SCIREA Journal of Geosciences

http://www.scirea.org/journal/Geosciences

November 25, 2020

Volume 4, Issue 3, June 2020

Source identification for potentially toxic metals using Pb isotopes and elemental ratios of road-deposited sediments, stream sediment, and soil from watershed in Busan, South Korea

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Abstract

Study on potentially toxic elements (PTEs; Cr, Ni, Cu, Zn, As, Cd, Sb, Pb and Hg) combined with Pb isotopes was conducted to evaluate the pollution status and to identify the sources of PTEs pollution in road-deposited sediments (RDS), soils and stream sediments in small watershed of Busan, Korea. Our results indicate that RDS was moderately to extremely polluted in Cu, Zn, Cd, Sb and Pb and highly polluted in sampling site with high traffic activity. According to the I_{geo} results, the Sb pollution caused by automobile brake pads was higher than that of other elements. Cd and Sb in RDS pose a serous ecological risk. The pollution degree of PTEs was in the order: RDS>stream sediment>soil. Pb isotopes of RDS of this study was clearly distinguished from the industrial region. In urban areas, traffic activities were found to have a larger contribution to PTEs pollution in RDS. $^{206}Pb/^{207}Pb$ ratio

showed the lowest value in RDS and increased in the order of stream sediments and soils. In particular, the results of biplot between Pb isotope and Zu/Cu ratio showed that it was possible to distinguish between industrial and traffic activities. Our results indicate that RDS is one of the main sources of PTEs pollution in stream sediments. Therefore, efficient management, such as RDS cleaning, is very important to reduce PTEs contamination that migrates to the stream environment as a non-point source.

Keywords: potentially toxic elements, road-deposited sediments, soils, stream sediments, pollution

1. Introduction

Roads are essential infrastructure for human activities and traffic activities are recognized as one of the significant pollution sources of potentially toxic elements (PTEs) in urban environments (Yuen et al. 2012; Admad et al. 2019). The road dust or road-deposited sediments (RDS) are used as an important environmental indicator of PTEs pollution (Suryawanshi et al. 2016; Jeong et al. 2020a; Logiewa et al. 2020). Traffic activities such as vehicle transportation can enrich PTEs in roadside soil and adversely affect the environment and plants (Zhang et al. 2015; Khalid et al. 2018). PTEs in RDS can become direct sources to atmosphere particle matters and can be reached directly to human population through inhalation, ingestion and dermal contact after resuspension by wind (Abu-Allaban et al. 2003; Chen et al. 2012; Du et al. 2013). Additionally, PTEs containing in RDS are transferred into the aquatic environments by wash-off during rainfall events (Logiewa et al., 2020). Therefore, RDS are one of important contributor of PTEs pollution in the urban environments (soils and stream sediments) and the coastal sediments (Suryawanshi et al. 2016; Jeong et al. 2020b).

The vehicle exhaust emission, the extensive use of brake pads and tires, the wear of road surface and roadside soil erosion are contributed to the PTEs pollution such as Cr, Ni, Cu, Zn, Cd, Sb and Pb (Khan et al. 2013; Loganathan et al. 2013; Adamiec et al. 2016; Baensch-Baltruschat et al. 2020). RDS have been reported to be highly polluted with PTEs because particulate matter generated by traffic transportation in urban areas accumulate on road surface (Swietlik et al. 2013; Cai et al. 2019).

The abrasion of brake pad and tire wear debris are particularly enriched with Cu, Zn, Sb and Pb in RDS (Thorpe and Harrison 2008; Doung and Lee 2011). Therefore, the elemental ratios of Zn/Cu and Cu/Sb ratio in RDS can indicate a relative contribution to the traffic activity of these metals in vehicle and non-vehicle sources (Iijima et al. 2007; Amato et al. 2011; Hwang et al. 2016; Bourotte et al. 2019; Jeong et al. 2020b). Pb stable isotopes are also used as tracers and suitable for identifying Pb sources in the environments (Wijaya et al. 2012; Nazarpour et al. 2019). Traffic-related Pb affected their geochemical signatures and RDS is more sensitive to record the anthropogenic contamination of Pb than soil (Kelepertzis et al. 2020). Several Pb isotope studies suggest that the soils and stream sediments were affected by RDS transported in stormwater runoff (Yu et al. 2016a; Jeong et al. 2018; 2020c; Kelepertzis et al. 2020).

The aims of this study are: 1) to investigate of PTEs (e.g., Cr, Ni, Cu, Zn, As, Cd, Sb, Pb and Hg) distribution in RDS, soils and stream sediments of small watershed regions; 2) to assess the pollution degree and ecological risk of PTEs pollution; 3) to discuss the pollution sources using Pb isotope composition and the elemental ratio such as Zu/Cu and Sb/Cu.

2. Materials and Methods

2.1. Sampling

Overall, 63 RDS, 39 soils and 50 stream sediments were collected from the watershed of Suyeong river and Oncheon stream in Busan of Korea in September 2015 (Fig. 1). RDS samples (R1~R63) were collected using a vacuum cleaner (DC35, Dyson Co., England) within a 0.7m ×0.7m from the road side curb. To avoid cross-contamination between samples, vacuum cleaner was cleaned and replaced after each sampling. RDS samples were collected from five zones per each site, mixed to ensure representativeness and stored in plastic bag until analysis. Surface soils (O1~O22, S1~S17) and the upstream sediments (O1~O23; Oncheon stream, S1~S18; the upstream of Suyeong river) were collected using PE scoop connected with PVC pipes. Stream sediments (S19~S27) in the downstream of Suyeong river were collected using van veen grab samplers in small boat. The collected RDS, soils and stream sediments were dried in an oven or freeze-dried.

