Environmental Pollution
April 2023, Volume 322, Pages 121176 (11p.)
https://doi.org/10.1016/j.envpol.2023.121176
https://archimer.ifremer.fr/doc/00819/93117/

Isotopic (Cu, Zn, and Pb) and elemental fingerprints of antifouling paints and their potential use for environmental forensic investigations

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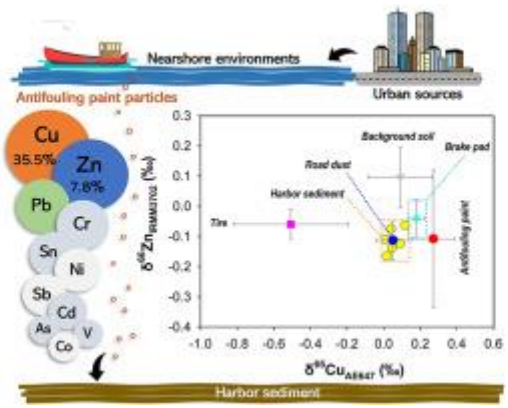
Abstract :

Antifouling paints (APs) are one of the important sources of Cu and Zn contamination in coastal environments. This study applied for the first-time a multi-isotope (Cu, Zn, and Pb) and multi-elemental characterization of different AP brands to improve their tracking in marine environments. The Cu and Zn contents of APs were shown to be remarkably high ∼35% and ∼8%, respectively. The δ65CuAE647, δ66ZnIRMM3702, and 206Pb/207Pb of the APs differed depending on the manufacturers and color (−0.16 to +0.36‰, −0.34 to +0.03‰, and 1.1158 to 1.2140, respectively). A PCA analysis indicates that APs, tires, and brake pads have also distinct elemental fingerprints. Combining isotopic and elemental ratios (e.g., Zn/Cu) allows to distinguish the environmental samples. Nevertheless, a first attempt to apply this approach in highly urbanized harbor areas demonstrates difficulties in source apportionments, because the sediment was chemically and isotopically homogeneous. The similarity of isotope ranges between the harbor and non-exhaust traffic emission sources suggests that most metals are highly affected by urban runoff, and that APs are not the main contributors of these metals. It is suspected that AP-borne contamination should be punctual rather than dispersed, because of APs low solubility properties. Nevertheless, this study shows that the common coastal anthropogenic sources display different elemental and isotopic fingerprints, hence the potential for isotope source tracking applications in marine environments. Further study cases, combined with laboratory experiments to investigate isotope fractionation during releasing the metal sources are necessary to improve non-traditional isotope applications in environmental forensics.

Graphical abstract



Highlights

► First multi-isotopic and elemental fingerprints of antifouling paints (APs). ► APs isotopic compositions vary depending on manufacturer and color. ► Unique chemical fingerprint of APs differentiates them from other pollutants. ► Major contribution of harbor sediments in Korea indicated urban sources than APs. ► Metal isotopic signatures may enable source discrimination in forensic studies.

Keywords : Metal pollution, Hazard materials, Metal isotopes, Isotopic signatures, Harbor sediment, Tracing pollution sources

1. Introduction

The adhesion of biofouling marine organisms to submerged surfaces, such as marine leisure and shipping vessels, is a serious socioeconomic issue (Ytreberg et al., 2016; Davidson et al., 2021) as it is a major cause of an increase in ship drag penalty and hence in fuel consumption (Utama and Nugroho, 2018). Additionally, it can lead to high vessel maintenance costs, while the frequent need to clean the hull can shorten the dry-docking interval (Ytreberg et al., 2021). The annual costs to the global shipping industry of biofouling, including its prevention, increased fuel consumption, and vessel maintenance, are in the billions of Euros range (Desher, 2018; Whitworth et al., 2022).

After the worldwide ban on biocidal organotin compounds, such as tributyltin (TBT), in antifouling paints (APs), the tin-free alternatives have consisted largely of Cu(I)-based biocidal substances, such as cuprous oxide (Cu_2O) and copper thiocyanate (CuSCN), with zinc oxide (ZnO), and zinc pyrithione (ZnPT) as booster biocides (Turner, 2010; Muller-Karanassos et al., 2021). The high contents of these toxic metals in APs imply a risk of their release into the marine environment at variable rates that depend on the physical and chemical parameters of the aqueous medium.

Cu and Zn are essential micronutrients for living organisms, but at high concentrations, their bioaccumulation can result in considerable toxicity, with negative impacts on benthic ecosystems and marine organisms as well as degradation of water quality. For example, high Cu bioavailability was shown to damage the endocrine systems of oysters at the larval life stage (Gamain et al., 2017; Mai et al., 2012; Sussarellu et al., 2018; Wang et al., 2018; Wijsman et al., 2019).

