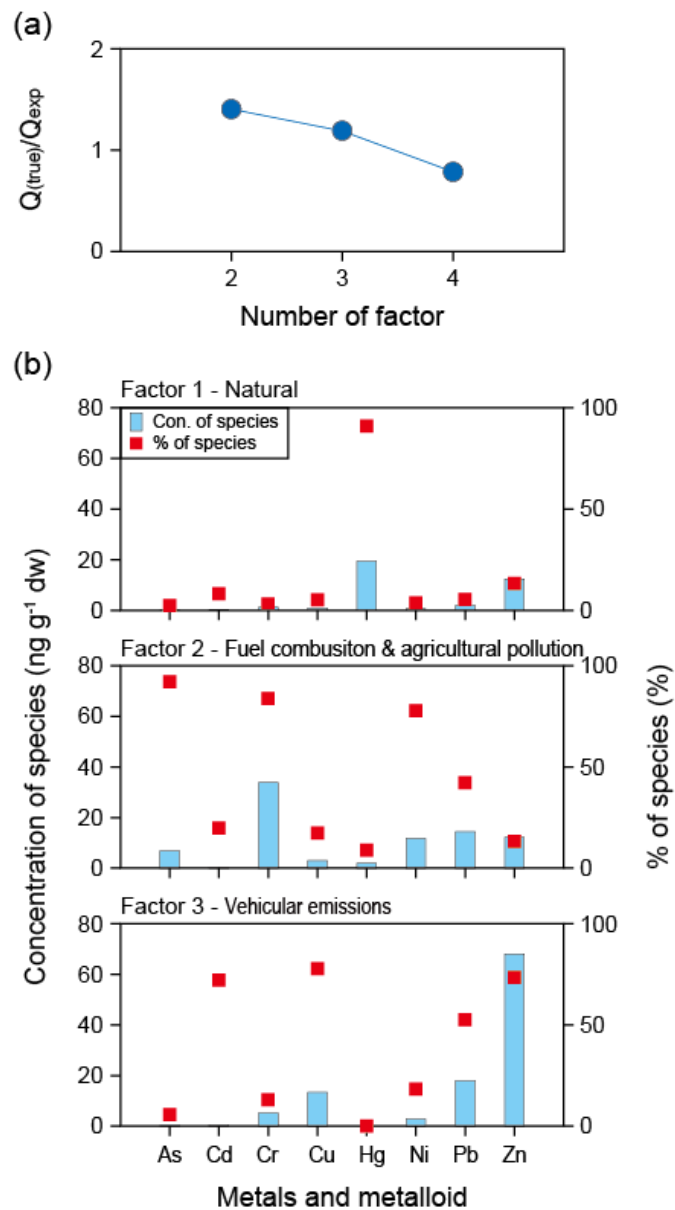


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