2.2. Particle size, PTEs and Pb isotope analysis

For determination of particle size, RDS, soil and stream sediment samples were used and organic matter and inorganic carbonate were removed with hydrogen peroxide and 1N hydrochloric acid, respectively. Then, particle size analysis was conducted using a laser particle-size analyzer (Mastersizer 2000, Malvern Instruments, UK) at the Korea Institute of Geoscience and Mineral Resources (KIGAM).

RDS, soil and stream sediment samples were pulverized using a mechanical mortar (Pulverisette 6, Fritsch Co., Germany) before the determinations of PTEs concentrations and Pb isotope. Approximately 0.2 g of the ground and homogenized samples was decomposed using high purity (Ultra-100, Kanto Chemical, Japan) of hydrofluoric acid, nitric acid and perchloric acid on a hot plate at 180°C for 24 h. The decomposed samples were nearly evaporated and re-dissolved in 1% nitric acid (v/v) for PTEs analysis. Cr, Ni, Cu, Zn, As, Cd, Sb and Pb were determined by inductively coupled plasma mass spectrometry (ICP-MS; iCAP-Q, Thermo Scientific Co., Germany) and Hg was determined using a mercury analyzer (Hydra-C, Teledyne Technology Co., USA. Duplicate analysis was performed to improve data quality. Recovery rates were calculated using two types of certified reference materials (MESS-4 and PACS-3, National Research Council of Canada) and ranged from 96% to 102%. Pb stable isotope analyses was carried out with multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS; Neptune plus, Thermo Scientific Co., Germany) at Korea Institute of Ocean Science and Technology (KIOST). Tl was used to correct Pb mass fractionation and the mass fractionation was corrected using standard-sample bracketing methods.

2.3. Pollution and ecological risk assessment

The geo-accumulation index (I_{geo}) is a useful indicator to determine each toxic element pollution and is proposed by Muller (1969) as follow equation:

$$I_{geo} = \log_2(C_n/1.5\times B_n)$$

where, C_n and B_n represent the element concentration in sediment sample of this study and the geological background value (Rudnick and Gao 2003). Factor 1.5 is adopted due to lithogenic variations. I_{geo} is divided into seven classes between unpolluted ($I_{geo}<0$) and extremely polluted ($I_{geo}>5$).

The nemerow index (P_N) is widely used to evaluate a comprehensive pollution levels of the measured toxic elements in soils and sediments (Nemerow 1991; Huang et al. 2020) as follow equation:

$$P_N = \sqrt{\frac{(PI^2_{average} + PI^2_{maximum})}{2}}$$

where, $PI=C_n/S_n$, C_n is the elemental concentrations in sediment samples and S_n is the residential soil quality guidelines for the protection of environmental and human health by CCME (2007). P_N is categorized into five classes ranging from no pollution ($P_N<0.7$) to high level of pollution ($P_N>3.0$) (Cheng et al. 2014).

The potential ecological risk factor (PER) is proposed by Hakanson (1980) to comprehensively evaluate the pollution degree of each toxic element by considering their toxicity and is the sum of single potential ecological risk factor (E^i_r) as follow equation:

$$PER = \sum_{i=1}^{9}(E^i_r) = \sum_{i=1}^{9}(T^i_r \times {}^{C_n}/_{B_n})$$

where, C_n and B_n are the same as geo-accumulation index. T^i_r is the element toxicity response factors (Hg=40, Cd=30, Sb=7, As=10, Cu=Ni=Pb=5 Cr=2, Zn=1) (Hakanson 1980; Lu et al. 2014; Wang et al. 2018). E^i_r values were categorized into five classes ranging from low potential ecological risk ($E^i_r<40$) to serious ecological risk ($E^i_r>320$). PER values were classified into four classes ranging from low risk (PER<150) to serious risk (PER>600).

3. Results and discussion

3.1. PTEs in road-deposited sediments

The average, minimum and maximum concentrations of PTEs in RDS are presented in Tab. 1. Zn has the highest value among PTEs and PTEs concentrations in RDS were in the following order: Zn>Cu>Cr>Pb>Ni>Sb>As>Cd>Hg. The highest values of Cu and Zn were observed in R2, R47 and R58 site nearby bus terminal and large department store where road traffic is high. Many studies were reported that Cu, Zn and Pb in RDS are largely affected traffic related sources, especially the abrasion of brake pad and tire wear (Grigoratos and Martini 2015; Jose and Srimuruganandam 2020).

Zn is used as a tracer of tire wear in urban environment and the main source of Zn are brake and corrosion galvanized parts as well as tire (Amato et al. 2009; Bhattacharya et al. 2013). Cu sources in RDS are bearing wear, engine part and brake emissions (Faiz et al. 2009; Lu et al. 2009; Varrica et al. 2003). Cr and Ni could be also released from traffic-related sources (Abassi et al. 2018; Jose et al. 2020). The highest Cr and Ni concentrations in RDS was found at R30 nearby subway station, baseball park, soccer field. However, Pb concentrations was highest at R48, where industrial facilities are located. Sb concentrations in RDS ranged from 8.5 to 7.8 mg/kg with mean of 27.6 mg/kg. Mean concentration of Sb is 13 times higher than in soils (Fig. 2). Brake pad contain high content of Sb in the form of antimony oxide and stibnite. When the vehicle is stopped, Sb is abraded and discharged into the road surface (Sinha et al. 2020). Therefore, the high Sb concentration in RDS indicate that traffic activities are the major pollution source. Other PTEs such as As, Cd and Hg also showed relatively higher concentrations in sampling site with high traffic activities. PTEs in RDS is 1.3~13 times higher than that of the surrounding soil (Fig. 2). For geoaccumulation index (I_{geo}), Sb has the highest value at 5.4 and decreased in the order of Sb>Cd>Zn>Pb>Cu>Cr>Hg>Ni (Tab. 2). Sb indicates extremely strong pollution with I_{geo}>5 over 80% of sampling sites. The average of I_{geo} values of Zn and Cd indicated strong pollution (3<I_{geo}<4). The average of I_{geo} for Cu and Pb in RDS was classified as moderate pollution to strong pollution (2<I_{geo}<3).

