Potentially toxic elements pollution in road deposited sediments around the active smelting industry of Korea

Hyeryeong Jeong1,2, Jin Young Choi2 & Kongtae Ra1,2*

Potentially toxic elements (PTEs) were investigated in the different sizes of road deposited sediments (RDS) around the active smelting industry to understand their sources and to assess the pollution and ecological risk levels. The highest PTEs concentrations was shown near the raw materials import port and the smelting facilities. The fine particles of RDS showed extremely high PTEs concentrations. Zn has the highest mean concentration in the < 63 μm particle size of RDS, followed by Pb > Cu > As > Cr > Ni > Cd > Hg. The PTEs concentrations of this study were the highest values compared to the soils around the smelter and the RDS in urban and industrial areas in the world. This indicates that these PTEs pollution in RDS were mainly attributed to the transportation of raw materials for the smelting industry. According to nemerow pollution index calculation, RDS at all sampling sites with particles of less than 250 mm was seriously polluted with PTEs. The ecological risk was also found to be very high in all RDS fractions and highly toxic elements such as Cd, Pb and Hg pose extremely risk. Given the total amounts PTEs in the road surface, it is necessary to apply RDS removal management plan to reduce the PTEs pollution.

Road infrastructure and transportation are important components of urban areas and have enabled the rapid development of industrialization and urbanization. Road deposited sediments (RDS) are highly contaminated with potentially toxic elements (PTEs) by various traffic and industry-related sources such as vehicular exhaust and non-exhaust sources, atmospheric deposition and surrounding soil erosion and spill of industrial raw materials during transportation1–4. Thus, roads are often a prominent point-source and non-point source of dissolved and sediment-associated PTEs6–10. The particle size distribution of RDS is a very important factor as it determines the behavior and mobility of the particles and shows the highest concentration of PTEs in fine particles11–13. Environmental concern related to RDS is that RDS containing high concentrations of PTEs on the road surface adversely affects the surrounding environments as well as human health14–16. The fine fractions of RDS are readily transported to the surrounding aquatic environments by stormwater runoff. Many studies reported that the fine particle (< 44 μm17, < 63 μm18, < 125 μm6) largely contributed of total suspended solids (TSS) load in stormwater runoff from urban and industrial areas. The finer RDS are also re-suspended by strong winds and the high-speed movement of the vehicles, therefore, PTEs bound to fine particles of RDS and surrounding soils can enter the human body via inhalation, ingestion and dermal absorption19–21. Our previous study reported that 14.3–15.8 g/m² (< 63 μm) and 3.2–4.2 g/m² (> 1000 μm) of RDS in urban area accumulate on the road surface in Korea22. On road surface, RDS are deposited of 11.7 g/m² in urban area17 and 174.6 g/m² in industrial area6. Industrial areas are characterized by a higher accumulation of road dust than urban areas. In Korea, the amounts and concentrations of PTEs in fine particle of RDS were much higher in industrial area than in urban areas22,23. Given the total length of road, a huge amount of PTEs would have been accumulated in road surface. Of course, PTEs pollution in industrial RDS is subjected to the complex influence of traffic and industrial activities. Lanzerstorfer13 reported that the PTEs concentrations in urban RDS can be used as a useful indicator for environmental pollution. The potential sources of PTEs can be identified by evaluating the PTEs concentrations in RDS from different land use types and the elemental ratios of them11,24–26. Although there are very few RDS studies in industrial areas compared to urban areas, the study of PTEs concentration in RDS from the industrial area will make it possible to differentiate between transport and industrial activities. The objectives of this study are to: (1) evaluate the PTEs

1Marine Environmental Research Center, Korea Institute of Ocean Science and Technology (KIOST), Busan 49111, Korea. 2Department of Ocean Science (Oceanography), KIOST School, University of Science and Technology (UST), Daejeon 34113, Korea. *email: ktra@kiost.ac.kr
pollution levels of different RDS sizes in the industrial area where the smelting industry is active; (2) identify the pollution sources of PTEs; (3) assess the potential ecological posed by PTEs.