Lead (Pb) compounds are also used in marine paints, due to their corrosion resistance, rapid curing, color, and opacity (Turner, 2014). Nonetheless, their harmful effects on human health (Turner, 2014), have led to the establishment in many countries of the following threshold values of Pb addition to paints: USA, Canada, Philippines, Nepal; 90 ppm, Switzerland, Thailand; 100 ppm, Brazil, the Republic of Korea, Argentina, Mexico; 600 ppm, New Zealand, Australia; 1000 ppm, as well as various countries have Pb restrictions on paints (UNEP, 2016). Furthermore, paint peelings from abandoned boats contained considerably high concentrations of Pb, Zn, and Cu (Rees et al., 2014), and may thus contaminate local sediments, transforming them into legacy pollution sources in marine environments. Major environmental and health risks for the biota and for humans may also arise from speciation changes during post-depositional processes in sediments, which modify the bioavailability and toxicity of these metals, especially Pb (Rees et al., 2014). Because the aquatic environment gradually leaches APs from treated surfaces, AP efficiency decreases over time, requiring to periodically renew them (Soroldoni et al., 2018). The dissolved components and particles in the APs can be disseminated into the local environment (e.g., harbors, shipyards, and marinas), as also occurs when old AP coatings are removed, such as during vessel repair, maintenance, repainting, and cleaning (Turner et al., 2009; Soroldoni et al., 2017; 2018). Once in the marine environment, AP particles undergo various hydrodynamic processes (e.g., deposition, resuspension and dredging, dissolution, advection, and ultimately burial) (Turner, 2010). The release of biocidal as a result of biogeochemical and physiochemical reactions can adversely affect the marine biota and benthic ecosystems (Jones and Turner, 2010; Lagerström et al., 2016; Soroldoni et al., 2020).

The behavior of metals released from APs under variable physicochemical conditions has been evaluated extensively, mostly for the purpose of implementing environmental regulatory policies regarding AP use (Turner et al., 2009; Turner, 2010, 2014; Ytreberg et al., 2016, 2021; Soroldoni et al., 2017, 2018, 2020). However, accurate metal-based quantification of AP fluxes in the coastal environment remains challenging, since other anthropogenic metal sources are often impossible to deconvolve with traditional elemental analysis. Over the last 15 years, the development of techniques based on metal stable isotopes, including the quantification of metals and the discrimination of their sources, has opened up new perspectives in environmental forensics (Weiss et al., 2008; Bartelink et al., 2019; Pontér et al., 2021).

Isotopic fingerprints using radiogenic and stable isotope systems are advantageous techniques to track contaminants and source identification (Cheng and Hu, 2010, Kumar et al., 2014; Bi et al., 2017; Wang et al., 2021; Chen et al., 2022). Pb isotopic compositions reflect geogenic origins and are unaltered by physiochemical fractionation during anthropic activities (Shiel et al., 2010; Longman et al., 2018). The radioactive decays of thorium (Th) and uranium (U) induce different Pb isotopic compositions, and ^{208}Pb, ^{207}Pb, and ^{206}Pb are radioactive decay products of ^{232}Th, ^{235}U, and ^{238}U, respectively (Komárek et al., 2008). Distinct Pb isotopic ratios characterize in various geochemical reservoirs, and geogenic origins are more radiogenic than anthropogenic sources (Sangster et al., 2000; Knowlton and Moran, 2010; Zhu et al., 2013;

Kelepertzis et al., 2020; Liang et al., 2021). Diverse environmental reactions can lead to Cu and Zn isotopic fractionation in the interconnected earth systems (e.g., biosphere, hydrosphere, atmosphere, and lithosphere) (Wang et al., 2017; Souto-Oliveira et al., 2018; Köbberich and Vance, 2019; Liu et al., 2019; Liu et al., 2021; Araújo et al., 2022a). In general, adsorption of Cu and Zn to oxides (Pokrovsky et al., 2008; Bryan et al., 2015), organic matter (Jouvin et al., 2009; Araújo et al., 2022b), and soils (Bigalke et al., 2010) tends to preferentially enrich the heavy isotope on the surfaces (Guinoiseau et al., 2018), with rare exceptions (kaolinite; Li et al., 2015). The isotope systems of Zn, Cu, and Pb have been successfully used to track anthropogenic contamination in marine environments impacted by metallurgic (Yin et al., 2016; Tonhá et al., 2021; Yu et al., 2021), agricultural (Peng et al., 2020; Chen et al., 2022), and urban emissions (Gonzalez et al., 2016; Nazarpour et al., 2019). Thus far, only one study has investigated the use of Cu isotopes to trace AP contamination in sedimentary archives (Briant et al., 2022). Combining different isotope systems would allow source discrimination with improved resolution, as demonstrated in investigations of atmospheric pollution in urban aerosols (Souto-Oliveira et al., 2018; 2019; Schleicher et al., 2020). However, few studies have examined the applicability of this approach to marine systems, although they are often the ultimate repository for land-originating metal release.