The average value of nemerow index (P_N) varied between 1.9 and 10.2 with average of 4.4. Over the 63 RDS samples, 82% (52 sites) and 16% (10 sites) had high and moderate level of pollution, indicating that RDS compared to residential soils was highly polluted with PTEs (Fig. 3). The average values of E^i_r for Cd and Sb were 694 and 483, respectively, indicating that RDS has serious risk with Cd and Sb (Tab. 3). Cd pose the most ecological risk of all nine toxic elements of this study. Cu, As, Pb and Hg also pose moderately to higher ecological risk (Tab. 4). Based on the PER values (mean of 1,426), there exist serious ecological risk from the presence of Cd, Sb, Hg, Pb, Cu and As in RDS.

3.2. PTEs in soils

Zn was the most abundant toxic elements in soils with an average of 282 ± 227 mg/kg. The average of PTEs concentrations were in the following decreasing order of Zn>Pb>Cr>Cu>Ni>As>Sb>Cd>Hg (Tab. 1). Most toxic elements except for Cr exhibited slightly high concentrations at S3 site nearby Seokdae Industrial Complex. Considerably high Zn concentrations (1,109 mg/kg) were found. Bhattacharya et al. (2013) reported that high

concentration of Zn in road dust has been affected by industrial sources such as electroplating industries and galvanization industries. At S3 site, Cu and Sb concentrations are 40 mg/kg and 2.6 mg/kg, which was lower than that of other sampling sites. It indicates that Zn pollution is caused by industrial activities rather than traffic activities. The relatively high concentrations of PTEs in soil were observed in the upstream of Suyeong river. However, the PTEs concentration in soils was significantly lower that that of stream sediments and RDS (Fig. 2). I_{geo} values of soil for Zn, Cd, Sb and Pb corresponded to the moderately pollution status, but the rest toxic elements such as Cr, Ni, Cu, As and Hg were not polluted (Tab. 2). P_N varied from 0.2 to 3.2 with average of 0.9, representing the warning line of PTEs pollution level (0.7<PN<1.0) (Fig. 3). The average of potential ecological risk factor (E^i_r) in soils decreased in the following order of Cd (218)>Hg(49)>Sb(37)>Pb(20)>As(12)>Cu(8)>Zn(4)>Cr≈Ni(1) (Tab. 3). The average of PER value was 349 ranged from 63 to 1194, representing severe ecological risk (300<PER<600).

3.3. PTEs in stream sediments

In stream sediments, the concentrations of PTEs with exception of Cr and Pb were 1.2-2.7 times higher than those of soil samples, but lower than RDS (Fig. 2). Zn was the most abundant PTEs in stream sediment, followed by Pb>Cu>Cr>Ni>As>Sb>Cd>Hg. Stream sediment at S2 site around industrial complex showed the highest Cr, Ni, Cn, As, Cd, Sb and Pb concentrations, indicating the presence of pollution from industrial activities. The average of PTEs concentrations from the upstream of Suyeong river was 1.9 (Cu) – 7.5 (Cd) times higher that that of Oncheon stream. All PTEs were found to have the lower concentration in Oncheon stream. I_{geo} values ranged from -2.5 (Ni) to 2.3 (Cd). The average of I_{geo} values revealed that stream sediments was moderate to strong polluted by Cd. Zn, Sb and Pb were moderate pollution level, whereas other toxic elements was not polluted in stream sediments.

P_N ranged from 0.3 to 15.1, indicating that PTEs pollution varies largely from sampling sites (Fig. 3). This is due to the flow rate of stream water and topography of the stream environments. The stream sediments nearby industrial complex showed high level of pollution with higher P_N value, exceeding 3. Similar to RDS, Cd shows the most ecological risk among PTEs in stream sediments. Stream sediments of Suyeong river has significantly higher PER values than that of Oncheon stream. Most of sampling sites from Suyeong river had higher PER value (>600), indicating a serious ecological risk.

3.4. Identification of PTEs pollution sources using Pb isotopes and elemental ratios

RDS is transported to the stream environments during rainfall events and RDS in runoff is one of the main sources to urban waterway contamination of toxic elements (Marshall et al. 2010; Ignatavičius et al. 2017). Fig. 2 compared the PTEs concentration of RDS, stream sediment and soil in this study as well as of total suspended solids (TSS) in urban runoff in our previous study. In most PTEs except for Ni and Cd, the concentrations of TSS in runoff was between RDS and stream sediments. The average particle size in stream sediments was 445 mm which is 2.7 times larger than that of RDS (162 mm). In addition, the PTEs concentrations in stream sediments is lower than that of TSS in runoff. The average particle size in soil was 423 mm, similar to that of river sediments, but the PTEs concentrations of stream sediments were hight than that of soils, indicating that both RDS and surrounding soil during stormwater runoff are introduced into the stream environment.