Materials and methods

Sampling and PTEs analysis. Total of 14 RDS samples were collected from Onsan Industrial complex including several smelting facilities of Korea (Fig. 1) during December 2013 following a dry weather periods of about 10 days. Average temperature, humidity, and wind speed were 4.3 °C, 52.0%rh, and 6.7 m/s respectively. The RDS were collected in four and more sub-sampling for each site using a cordless vacuum cleaner (DC-35, Dyson Co., UK) with 0.5 m × 0.5 m space along the curb of the road. This vacuum cleaner can collect dust with high efficiency using powerful centrifugal forces spin. After collecting RDS samples, the vacuum cleaner was disassembled and cleaned, and the parts that were difficult to clean were replaced with new ones to prevent cross-contamination. Each RDS sample were sieved individually using < 63 μm, 63–125 μm, 125–250 μm, 250–500 μm, 500–1000 μm, >1000 μm by using vibratory sieve shaker (Analysette 3 pro, Fritsch Co., Germany) with nylon sieves in laboratory. Each fraction of RDS sample was weighted, pulverized (Pulverisette 6, Fritsch Co., Germany) and stored separately into pre-acid cleaned polyethylene bottle until metal analysis. The weight (g) of each RDS size fraction accounted for 7.3% (< 63 μm), 11.8% (63–125 μm), 23.2% (125–250 μm), 31.8% (250–500 μm), 17.1% (500–1000 μm), and 8.9% (>1000 μm) of the total RDS samples. About 0.1 g of each ground and homogenized RDS sample was weighted in Teflon digestion vessel added with high purity (Ultra-100 grade, Kanto Chemical, Japan) of HNO₃, HF and HClO₄ on a hot plate at 180 °C for 24 h for total digestion. After evaporation and redissolution with 2% HNO₃, heavy metals of Cr, Ni, Cu, Zn, As, Cd and Pb were analyzed using inductively coupled plasma mass spectrometry (ICP-MS, iCAP-Q, Thermo Scientific Co., Germany). Hg was determined using Hg analyzer (Hydra-C, Leeman Labs, USA) based on the USEPA 7473 method. The blanks and duplicate measurements were performed for quality control. Two types of certified reference materials for MESS-4 and PACS-3 (National Research Council, Canada) were used to check data accuracy. Recoveries ranged between 96.4% and 102.1% for MESS-4 and between 93.9% and 106.0% for PACS-3, respectively.

Pollution level assessment. The geo-accumulation index (Igeo), proposed by Muller²⁸, can be used to assess the pollution level of individual metal using the following equation:

\[ I_{geo} = \log_2 \left( \frac{C_i}{(1.5 \times B_i)} \right) \]

where \( C_i \) and \( B_i \) are the concentrations of RDS samples and the geochemical background values²⁹, 1.5 is the background correction efficient. \( I_{geo} \) value were classified into seven categories²⁸,³⁰.

The nemerow index \( (P_N) \) are widely used to make a comprehensive evaluation of the pollution levels of heavy metals in soils and sediments³¹–³⁵ and was calculated using the following equation:

\[ P_N = \sqrt{\frac{1}{n} \sum_{i=1}^{n} P_i^2 + (\text{Max } P_i)^2} \]