Estuaries frequently receive anthropogenic effluents, including urban, industrial, and food production (agriculture, aquafarming, and fishing) activities (Araújo et al., 2019; Briant et al., 2021; Nel et al., 2022). Urban emissions are the dominant source of metal contamination in local aquatic environments, and they can distinctly affect the water quality (Deycard et al., 2014). Most coastal cities are densely populated, and many are geographically advantaged by their proximity to the mouths of large rivers (Wijesiri et al., 2019). However, adjacent maritime environments are thus more vulnerable to the deleterious effects of uncontrolled stormwater discharges (Jeong et al., 2020; Buzzi et al., 2022). Strongly urbanized estuaries tend to be susceptible to increased fluxes of metal-based compounds released from cities and urban structures (Deycard et al., 2014), such as non-exhaust traffic emission sources (e.g., wear of brake pads, tires, road paints, and road pavement) (Adamiec et al., 2016; Piscitello et al., 2021; Jeong et al., 2022). This multi-source road dust is transported together with surface soils into water systems vis stormwater runoff (Loganathan et al., 2013; Hwang et al., 2016; Wang et al., 2019).

The present study provides for the first time a multi-isotopic (Cu, Zn, and Pb) characterization in commercial APs. The isotopic fingerprints of APs are compared with other metal contamination sources including non-exhaust traffic emission sources. Furthermore, harbor sediment from a Korean marina is used to identify the potential useability of these isotopic and elemental fingerprints in a real-world environment.

2. Materials and methods

2.1. Anthropogenic source sampling

2.1.1 Antifouling paints

The 25 APs examined in this study are those generally used in Korea. The 11 domestic (Korean) APs were purchased from 5 different manufacturers (A, B, C, D, E). These were compared with 14 APs imported from different counties and produced by 4 manufacturers (F, G, H, I). Together, these 25 paints represent > 80% of the APs used in Korea. A 1- to 2-mm-thick layer of each AP was painted onto a Teflon sheet, which was then dried completely by placement on a 60 °C hot plate for several days.

2.1.2. Road dust, tire wear, and brake pads

Published data on road dust and particles from tire and brake pad wear were used for comparisons with potential sources in the estuarine environment. Road dust (25 samples) was vacuumed from an area of ~0.25 m^2 in Busan Metropolitan City. Brake pad and tire samples (from brands accounting for the majority of Korean market share) were broken up or cut into small pieces for homogenization and total digestion (Jeong et al., 2022; Jeong, 2022). Details of the sampling processes can be found in Jeong and Ra (2021), Jeong et al. (2022), and Jeong (2022).

2.2. Harbor sediments

Busan is the largest port city in Korea and the 6th largest container port in the world (WSC, 2019). Among Korean ports, it has the highest total traffic volume, largely due to the high density of trans-shipment and ship repair facilities. Based on a previous study (Jeong et al., 2020), seven sampling sites were selected and the harbor sediments were collected using a grab-sampler in February 2020 (Fig. S1). The collected sediments were freeze-dried, homogenized, and stored in pre-acid cleaned PE bottles until the metal concentration and isotope measurements.

2.3. Sample preparation and elemental analysis

The dried APs were cut into small pieces and aliquots of ~50 mg were digested in Savillex digestion vessels. In the first step of the digestion procedure, high-purity nitric acid (HNO_3, Ultra-100, Kanto Chemical Co., Japan) was added, followed by evaporation of the samples to near dryness on a hot plate at 180 ºC; this step was then repeated. In the second step, the samples were treated with a mixed acid solution ($HF:HNO_3:HClO_4$ = 4:3:1; v/v) to achieve total digestion (Jeong et al., 2022), followed by evaporation as described above. The samples were then redissolved using 2% HNO_3. The same procedure was used to digest 50 mg amounts of the harbor sediment. All samples were prepared in duplicate. Metals were analyzed using an inductively coupled plasma mass spectrometer (ICP-MS; iCAP-Q, Thermo Scientific Co., Germany). All pre-treatment steps and analysis were performed in a clean room. The analytical quality of the metal analysis was confirmed by decomposing two certified reference materials (CRMs), MESS-4 and BCR-667, together with the environmental samples. The experimental concentrations obtained for CRMs were within ±10% of their certified values.

2.4. Metal stable isotope (Cu, Zn, and Pb) chromatography and analysis

Prior to measurements of the isotopic composition of Cu and Zn in APs and harbor sediments, the Cu and Zn digests were separated and purified on a 1 mL Teflon column (3.2 mm ID × 4.7 mm OD, Savillex, USA) filled with a Bio-Rad AG-MP1 anion exchange resin (analytical grade, 100–200 mesh, USA). The retained matrix was removed by the addition of 5 mL, and the Cu fraction by subsequent elution with 19 mL 7 mol/L HCl + 0.001% H_2O_2. The Fe fraction was removed using 16 mL 1 mol/L HCl + 0.001% H_2O_2. Finally, the Zn fraction was eluted in 10 mL 0.5 mol/L HNO_3. Cu was obtained on a second column to avoid element interference. The column separation protocols are described in detail in Jeong et al. (2021). In some paint samples, high concentrations of Ti and Ba interferents remained in the purified fractions even after two-step column separation. Therefore, the Cu samples were purified on a third column using the same protocol described for the second column. For the Pb isotope analyses, Pb was purified using a 2 mL Eichrom column with a Pb-specific resin (100–150 μm particle size, Eichrom, France) (Jeong et al., 2021).