Pb is widely used to balance wheel and tires as a wheel weight. Duzgoren-Aydin (2007) reported that lead wheel weight was a major source of lead contamination in the surrounding road-side soil. Pb isotope compositions were used for tracing Pb sources (Yu et al. 2016b; Gmochowska et al. 2019; Lin et al. 2019). The average of $^{208}Pb/^{206}Pb$ and $^{206}Pb/^{207}Pb$ in RDS were 2.1066 and 1.1576, respectively. In this study, the $^{208}Pb/^{206}Pb$ ratio of RDS is higher than that of stream sediment and soil, and the $^{206}Pb/^{207}Pb$ ratio is characterized by lower value of RDS. In particular, the Pb isotope compositions of stream sediments have a value close to that of RDS compared to soil (Tab. 1 and Fig. 2). A comparison of the Pb isotope composition from stream sediments indicated that $^{208}Pb/^{206}Pb$ ratio in the upstream of Suyeong river were the higher value, whereas Oncheon stream had the lower $^{208}Pb/^{206}Pb$ value. This indicates that stream sediments are present in various pollution sources from the surrounding environments. Biplot of $^{208}Pb/^{206}Pb$ vs $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{207}Pb$ vs Li/Pb elemental ratio in RDS, stream sediment and soil were shown in Fig. 4. RDS in urban areas of this study is clearly distinguished from RDS in industrial areas. It also shows that Pb isotopes in stream sediment are distributed closer to RDS.

The elemental ratios between Zn, Cu and Sb are used as good indicator to assess the contribution of traffic activities in urban environment (Pio et al. 2013; Hwang et al. 2016; Choi et al. 2020). The Zn/Cu ratio in RDS of urban area is reported to be 2.6-5.1 (Hwang et al. 2016; Bourotte et al. 2019; Jeong et al. 2020b). In this study, the average of Zn/Cu ratio in RDS was 5.1, implying that these elements affected by traffic activities related to the abrasion

of tires and brake pad. Fig. 5 showed the relationship between Pb isotope composition and Zn/Cu and Cu/Sb elemental ratios.

Although $^{206}Pb/^{207}Pb$ and Zn/Cu ratio were dispersed, RDS and soils were clearly distinguished. However, some of stream sediments showed similar characteristics to RDS. Stream sediments and soil around the industrial complex at the upstream of Suyeong river had low $^{206}Pb/^{207}Pb$ and high Zn/Cu ratio (>20) and were clearly distinguished from most sediment samples affected by traffic activity. This means that PTEs accumulated inside of industrial facilities have transported into the streams during rainfall.

Cu is also used has been used as a potential tracer for aerosol emission related to traffic activities (Pio et al. 2013). Iijima et al. (2007) reported that Cu/Sb ratio in brake pads ranged from 9.1 to 20. They also discussed that different brands of brake pads may have different Cu/Sb ratio. The Cu/Sb ratios reported a value of 2.17 ± 0.83 for fine PM and 9.1 ± 1.8 for coarse PM in road dust (Lin et al. 2005). In this study, the Cu/Sb ratio in RDS showed an average value of 10.9 ± 5.7 and is comparable to those in published data (Iijima et al. 2007, Lin et al. 2005). The I_{geo} value of Sb in RDS was very high compare to other toxic elements in this study. Therefore, most of RDS is considered to be polluted by traffic activities.

The Cu/Sb ratio in stream sediments and soils were 22.3 and 21.8, respectively, which was higher than the RDS. However, the Igeo result of Sb corresponds to the moderately pollution level in stream sediments and soil. Our previous study reported that the Sb concentration in TSS in urban runoff was 32 times higher that compared to before rainfall event and the high concentration exceeding 2.0 mg/kg in the marine sediments connected the Suyeong river was observed (Jeong et al. 2019; 2020b). Thus, RDS polluted with PTEs enter into the stream or coastal environments during rainfall.

Many studies have reported that the transportation by stormwater runoff and re-suspension of deposited particle including RDS in impervious layer of urban environments are important causes of PTEs pollution in aquatic environments and atmosphere, thus environmental concerns are recently increasing (Ram et al. 2014; Jeong et al. 2020a; 2020b; Lanzerstorfer 2020). High level of PTEs in RDS existing in urban road can transport the marine environments through stream and river during rainfall and also spreads into the atmosphere, adversely affecting human health. Further studies are needed to efficiently remove the RDS accumulated on the road surface and accurately identify and manage for PTEs pollution sources in urban environment.

4. Conclusions

We investigated the PTEs concentration in RDS, stream sediments and soils. The level of pollution and ecological risk for PTES were evaluated using various pollution assessment indices. Potential pollution sources for PTEs in RDS, stream sediment and soil were also discussed using Pb isotope composition and elemental ratio in sediment samples of this study. The concentrations of PTEs in RDS was much higher compared to stream sediment and soil. Based on Igeo results, the pollution degree of Sb, Cd, Zn, Cu and Pb related to traffic activity is much higher than other toxic elements (Cr, Ni and Hg). The PER values for the nine PTEs in RDS are high enough to bring serious ecological risk and Sb and Cd are particularly serious. Therefore, the PTEs pollution in RDS is mostly attributed to traffic activities such as the abrasion of tire and brake pad.

$^{206}Pb/^{207}Pb$ ratio showed the lowest value in RDS and increased in the order of stream sediments and soils, implying that RDS is one the main sources of PTEs pollution in stream sediments. The results of Pb isotope composition and elemental ratio of Zn/Cu and Cu/Sb suggest that the PTEs in urban environments are mostly derived from traffic sources. The PTEs pollution source of stream sediment was found to be related to RDS rather than soil. However, the stream sediments and soils around the industrial complex showed high PTEs concentrations. The combination of Pb isotope composition and Zn/Cu ratio appeared as a good tool to distinguish the influence of traffic and industrial activities.

Our study indicates that RDS contaminated with PTEs accumulated in the impermeable layer of urban environment could flows into stream in the form of non-point sources during precipitation. Therefore, efficient management of RDS is very important to reduce PTEs contamination that migrates to the stream environment as a non-point source.

Acknowledgements

This research was supported by project from Korea Institute of Ocean Science and Technology (PE99812).

Figure captions

Fig. 1 Sampling sites of RDS (left), soil, and stream sediments (right) in Busan, South Korea.

Fig. 2 Comparison of PTEs concentrations and Pb isotopic ratios in RDS, stream sediment (SS), soil of this study with our published data for total suspended solids (TSS) in rainfall runoff samples by Jeong et al. (2019).