where \( P_i \) represent a single pollution index of metal \( i \), \( P_i = C_i/S_i \), \( C_i \) is the measured concentration of each metal \( i \). The calculated results of \( P_N \) using the geological background value can be overestimated the magnitude of metal pollution³⁶. Therefore, the soil quality guideline values were used in this study to better reflect the comprehensive pollution level of heavy metals in Korea. \( S_i \) is the soil pollution concern standard for road and factory
site in Korea and its values (mg/kg) of Cr\textsuperscript{6+}, Ni, Cu, Zn, As, Cd, Pb and Hg were 40, 500, 2000, 2000, 200, 60, 700 and 20, respectively\textsuperscript{27}. In Korea, soil samples are sieved with a 150 μm mesh. PTEs in soils (< 150 μm) are analyzed and compared with the soil pollution concern standard. In case of Cr, in Korea soil quality guideline, the concentration of Cr\textsuperscript{6+} is recommended. Lazo\textsuperscript{38} reported that the content of Cr\textsuperscript{6+} accounts for more than 90% of total Cr in the contaminated area. Therefore, the application of total Cr concentration instead of Cr\textsuperscript{6+} of this study did not significantly affect the results of pollution evaluation for eight metals using P\textsubscript{cr}. This index divides pollution into five grades\textsuperscript{39}.

**Potential ecological risk assessment.** Potential ecological risk index (PER), proposed by Hakansson\textsuperscript{40} can be used to assess the risk of eight metals based on their toxicity response using the following equations:

\[
E_i^r = T_i^r \times (G_i/B_i)
\]

\[
PER = \sum_{i=1}^{n} E_i^r
\]

where C\textsubscript{i} and B\textsubscript{i} were the same as those in I\textsubscript{geo} calculation. E\textsubscript{i}\textsuperscript{r} is the single factor ecological risk degree for PTEs. T\textsubscript{i}\textsuperscript{r} is the toxic response factor for a single metal pollution (Hg = 40, Cd = 30, As = 10, Cu = Ni = Pb = 5, Cr = 2, Zn = 1)\textsuperscript{40,41}. E\textsubscript{i} were classified into five classes\textsuperscript{42} and the PER value were classified into four classes\textsuperscript{40,43}. PASW statistics program (version 18) was used for the Pearson's correlation analysis and principal component analysis (PCA) to extract correlation among PTEs in this study. Hierarchical cluster analysis (HCA) was also performed to understand the relationship between different size fractions of RDS.

**Grain size fraction loading.** The grain size fraction loading (GS\textsubscript{floading}) was calculated using the relative mass loads of PTEs in the six particle size fractions of the RDS, which is expressed as follows:

\[
\text{GSF}_{\text{loading}} = 100 \times \left( \frac{X_i \times GS_i}{\sum_{i=1}^{6} X_i \times GS_i} \right)
\]

where X\textsubscript{i} is the concentration of PTEs by particle size fraction separated from each RDS sample, and GS\textsubscript{i} is the mass percentage of each particle size fraction. The sum of the GS\textsubscript{floading} values for each RDS sample is always 100%\textsuperscript{44}.

**Results and discussion**

**PTEs contents in different sizes of RDS.** The minimum, maximum and mean values of the total RDS amount and Cr, Ni, Cu, Zn, As, Cd, Pb, and Hg concentrations are shown in Table 1. Crustal elements such as Al, Fe, and Li showed no significant difference depending on different sizes of RDS (Table S1). The Cu, Zn, As, Cd, Pb, and Hg concentrations significantly increased with decreasing in particle size of RDS (Fig. 2). Mean PTE concentrations in the fine particle size (< 63 μm) of RDS was 5.0 (Cr) ~ 55.5 (Zn) times higher than those in the large particle size (> 1000 μm). The mean concentration of RDS (63 μm) was highest for Zn at 34,592 mg/kg, followed by Pb (13,561 > Cu (7071) > As (961) > Cr (596) > Ni (364) > Cd (225) > Hg (17). The Cr and Ni concentrations in the fine particle size (< 63 μm) showed highest values at S6 site, but the highest concentrations for Cu, Zn, As, Cd were observed in S4 and S5 sites which the smelting facilities exist (Fig. S1 and S2).