For precise isotope measurements, the standard-sample bracketing method and instrumental mass bias correction method were adopted by spiking Zn for Cu isotopes (and vice versa) and Tl for Pb isotopes. The average uncertainty (2sd) in duplicate samples was ±0.05‰ for $\delta^{65}Cu_{AE647}$, ±0.02‰ for $\delta^{66}Zn_{IRMM3702}$, and ±0.0002 for the $^{206}Pb/^{207}Pb$ ratio. The isotope analyses were conducted in samples containing 100 μg/L for Cu, 200 μg/L for Zn, and 50 μg/L for Pb. The Cu, Zn, and Pb isotopic compositions were measured using a multi-collector ICP-MS (MC-ICP-MS, Neptune Plus, Thermo Scientific Co., Germany) at the Korea Institute of Ocean Science and Technology (KIOST).

In-house standard solutions were used for quality control to ensure the accuracy of the isotope measurements. ERM-AE633 and Kanto Cu solution were used for the determination of Cu, yielding average $\delta^{65}Cu_{AE647}$ values of –0.21 ± 0.03‰ (2sd, n = 8) and +0.12 ± 0.01‰ (2sd, n = 8), respectively. IRMM-651 and Kanto Zn solution were used for the determination of Zn, yielding average $\delta^{66}Zn_{IRMM3702}$ values of –11.59 ± 0.01‰ (2sd, n = 4) and –0.07 ± 0.02‰ (2sd, n = 5) respectively. The average values for $\delta^{65}Cu_{AE647}$ and $\delta^{66}Zn_{IRMM3702}$ obtained using BHVO-2 were –0.08 ± 0.03‰ (2sd, n = 3) and –0.05 ± 0.09‰ (2sd, n = 3), respectively; these values were within the range of previously reported values (Sossi et al., 2015; Wang et al., 2020; Jeong et al., 2021) (Table 1).

The isotopic compositions of Cu and Zn are expressed in δ notation as the per mil (‰) deviation from the reference material:

$$\delta^{65}Cu\ (‰) = \left(\frac{(^{65}Cu/^{63}Cu)_{sample}}{(^{65}Cu/^{63}Cu)_{ERM-AE647}} - 1\right) \times 1000$$

$$\delta^{66}Zn\ (‰) = \left(\frac{(^{66}Zn/^{64}Zn)_{sample}}{(^{66}Zn/^{64}Zn)_{IRMM-3702}} - 1\right) \times 1000$$

Cu and Zn isotopic values were converted as follows to compare with previously reported values (Moeller et al., 2012; Araújo et al., 2017):

$$\delta^{65}Cu_{ERM-AE647} = \delta^{65}Cu_{NIST976} - 0.21‰$$

$$\delta^{66}Zn_{IRMM3702} = \delta^{66}Zn_{JMC} - 0.27‰$$

For Pb isotopes, the relative ratios of four stable isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb) are reported.

2.5. Enrichment factor calculation

The enrichment factor (EF) is commonly used to assess the anthropogenic impact of metal contamination in sediments, and to classify contamination levels. It is calculated as follows (Ra et al., 2014):

$$\mathrm{EF} = \frac{\left({}^{metal}/_{Al}\right)_{sample}}{\left({}^{metal}/_{Al}\right)_{background}}$$

where metal/Al_{sample} and metal/$Al_{background}$ are the ratios of sediment and continental crust (Rudnick and Gao, 2003), respectively.

2.6. Principal component analysis

Principal component analysis (PCA) is used to recombine variables in multivariate data, with most of the variance explained by the first few variables (Xue et al., 2011). In this study, PCA was performed to identify the intercorrelations of potential sources of metal contamination (i.e., APs, brake pads, tires, and road dust) using PASW Statistics version 18. Eigenvalues > 1 were extracted for the first two components. To improve the accuracy of the results, the variables were varimax rotated.