Fig. 3 Spatial distributions of nemerow pollution index (P_N) in RDS, stream sediment, and soil samples.

Fig. 4 Diagram of $^{206}Pb/^{207}Pb$ vs $^{208}Pb/^{206}Pb$ (left) and Li/Pb vs $^{207}Pb/^{206}Pb$ (right) in RDS, soil, stream sediment (this study), and the literature data in Korea (RDS from industrial region; Jeong et al., 2018).

Fig. 5 Diagram of Zu/Cu (left) and Cu/Sb vs $^{206}Pb/^{207}Pb$ in RDS, soil, stream sediment of this study.

Table captions

Tab. 1 Average (mean ± SD) of particle size(μm), PTEs concentrations (mg/kg), and Pb isotopic ratios in RDS, soil, stream sediment, and TSS in rainfall runoff.

Tab. 2 Assessment of pollution level for each toxic element using I_{geo} values in RDS, soil, steam sediment, and TSS in runoff.

Tab. 3 Assessment of ecological risk using single potential risk factor (E^i_r) values in RDS, soil, steam sediment, and TSS in runoff.

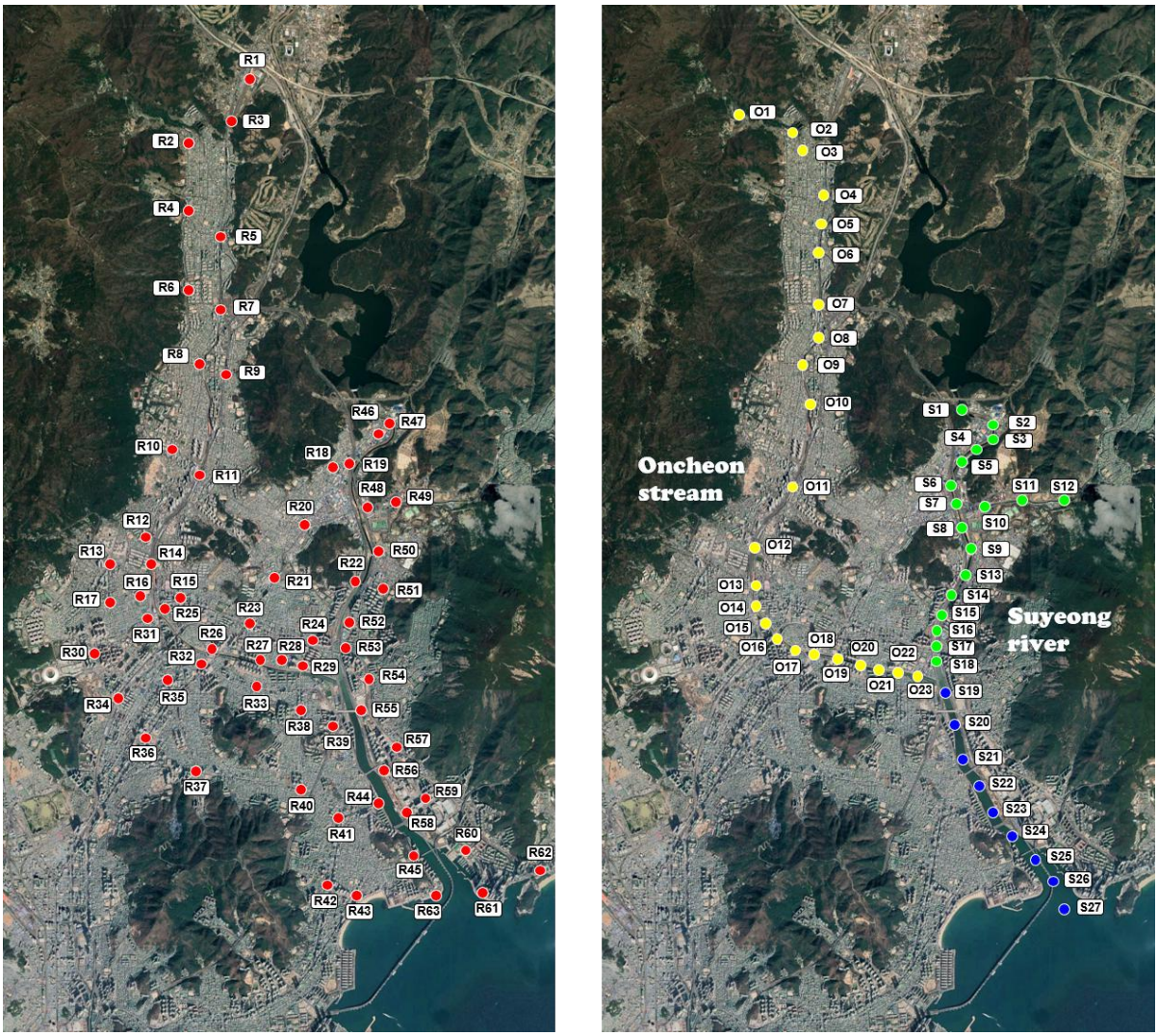


Fig. 1. Sampling sites of RDS (left), soil, and stream sediments (right) in Busan, South Korea.