The study area, Onsan industrial complex, has concentrated non-ferrous metal production industry of Korea. There are many smelting facilities in operation that produces 1.2 Mt of nonferrous metals annually, including Cu, Zn, Cd and Pb. The largest smelter in this study region produces high-purity ingots for Cu 25,800 t, Zn 650,100 t, and Pb 413,000 t. Garmash (1985)\textsuperscript{45} found that nonferrous metal smelters are more contaminated with Zn, Pb, and Cd in soils than iron smelters. The amount of RDS accumulated on road surface in the study area is higher than that in urban areas. There are raw material import ports and outdoor raw material storages for smelting industry on the north of S4 site.

The PCA results indicated that the two principal components explaining 72.498% of the total variance (Table S2). Kaiser–Meyer–Olkin (KMO) value was found to be 0.745 and Bartlett's test value was 0 (p<0.001), confirming to be suitable for PCA analysis. PC1 was dominated by Cu, Zn, As, Cd, and Pb, accounting for 50.034% of the total variance (Table S2). RDS of this study is significantly correlated with among Cu, Zn, As, Cd, and Pb. Raw materials are transported using a large truck. The highest PTEs concentrations were observed in all particle sizes of RDS around the smelting facilities, indicating that raw materials for the smelting industry were spilled onto the road surface during transportation. PC2 consisted of Cr and Ni, explaining 22.464% of the total variance (Table S2). A high correlation between Cr and Ni was observed. Cr and Ni are discharged from furnaces during the manufacture of iron and steel, and also used in alloy manufactures such as stainless steel and chromium plating\textsuperscript{46}. Jo et al.\textsuperscript{47} reported that Cr and Ni contamination in roadside soil was affected by traffic and industrial activities in Korea. Generally, Cr is used in vehicle parts including metal plating, wrist pins, and connecting rods\textsuperscript{48}. Adamiec et al.\textsuperscript{49} reported that the urban and motorway road dust were contaminated with Cr from the abrasion of brake and alloys (wrist pins and connecting rods). In this study, the contamination of Cr and Ni was lower than that of other metals, indicating that Cr and Ni contamination was not directly related to the smelting industry. The highest concentrations of Cr and Ni were observed at S11 site, with high traffic activity connected to the highway. Therefore, Cr and Ni were more related to traffic activities in this area.

Hierarchical cluster analysis was also conducted to understand the relationship among the different sizes of RDS. The dendrogram of the different particle sizes of RDS shows two cluster groups (Fig. S3). Group 1 comprises...
two particle size fractions (< 125 μm) with significant PTEs contamination. Group 2 corresponded to the particle size of < 125 μm with moderate PTEs contamination. The PTEs concentrations of this study are higher than those of RDS in urban area of Korea 10,22,23, indicating that RDS of industrial area are mainly influenced by industrial activities related to transportation of raw materials for smelting industry. In particular, the concentration of PTEs in the fine (< 63 μm) size of RDS in this study were the highest values compared to the RDS in urban cities3,22,49–51 and the soils around the smelter52–62 in the world (Table 2).

Pollution assessment in industrial RDS. Based on PTEs concentrations in different particle sizes of RDS, quantification of PTEs pollution was conducted using the Igeo and PN indices. Comparison of mean Igeo values in different particles size of RDS is shown in Table 3. RDS of less than 63 μm had the highest Igeo value for all PTEs. The mean of Igeo values of PTEs for < 63 μm size of RDS are arranged in the following order: Cd > Pb > Zn > Hg > Cu > As > Ni > Cr. The mean values of Igeo for Cr and Ni show that the large particle (> 125 μm) is not polluted, but the fine particle (< 125 μm) is characterized as medium to heavily pollution. The mean values of Igeo showed that the RDS less than 1000 μm have an extremely heavy pollution for Cu, Zn, Cd, and Pb. For the case of As and Hg, the mean values of Igeo in RDS less than 125 μm exceeded 5 corresponding extremely heavy pollution, and RDS larger than 500 μm had relatively low pollution levels.