3. Results and discussion

3.1. Elemental and isotope compositions of anthropogenic sources

3.1.1 Antifouling paints

Overall, the mean metal concentrations in domestic APs ranked as follows: Cu (30.46%) > Zn (6.58%) > Fe (1.97%) > Ti (1.64%) > Al (0.24%) > Sn (374.8 mg/kg) > Pb (143.4 mg/kg) > Ni (83.0 mg/kg) > Cr (51.7 mg/kg) > Mn (46.8 mg/kg) > Sb (5.61 mg/kg) > Mo (3.58 mg/kg) > V (3.15 mg/kg) > As (2.69 mg/kg) > Co (2.16 mg/kg) > Cd (0.93 mg/kg). Domestic APs had higher concentrations of Fe, Mn, V, Cr, Co, Sn, and Sb compared with imported APs (Table 2). The concentrations of Al, Ni, and Mo were similar between domestic and imported APs, while the concentrations of of Cu, Zn, As, Cd, and Pb were slightly higher in imported than domestic APs. The metal composition of APs produced by the same manufacturer varied depending on the paint color, with white APs having a higher Ti concentration (8.97%), but lower concentrations of other elements compared with blue, red, and black paints (Table S1). The concentrations of many metals (Cr, Ni, Cu, Zn, Cd, Sn, and Pb) were higher in APs than in either road paint (Jeong et al., 2022) or car paint (Hsu et al., 2018). Our data are consistent with other studies in which even higher Cu and Zn concentrations in APs were reported. Nevertheless, the Cu, Zn, and Pb concentrations in the APs differed by 3-, 1700-, and 26-fold, respectively, depending on the manufacturer.

The isotopic compositions of Cu, Zn, and Pb in domestic and imported APs are shown in Table 3. The Cu concentration in all APs ranged widely, from 17.33% to 52.12% (Fig. 1a); $\delta^{65}Cu_{AE647}$ values ranged from –0.16 to +0.36‰, except for two outliers (AP-H and AP-G, Table 3), with most of APs falling within a narrow isotope range of +0.18 to +0.36‰, close to that previously reported for these products (mean $\delta^{65}Cu_{AE647}$: +0.33‰ ± 0.10, 2sd, n = 3; Briant et al., 2022). The $^{206}Pb/^{207}Pb$ ratio in domestic APs was overall homogenous, ranging from 1.17 (AP-B) to 1.20 (AP-C), with an average of 1.1829 ± 0.0267 (2sd, n = 11). The average $^{206}Pb/^{207}Pb$ ratio in imported APs was 1.1870 ± 0.0559 (2sd, n = 14), which was similar to that in domestic APs (Fig. 1b). Sample AP-H was an outlier with respect to the isotopic values of Cu and Pb (Table 3). The Zn isotopic composition ($\delta^{66}Zn_{IRMM3702}$) showed a variability of approximately 0.4‰ and the mean $\delta^{66}Zn_{IRMM3702}$ value of all APs was –0.10 ± 0.20‰ (2sd, n = 25). The Zn isotopic values were simailr between domestic (–0.11 ± 0.23‰; 2sd, n = 11) and imported products (–0.09 ± 0.18‰; 2sd, n = 14) (Fig. 1c). White APs had a lower Cu concentration and the lightest Cu isotopic value (mean: +0.09 ± 0.35‰; 2sd, n = 2) compared with those of other colors (blue, red, and blank) (Table S2). Blue APs had a relatively lighter Zn isotopic composition, while red APs had a distinct Pb isotopic composition compared with those of other colors.

3.1.2 Non-exhaust urban sources: road dust, tire, and brake pads

Urban sources were adopted to compare with different potential sources as reported in previous studies. Non-exhaust traffic emission sources (e.g., wear of brake pads, tires, road paints, road pavement, and railway) are major sources of metal contamination in urban environments (Adamiec et al., 2016; Piscitello et al., 2021; Jeong et al., 2022). Road dust, brake pads, and tires were considered dominant urban sources in this study. Isotopic compositions of road dust in Busan were +0.05 ± 0.09‰, (2sd, n = 25; $\delta^{65}Cu_{AE647}$), –0.11 ± 0.06‰ (2sd, n = 25; $\delta^{66}Zn_{IRMM3702}$), and 1.1514 ± 0.0073 (2sd, n = 25, $^{206}Pb/^{207}Pb$) (Jeong and Ra, 2021). The isotopic values of particles from Korean tires were –0.51 ± 0.31‰ (2sd, n = 12; $\delta^{65}Cu_{AE647}$), –0.06 ± 0.05‰ (2sd, n = 12; $\delta^{66}Zn_{IRMM3702}$), and 1.1568 ± 0.0294 (2sd, n = 12; $^{206}Pb/^{207}Pb$) (Jeong, 2022). The $\delta^{65}Cu_{AE647}$, $\delta^{66}Zn_{IRMM3702}$, and $^{206}Pb/^{207}Pb$ values in particles from Korean brake pads were +0.18 ± 0.04‰ (2sd, n = 9), –0.04 ± 0.06‰ (2sd, n = 9), and 1.2645 ± 0.2865 (2sd, n = 9), respectively (Jeong et al., 2022). Excluding a single high Pb isotopic ratio ($^{206}Pb/^{207}Pb$) of brake pads, the average is 1.2199 ± 0.1010 (2sd, n = 8).

3.2. Harbor sediments

The mean metal concentrations in harbor sediments (Table 2) decreased in the order Zn > Cu > V > Cr > Pb > Ni > Co > As > Sn > Mo > Sb > Cd. Notably, the Cu concentration in coastal sediment outside of harbor area (35.6 mg/kg, Jeong et al., 2020) was 5.5 times lower than that measured in the harbor sediment in this study.