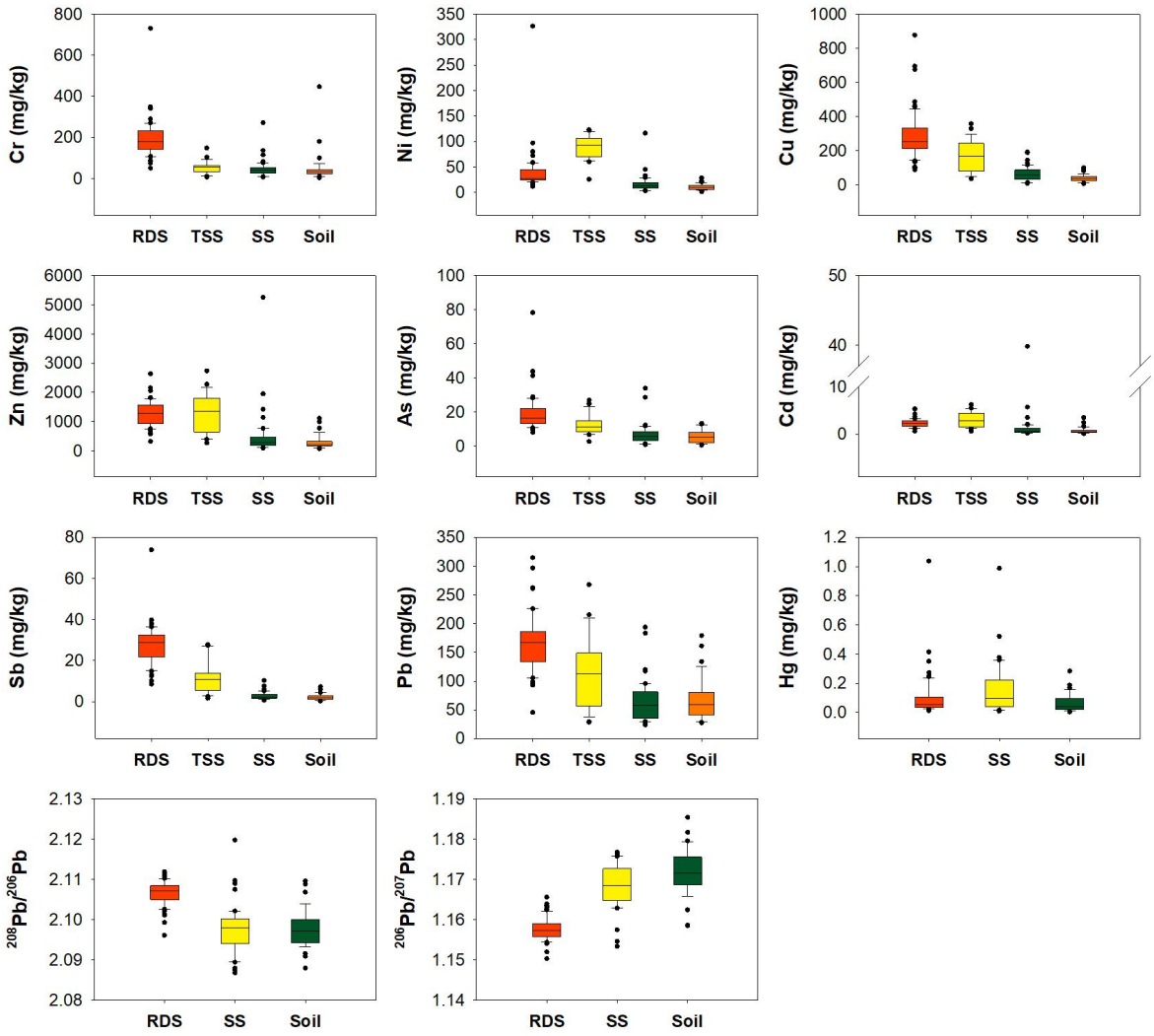
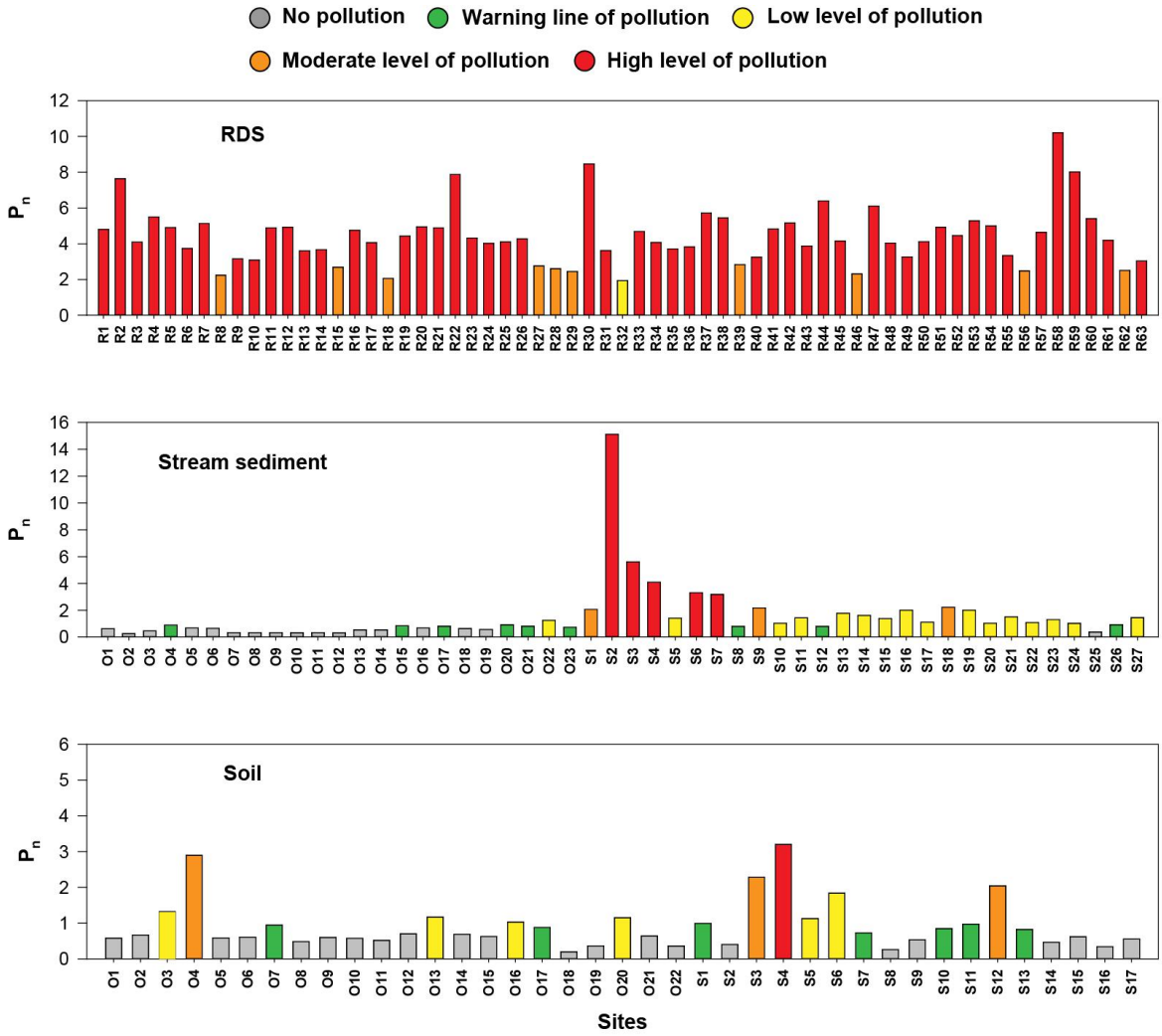