The results of nemerow index (PN) showed that the mean values were in the descending order of less than 63 μm (23.2) > 63–125 μm (12.8) > 125–250 μm (5.8) > 250–500 μm (4.7) > 500–1000 μm (7.5) > above 1000 μm (2.2). As the RDS size decreased, the PN value increases. Generally, fine particle sizes of RDS have high concentrations of PTEs than coarse particles6,17. For the RDS size less than 250 μm, PN values are significantly exceeding 3 at all sampling sites, representing serious polluted with PTEs (Fig. 3).

| Size (μm) | RDS (g/m²) | Cr (mg/kg) | Ni (mg/kg) | Cu (mg/kg) | Zn (mg/kg) | As (mg/kg) | Cd (mg/kg) | Pb (mg/kg) | Hg (mg/kg) |
|----------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| > 1000   |            |            |            |            |            |            |            |            |            |
| Min      | 4          | 51         | 26         | 71         | 256        | 3          | 0.9        | 65         | 0.01       |
| Max      | 298        | 220        | 68         | 3212       | 3735       | 100        | 20.9       | 1685       | 27.9       |
| Mean     | 104        | 120        | 46         | 623        | 623        | 46         | 6.3        | 470        | 2.5        |
| SD       | 92         | 56         | 15         | 846        | 846        | 28         | 5.0        | 418        | 7.4        |
| 500–1000 |            |            |            |            |            |            |            |            |            |
| Min      | 30         | 76         | 28         | 249        | 1177       | 10         | 2.0        | 209        | 0.1        |
| Max      | 688        | 2262       | 1156       | 7537       | 16,579     | 187        | 45.9       | 4083       | 54.6       |
| Mean     | 200        | 410        | 166        | 2243       | 7167       | 67         | 11.5       | 1483       | 4.5        |
| SD       | 193        | 552        | 287        | 2016       | 5186       | 49         | 11.2       | 1107       | 14.4       |
| 250–500  |            |            |            |            |            |            |            |            |            |
| Min      | 85         | 80         | 23         | 294        | 1518       | 25         | 2.2        | 240        | 0.1        |
| Max      | 1104       | 435        | 187        | 8477       | 20,034     | 341        | 64.2       | 6264       | 62.4       |
| Mean     | 373        | 249        | 111        | 2782       | 8646       | 92         | 18.8       | 2171       | 5.5        |
| SD       | 330        | 107        | 50         | 2170       | 5708       | 85         | 16.9       | 1560       | 16.4       |
| 125–250  |            |            |            |            |            |            |            |            |            |
| Min      | 72         | 100        | 23         | 284        | 1279       | 12         | 3.7        | 268        | 0.3        |
| Max      | 704        | 678        | 556        | 10,875     | 26,279     | 374        | 157.9      | 10,311     | 69.6       |
| Mean     | 272        | 285        | 147        | 2978       | 6743       | 141        | 38.0       | 3072       | 7.2        |
| SD       | 223        | 138        | 127        | 2708       | 6135       | 110        | 39.4       | 2718       | 18.1       |
| 63–125   |            |            |            |            |            |            |            |            |            |
| Min      | 53         | 199        | 54         | 348        | 2152       | 59         | 7.4        | 463        | 0.4        |
| Max      | 335        | 921        | 645        | 16,511     | 112,751    | 840        | 644.1      | 23,536     | 46.4       |
| Mean     | 138        | 476        | 222        | 5265       | 19,620     | 330        | 128.7      | 7924       | 8.9        |
| SD       | 94         | 217        | 153        | 4258       | 28,085     | 204        | 162.6      | 6927       | 11.9       |
| <63      |            |            |            |            |            |            |            |            |            |
| Min      | 28         | 200        | 106        | 975        | 4400       | 110        | 17.6       | 1253       | 1.2        |
| Max      | 197        | 1416       | 1081       | 18,873     | 166,457    | 2721       | 975.6      | 44,667     | 45.1       |
| Mean     | 85         | 596        | 364        | 7071       | 34,592     | 961        | 225.1      | 13,561     | 17.0       |
| SD       | 50         | 368        | 299        | 5552       | 44,856     | 744        | 278.6      | 12,438     | 13.2       |