At site H7, the Cu concentration was 282.4 mg/kg, and thus higher than that of Zn (238.2 mg/kg). The mean $\delta^{65}Cu_{AE647}$ and $\delta^{66}Zn_{IRMM3702}$ values in harbor sediments were +0.06 ± 0.08‰ (2sd, n = 7) and –0.11 ± 0.07 ‰ (2sd, n = 7), respectively. The mean Pb isotopic ratio ($^{206}Pb/^{207}Pb$) was 1.1694 ± 0.0079 (2sd, n = 7), with a range of 1.1630 to 1.1733.

Among metals, Cu had the highest mean EF (7.2), ranging from 4.1 to 11.0, indicative of moderate to significant Cu contamination. The mean EF in harbor sediments decreased as follows: Cu > Zn > Cd > Pb > Sn > Sb > As > Mo > V > Cr > Co > Ni. Cu contamination was higher than Zn contamination, indicating anthropogenic Cu sources from harbor activities. In the drainage basin of the study area, there is a high volume of vessel traffic in addition to many ship repair facilities along its coastline.

3.3. Source discrimination and comparison of isotopic and elemental fingerprints from coastal anthropogenic sources

The elemental and isotope information described for anthropogenic sources in previous sections are used here to examine whether the isotopic and elemental fingerprints can be used for source discrimination in the marine environment. To trace the sources of observed elevated a PCA yield two principal components explaining > 80% (PC1 65% and PC2 20%), (Fig. 2). PC1 had a strongly positive correlation with road dust and brake pads, and PC2 indicated a significantly positive correlation with tires. The differences in clusters according to specific anthropic material as determined in the PCA enabled the differentiation of these sources in the coastal environment (Fig. 2). The isotopic and elemental proxies of these sources and their use in tracking their potential contributions on harbor sediment are described below.

Elemental ratios are also widely used as a proxy for metal sources (Abbasi et al., 2021; Hong et al., 2018; Wu and Huang, 2021; Zhang et al., 2014). For example, Zn/Cu and Cu/Sb have been successfully applied to discriminate among traffic-activity-related sources in urban environments (Iijima et al. 2007; Hwang et al., 2016; Jeong et al., 2020; McKenzie et al., 2009). As noted above, anthropic materials can be discriminated according to their chemical composition, and specifically by their different relative contents of Cu and Zn. Therefore, the Zn/Cu ratio may be used to estimate potential sources of metal contamination in harbor sediments. Figure 3 shows the relationship between the Zn/Cu ratio and the isotopic compositions of Cu, Zn, and Pb. The mean Zn/Cu ratio of harbor sediment in this study was 1.6 (range: 0.8–2.6). This was slightly higher than the mean Zn/Cu ratio of APs and lower than the Zn/Cu ratio of soil and road dust. Brake pads and APs with extremely high Cu concentrations 47.3% and 36.0%, respectively, had similar Cu isotopic compositions. However, the Zn/Cu ratio of brake pads was lower than that of APs, indicating that these two sources can be distinguished (Fig. 3a). As shown in Fig. 3b, anthropogenic Zn tended to have an isotopically light composition, and its elemental ratio (Zn/Cu) enable to discriminate among the different sources (APs, road dust, brake pads, tires, and background soils). By contrast, it is difficult to find distinct characteristics of potential sources using Pb isotopic ratios ($^{206}Pb/^{207}Pb$) due to their homogeneity (Fig. 3c). Considering the Cu and Zn contamination levels in harbor sediments, the contribution of road dust to the estuarine environment is likely to be greater than that of APs. The result of this study also showed that Cu contamination in harbor sediments was affected by road dust, soil, and APs, simultaneously.

3.4. Metal isotope tracking in a Korean harbor

The relationships between the isotopic compositions of Cu, Zn, and Pb in harbor sediments and those of other potential sources, including APs, are shown in Fig. 4. The mean of $\delta^{65}Cu_{AE647}$ values was lower in harbor sediments than in domestic APs (+0.27‰, Table 3). The Zn isotopic composition was similar between the harbor sediments and APs, whereas the Pb isotopic ratio ($^{206}Pb/^{207}Pb$) was lower in harbor sediments. The mean $\delta^{65}Cu_{AE647}$ and $\delta^{66}Zn_{IRMM3702}$ were similar between harbor sediments and road dust (Jeong and Ra, 2021) (Fig. 4a). Cu and Zn isotopes in harbor sediments quite differed from those in non-exhaust emission sources in Korea, such as tire (Jeong, 2022) and brake pads (Jeong et al., 2022). Figure 4b shows the relationship between $^{206}Pb/^{207}Pb$ and $\delta^{66}Zn_{IRMM3702}$ values. The $\delta^{66}Zn_{IRMM3702}$ values in harbor sediments were similar to those in road dust and APs. The mean of $^{206}Pb/^{207}Pb$ values in harbor sediments was 1.1690, which was within the range of 1.1488 (road dust) and 1.1809 (APs). However, the isotopic composition of Zn and Pb in harbor sediments strongly differed from that in uncontaminated background soil ($\delta^{66}Zn_{IRMM3702}$: +0.10 ± 0.10‰, 2sd, n=6 and $^{206}Pb/^{207}Pb$: 1.1827 ± 0.0043, 2sd, n=6; Jeong and Ra, 2021). In the $^{206}Pb/^{207}Pb$ vs. $\delta^{65}Cu_{AE647}$ plot, the harbor sediment may have been affected by both geogenic (background soil) and anthropogenic (APs and road dust) sources (Fig. 4c). The isotopic compositions suggest that harbor sediments are not solely affected by APs, and that several other environmental sources affect surface sediments simultaneously.