Fig. 2. Comparison of PTEs concentrations and Pb isotopic ratios in RDS, stream sediment (SS), soil of this study with our published data for total suspended solids (TSS) in rainfall runoff samples (Jeong et al., 2019).



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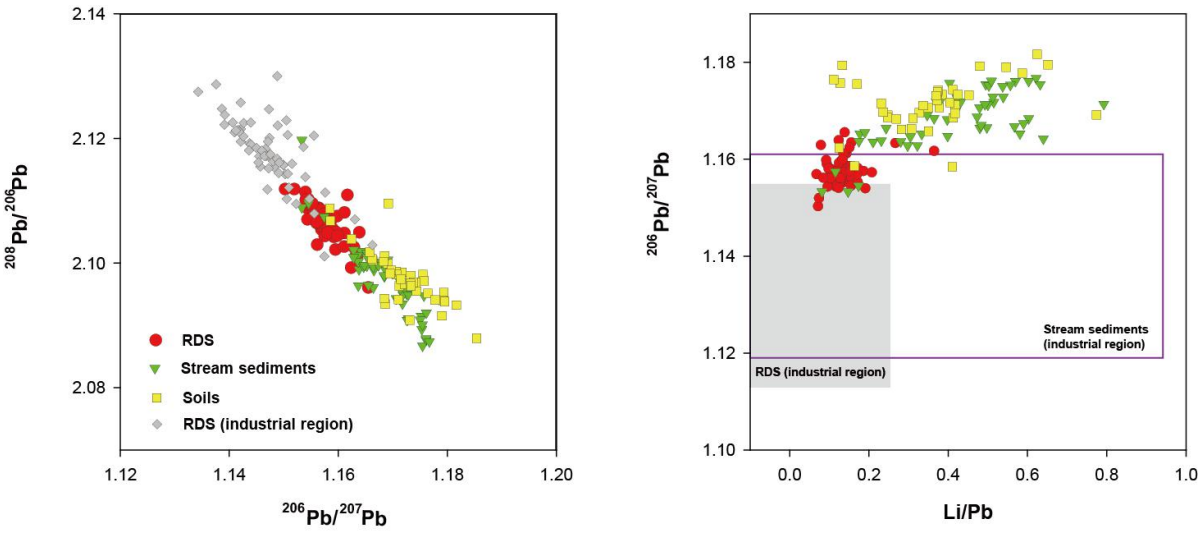

Fig. 4. Diagram of $^{206}Pb/^{207}Pb$ *vs* $^{208}Pb/^{206}Pb$ (left) and Li/Pb *vs* $^{207}Pb/^{206}Pb$ (right) in RDS, soil, stream sediment (this study), and the literature data in Korea (RDS from industrial region; Jeong et al., 2018).

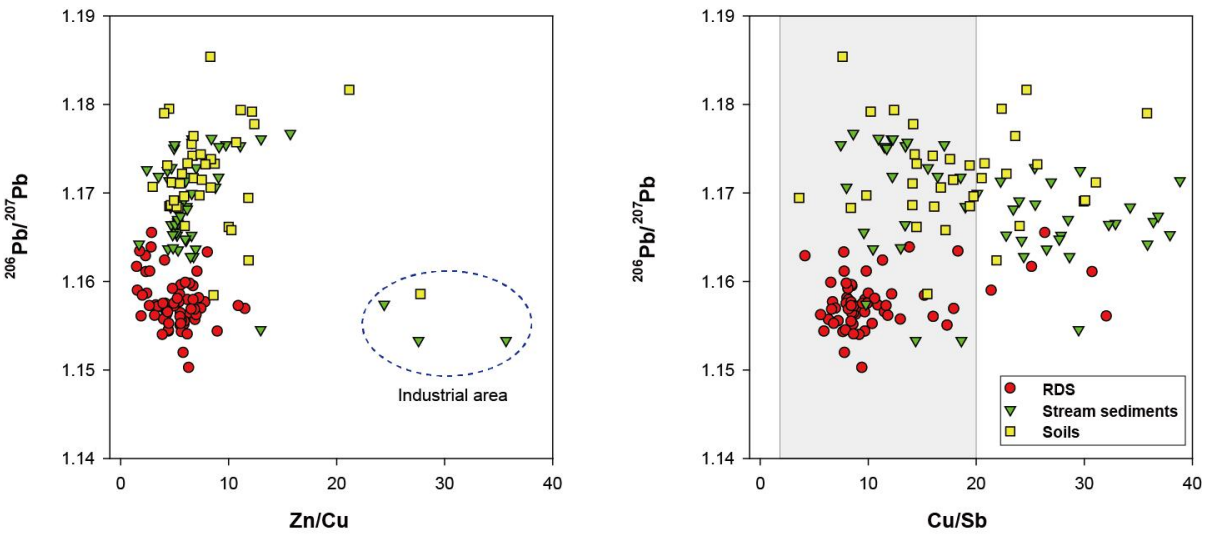

Fig. 5. Diagram of Zu/Cu (left) and Cu/Sb *vs* $^{206}Pb/^{207}Pb$ in RDS, soil, stream sediment of this study.