Table 1. Minimum, maximum, and mean values of PTEs in the different sizes of road deposited sediments of this study.
Figure 4 shows the spatial distribution of PN values in the different sizes of RDS. The spatial distribution of PN values for < 125 μm was high around the smelting facilities, but relatively low at the sampling sites away from the smelters. The high pollution degree of RDS (< 125 μm) indicates that the fine particles of RDS are attached to the tires according to vehicle transport and spreads through the entire road surface. Additionally, the chimney of smelter and vehicle emissions are other potential sources of PTEs in RDS. Bennett and Knapp reported that the median particle size emitted from Cu, Zn, and Pb smelter ranged from 0.1 to 2.2 μm. The particle size emitted by engine combustion of a vehicle is very small in the size range of 20–150 nm. Given the RDS amounts and spatial distribution of PTEs deposited in the road surface and, the major cause of PTEs contamination in RDS of this study is probably due to spillage and diffusion of raw ore minerals during transportation rather than particulate emissions from smelters.

Ecological risk assessment in industrial RDS. The results of single factor ecological risk degree (Ei) are presented in Table 4. The highest mean Ei value was observed for Cd (75,044) in < 63 μm of RDS and the lowest Ei value was observed for Cr (2.6) in > 1000 μm of RDS. Similar to the PTEs concentrations, the single ecological risk was higher as the particle size of RDS decreased. The mean of single factor ecological risk degree (Ei) values of Cr and Ni in all particle sizes was less than 40, which indicated that Cr and Ni concentrations of RDS correspond to the low ecological risk level. The mean values of Ei of Cd were the highest among those of all PTEs for all sampling sites and ranged from 2095 (> 1000 μm) to 75,044 (< 63 μm), indicating extremely...
potential risk levels ($E_i^r > 320$). Hg has the second highest $E_i^r$ values and exceed 320 in all particle sizes of RDS, showing extremely potential risk. For Cu and Pb, the mean of $E_i^r$ values were also obtained extremely potential risk except for the large RDS size > 1000 μm. Generally, the $E_i^r$ values were ranked in the following order: Cd > Hg > Pb > Cu > As > Zn > Ni > Cr. The mean of PER values, the comprehensive ecological risk of eight PTEs, ranged from 4434 (> 1000 μm) to 96,435 (< 63 μm) and the fine particle was 21.7 times higher that large particle. The PER values exceeded 600, indicating very high ecological risk for all studied sites and particle size of RDS except for > 1000 μm at S11 site (Fig. 3).

PTEs loads in RDS on the road surface around the active smelting industry. The mean of RDS amount in road surface were 104 for > 1000 μm, 200 for 500–1000 μm, 373 for 250–500 μm, 272 for 125–250 μm, 138 for 63–125 μm, 85 g/m² for < 63 μm, respectively (Table 1). Spatial distribution of amounts in different particle sizes of RDS is shown in Fig. S4. The amount of RDS with particle size of 250–500 μm was the most abundant in this study. We also calculated the PTEs loads and the contribution of each particle size fraction using $G_{SFloading}$ (Fig. 5). A significant amount of PTEs (21,872 mg/m²) has accumulated on the road surface in industrial area. The each PTEs load in industrial RDS was much higher than in urban RDS17. The order of the sum PTEs loading value in RDS for all measured PTEs was less than 63 μm (26.3%) > 250–500 μm (23.6%) > 63–125 μm (22.5%) > 125–250 μm (16.7%) > 500–1000 μm (9.6%) > above 1000 μm (1.3%). Among the eight PTEs, Zn had the highest $G_{SFloading}$ value per unit area (11,802 mg/m²) of road surface, in the order of Cu (4984) > Pb (4177) > Cr (370) > As (215) > Ni (169) > Cd (47) > Hg (4). Given the $G_{SFloading}$ and PTEs concentrations, particles of 250–500 mm showed the highest contribution for Cr, Ni, Cu and Zn, but the mean values of $G_{SFloading}$ were dominant in the < 63 μm fraction for As, Cd, Pb, and Hg (Fig. 6).