Cu and Zn isotope mixing models have been successfully used to quantify source contributions in several pollution contexts: soils (Wang et al., 2021; Wang et al., 2022), sediments (Araújo et al., 2019; Nitzsche et al., 2022), water (Chen et al., 2008), and aerosols (Souto-Oliveira et al., 2018). It has been demonstrated that sources tend to be recorded almost conservatively in natural archives. This study shows that isotope fractionation during transport and post-deposition processes is not significant enough to obscure the source record. This should be related to small fractionation related in releasing of Cu and Zn by these materials. Briant et al.

(2022) reported similar Cu isotopic signatures between underlying sediment and APs ($\delta^{65}Cu_{NIST976}$: +0.44‰ and +0.54‰, respectively). This small difference is consistent with experimental works about adsorption onto surfaces (Komárek et al., 2022). Understanding the specific isotopic fractionation of each material is out of this present scope, but it remains an important step for advancing environmental forensic applications using isotopic tools in marine environments.

Pb isotope ratios are unaffected by biogeochemical processes (Komárek et al., 2008) and therefore, they are conservative in terms of Pb source recording. In contrast, Cu and Zn isotope ratios can change along their biogeochemical cycling. After releasing Cu and Zn in the marine environment, they are partitioned into different phases or compartments. Cu isotopic fractionation can occur by preferential organic complexation and light Cu isotope scavenging to the particles (Little et al., 2018). Theoretically, substances with stronger bonds (shorter bond length) tend to be enriched in heavier isotopes in equilibrium (Schauble, 2004; Wiederhold, 2015; Gou et al., 2018). In terms of sorption on mineral surfaces, Zn isotopic fractionation can be related to the ionic strength of the suspension, aqueous speciation, and molecular coordination environment (Veeramani et al., 2015). Moreover, isotopic fractionation can be affected by kinetics, isotope equilibrium effects, and many aspects of environmental processes (e.g., physical, chemical, and biological processes) (Cloquet et al., 2008; Desaulty and Petelet-Giraud, 2020).

Potential isotope fractionation during the transport of different environmental compartments remains uncertainty in the Cu isotope systems (Araújo et al., 2021). Cu and Zn isotope ratios behave conservatively in particulate phases during transport and post-depositional processes. This has been confirmed in highly dynamic environments like mangroves (Araújo et al., 2018), and the largest water flux river confluence in the world (Guinoiseau et al., 2018). As well, isotope records of sources in atmospheric and soil particles seems not be also significantly changed (Schleicher et al., 2020; Wang et al., 2021). Isotope systematics of sediments, suspended particulate matters, aerosols, and soils profiles are well explained by mixing models. Although these isotopic shifts in biogeochemical process are relatively small, sediment can preserve its contamination record, and is pertinent for source identification (Thapalia et al., 2010; 2015; Pontér et al., 2021). Nevertheless, these results show that the consideration of various environmental factors (size, shape, and density of AP particles) is needed for future research, since these particles can be involved in mobility into the estuarine environments (Soroldoni et al., 2018).

Conclusions

The establishment of databases on elemental and metal isotopes from anthropogenic sources is a prerequisite for source apportionment studies in the field of environmental forensics. This work provides the first multi-isotope and elemental characterization of APs. These materials contain extremely high levels of Cu and Zn, and their progressive dispersion in the marine environment leads to the release of these toxic metals, with damage to marine ecosystems. The mean Cu ($\delta^{65}Cu_{AE647}$), Zn ($\delta^{66}Zn_{IRMM3702}$), and Pb ($^{206}Pb/^{207}Pb$) isotopic compositions of APs were +0.22 ± 0.26‰ (2sd), −0.10 ± 0.20‰ (2sd), and 1.1852 ± 0.0448 (2sd), respectively. While the concentrations of Cu, Zn, and Pb in APs differed widely depending on the manufacturer, the isotopic compositions of the metals fell within a relatively narrow range, with similar values for Korean-made and Korean-imported APs. Taken together, the elemental and isotopic characterization of APs provided fingerprints that allowed them to be distinguished from other sources (road dust, brake pads, and tires). These new data for APs extend the isotope catalog for anthropic materials reported in the literature. It also demonstrated that anthropogenic sources can be differentiated based on their chemical composition to track contaminants in the coastal environment. The fingerprint of harbor sediment was close to that of road dust. Because this study area is a densely populated port city and is highly influenced by not only shipping but also urban (especially, traffic-related) activities. These results demonstrate the feasibility of source identification using isotopic and elemental ratios in real-world environments.