Tab. 1. Average (mean ± SD) of particle size(μm), PTEs concentrations (mg/kg), and Pb isotopic ratios in RDS, soil, stream sediment, and TSS in rainfall runoff.

	RDS (n=63)	**Soil** (n=39)	**Stream sediment** (n=50)	TSS in runoff[a]	SQG[b]
Particle size (μm)	162 ± 58 (68–315)	423 ± 216 (10–749)	445 ± 244 (10–771)	-	-
Li (mg/kg)	20.6 ± 3.3 (13.3–33.4)	20.8 ± 5.3 (12.5–39.7)	22.6 ± 9.6 (13.8–62.7)	21.3 ± 10.5 (2.0–45.2)	-
Cr (mg/kg)	195 ± 94 (50–730)	49 ± 72 (2–446)	47 ± 41 (6–271)	68 ± 36 (11–167)	64
Ni (mg/kg)	39.2 ± 40.2 (11.4–326.0)	11.0 ± 5.8 (1.0–28.3)	16.5 ± 17.0 (2.8–116.2)	21.5 ± 7.7 (9.1–36.6)	45
Cu (mg/kg)	284 ± 138 (87–876)	43 ± 38 (5–233)	61 ± 42 (7–191)	199 ± 116 (43–434)	63
Zn (mg/kg)	1275 ± 428 (315–2634)	282 ± 227 (63–1109)	482 ± 771 (81–5254)	1514 ± 859 (328–3571)	250
As (mg/kg)	19.3 ± 10.2 (8.1–78.3)	5.7 ± 3.6 (0.6–13.4)	6.8 ± 6.0 (0.8–34.0)	14.8 ± 6.3 (3.8–29.1)	12
Cd (mg/kg)	2.3 ± 0.9 (0.6–5.3)	0.7 ± 0.6 (0.1–3.5)	1.7 ± 5.6 (0.2–39.8)	3.2 ± 1.8 (0.7–6.9)	10
Sb (mg/kg)	27.6 ± 9.5 (8.5–73.8)	2.1 ± 1.5 (0.2–7.2)	2.8 ± 1.8 (0.7–10.2)	11.8 ± 8.1 (1.6–27.7)	20
Pb (mg/kg)	166 ± 49 (45–314)	68 ± 37 (27–179)	63 ± 36 (24–194)	112 ± 66 (25–253)	140
Hg (mg/kg)	0.10 ± 0.14 (0.01–1.04)	0.06 ± 0.06 (0.00–0.28)	0.16 ± 0.18 (0.01–0.99)	-	6.6
$^{208}Pb/^{206}Pb$	2.1066 ± 0.0029 (2.0961–2.1119)	2.0977 ± 0.0045 (2.0879–2.1096)	2.0975 ± 0.0061 (2.0867–2.1197)	-	-

$^{206}Pb/^{207}Pb$	1.1576 ± 0.0029 (1.1503–1.1655)	1.1719 ± 0.0057 (1.1585–1.1854)	1.1683 ± 0.0059 (1.1533–1.1767)	-	-

[a]Jeong et al., 2019; [b]CCME2007

Tab. 2. Assessment of pollution level for each toxic element using I_{geo} values in RDS, soil, steam sediment, and TSS in runoff.

	Cr	Ni	Cu	Zn	As	Cd	Sb	Pb	Hg
RDS[a]	0.4	-1.1	2.6	3.6	1.3	3.8	5.4	2.6	-0.2
Soil[a]	-2.1	-2.9	-0.4	1.2	-0.7	1.9	1.5	1.2	-1.0
Stream sediment[a]	-2.0	-2.5	0.2	1.6	-0.5	2.3	2.0	1.1	0.2
TSS in Runoff[b]	-1.3	-1.8	1.9	3.7	0.9	4.2	3.9	1.9	-
	I_{geo}<0; No pollution				0<I_{geo}<1; No pollution ~ moderate pollution				
	1<I_{geo}<2; Moderate pollution				2<I_{geo}<3; Moderate pollution ~ strong pollution				
	3<I_{geo}<4; Strong pollution				4<I_{geo}<5; Strong pollution ~ extremely strong pollution				
	I_{geo}>5; Extremely strong pollution								

a: this study, b: Jeong et al., 2019

Tab. 3. Assessment of ecological risk using single potential risk factor (E^i_r) values in RDS, soil, steam sediment, and TSS in runoff.

	Cr	Ni	Cu	Zn	As	Cd	Sb	Pb	Hg
RDS[a]	4	4	51	19	40	694	483	49	82

Soil[a]	1	1	8	4	12	218	37	20	49
Stream sediment[a]	1	2	11	7	14	518	49	19	128
TSS in Runoff[b]	1	2	35	23	31	964	207	33	-
	E^i_r<40; Low ecological risk					40<E^i_r<80; Moderate ecological risk			
	80<E^i_r<160; Higher ecological risk					160<E^i_r<320; High ecological risk			
	E^i_r>320; Serious ecological risk								

a: this study, b: Jeong et al., 2019

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