Table 2. Comparison between the average (median value in parenthesis) PTEs concentrations (mg/kg) in the road deposited sediment (< 63 μm) and those in the other published data.

| Cr   | Ni  | Cu   | Zn   | As   | Cd  | Pb   | Hg   | Sample types | References                      |
|------|-----|------|------|------|-----|------|------|--------------|--------------------------------|
| 596  | 364 | 7071 | 34,592 | 18,362 | 961 | 1228 | 13,561 | <63 μm, RDS | This study (N = 14)               |
| 167  | 50  | 160  | 907   | 955  | 15.7 | 14.0 | 207 (181) | <63 μm, RDS | Urban, Korea (N = 5)             |
| 841  | 246 | 193  | 2982  | 2739 | 16.0 | 15.7 | 221 (159) | <63 μm, RDS | Industrial, Korea               |
| 52.1 | 345 | 1271 | 2.3   | 223  | <75 μm RDS | Urban, Korea               |
| 124  | 630 | 38   | 350  | <63 μm, RDS | Urban, Spain              |
| 182  | 109 | 287  | 1829  | 456  | 20 μm, RDS | Motorway, Poland (N = 3) |
| 78   | 1062| 5.54 | 363   | 4011 | 1503 | 333  | 1503  | Soil (10–30 cm) | Cu smelter, Poland |
| 7366 | 8285| 102 (120)| 2401 (2340)| Top soil (0–36 cm) | Pb/Zn smelter, France (N = 3) |
| 161  | 3630| 54.5 | 1740  | 39   | 597 | 22.1 | 992   | Top soil (0–5 cm) | Pb/Zn smelter, China (N = 9) |
| 118  | 2558| 76   | 31.7  | 953  | 2.27 | Top soil (0–20 cm) | Pb/Zn smelter, China (N = 12) |
| 39   | 397 | 22.1 | 992   | 182  | 109 | 287  | 1829  | <63 μm, RDS | Urban, Korea (N = 5)             |
| 160  | 54  | 44   | 280   | 9.8  | 9.2 | 7.7  | 6.4   | Top soil (0–5 cm) | Pb/Zn smelter, Macedonia (N = 159) |
| 4575 | 5350| 1780 | 16500 | 128 (122)| 5925 (5990)| Top soil (0–10 cm) | Cu/Pb smelter, Namibia (N = 4) |

Road surface is a pollution hotspot where enormous PTEs accumulate in RDS and transport to surrounding environments via stormwater runoff and wind. The curb is the most RDS-accumulated area on a road surface66. Tobin and Brinkmann66 reported that the rotary
Table 3. Mean values of geo-accumulation index (Igeo) of PTEs in the different size of road deposited sediments.

| Size (μm) | Cr  | Ni  | Cu  | Zn  | As  | Cd  | Pb  | Hg  |
|-----------|-----|-----|-----|-----|-----|-----|-----|-----|
| >1000     | -0.3| -0.7| 3.0 | 3.6 | 2.3 | 5.1 | 3.7 | 1.4 |
| 500–1000  | 1.0 | 0.5 | 5.2 | 5.7 | 2.9 | 5.9 | 5.4 | 2.8 |
| 250–500   | 0.7 | 0.4 | 5.5 | 6.0 | 3.3 | 6.6 | 6.0 | 3.6 |
| 125–250   | 0.9 | 0.7 | 5.7 | 5.7 | 3.8 | 7.5 | 6.4 | 4.8 |
| 63–125    | 1.7 | 1.4 | 6.5 | 6.8 | 5.2 | 9.1 | 7.6 | 6.0 |
| <63       | 1.9 | 2.0 | 7.0 | 7.6 | 6.6 | 9.9 | 8.5 | 7.3 |

Igeo < 0, practically unpolluted
0 < Igeo < 1, unpolluted to medium polluted
1 < Igeo < 2, medium pollution
2 < Igeo < 3, medium to heavy pollution
3 < Igeo < 4, heavy pollution
4 < Igeo < 5, heavy to extremely heavy pollution
Igeo > 5, extremely heavy pollution

Figure 3. Comparison of nemerow index (PN) and potential ecological risk index (PER) of the different sizes of road deposited sediments of this study.

Conclusions
RDS is highly polluted by various pollutants, especially PTEs, and has received much attention as one of the important pollution sources in the terrestrial, coastal, and atmospheric environments as well as human health problems. We studied the concentrations and loadings of PTEs in different particle sizes of RDS around the active smelting industry to figure out their pollution source and to assess the pollution and potential ecological risk levels. PTE concentration in RDS increased with decreasing in particle size and the fine size (<63 μm) of RDS was heavily polluted with PTEs. Mean metal concentrations (mg/kg) in the fine size (<63 μm) were on the order of Zn (34,592) > Pb (13,561) > Cu (7071) > As (961) > Cr (596) > Ni (364) > Cd (225) > Hg (17). These concentrations of...
Figure 4. Spatial distribution of nemerow index (PN) values in the different sizes of road deposited sediments. Blue star symbol means a smelting facility. Figure created using Microsoft Office PowerPoint 2016 based on Google Maps (available at https://www.google.com/maps).

Table 4. Mean values of single factor ecological risk degree (E_i) of PTEs in the different size of road deposited sediments.
PTEs in this study were the highest values compared to the soils around the smelter and the RDS in urban cities in the world. The PTEs in RDS could be derived from both particulate emissions from chimney and truck spills during the transportation of raw ore for smelting activity. The spatial distribution of PTEs for < 125 μm was high around the smelting facilities, but relatively low at the sampling sites away from the smelters. Our results indicate that the PTEs in RDS might be affected by spillage and diffusion of raw ore minerals during transportation rather than particulate emission from the smelters. Road surface around the smelter has a significant amount of RDS accumulated with a mean of 21,678 mg/m² compared to urban areas. Cr, Ni, Cu, Zn, As, Cd, Pb, and Hg were accumulated per unit area in amounts of 370, 169, 4984, 11,802, 215, 47, 4177, and 4 mg/m² in the road surface of the study area. The relative contributions of Zn, As, Cd, Pb and Hg in the fraction (< 125 μm) that could transport to the surrounding environments via runoff and resuspension accounted for 39.6% (Zn), 57.9% (As), 63.8% (Cd), 52.3% (Pb) and 51.3% (Hg) of the total RDS. Given the amount of PTEs deposited on the road surface, it is necessary to apply an RDS removal management plan to reduce the PTEs pollution.

Figure 5. Comparison of mean PTEs loads (mg/m²) with standard deviation in the different sizes of road deposited sediments of this study.
Figure 6. PTEs loading percentages of different sizes of road deposited sediments in this study.

Data availability
All Data for this study are available from the corresponding author on request.

Received: 12 November 2020; Accepted: 25 February 2021
Published online: 31 March 2021

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Acknowledgements
The authors declare that they have no conflict of interest. This research was supported by grant (PE99912) from Korea Institute of Ocean Science and Technology (KIOST).

Author contributions
H.J and K.R conceptualized, conducted the PTEs measurements, prepared all figures and tables and wrote original manuscript. J.C performed RDS sampling and reviewed the manuscript. All authors reviewed the manuscript.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary Information The online version contains supplementary material available at https://doi.org/10.1038/s41598-021-86698-x.

Correspondence and requests for materials should be addressed to K.R.

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