CRediT authorship contribution statement

Hyeryeong Jeong: Conceptualization, Investigation, Metal and Isotope analysis, Visualization, Validation, Writing-original draft. **Daniel F. Araújo:** Validation, Writing-Review & Editing. **Joël Knœry:** Validation, Writing-Review & Editing. **Nicolas Briant:** Validation, Writing-Review & Editing. **Kongtae Ra:** Methodology, Sampling, Metal and Isotope analysis, Visualization, Funding acquisition, Writing-Review & Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests that could have appeared to influence the work reported in this manuscript and have no conflicts of interest to declare that are relevant to this study.

Acknowledgements

This research was supported by a grant (PEA0023) from the Korea Institute of Ocean Science and Technology (KIOST): it was also supported by the "Development of source identification and apportionment methods for toxic substances in marine environments" program of the Korea Institute of Marine Science & Technology Promotion (KIMST) funded by the Ministry of Oceans and Fisheries (KIMST-20220534).

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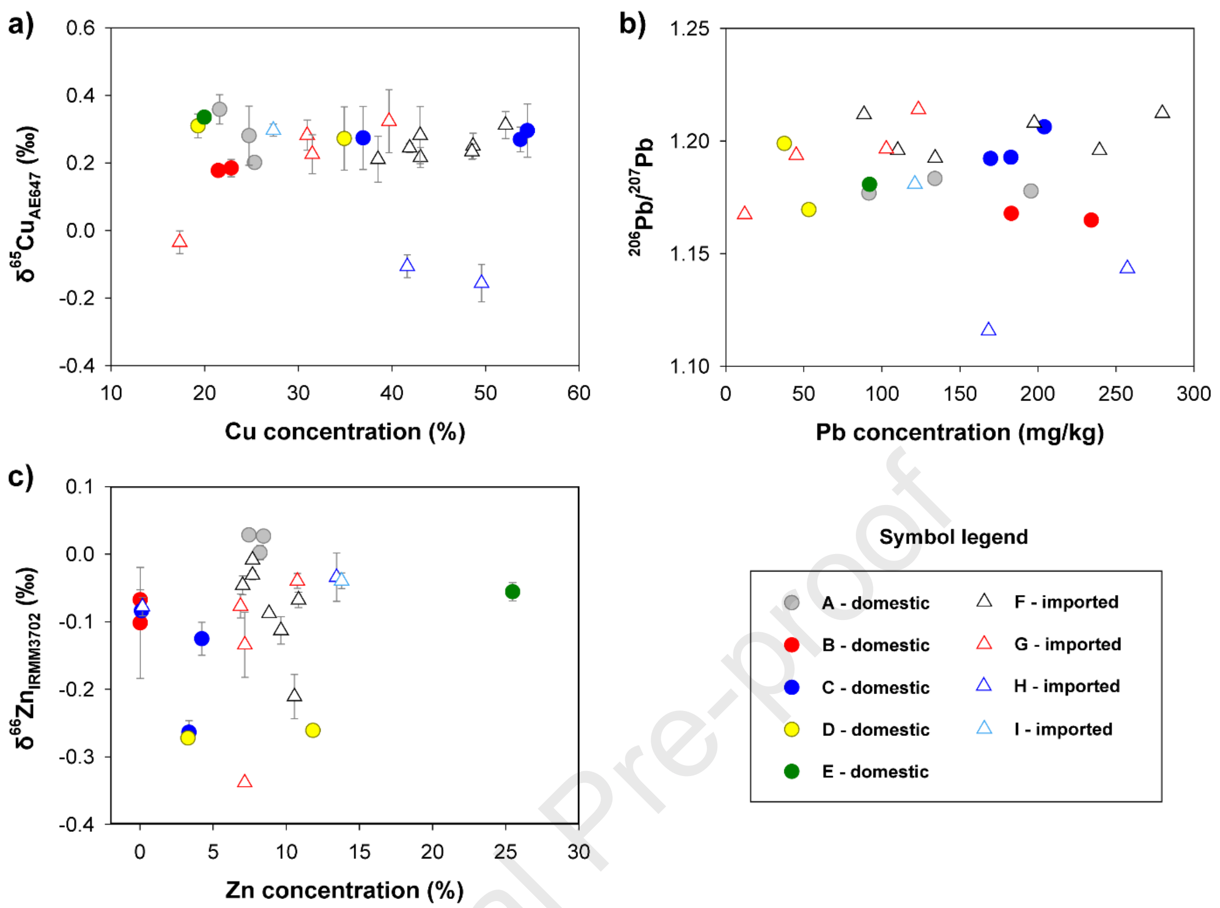
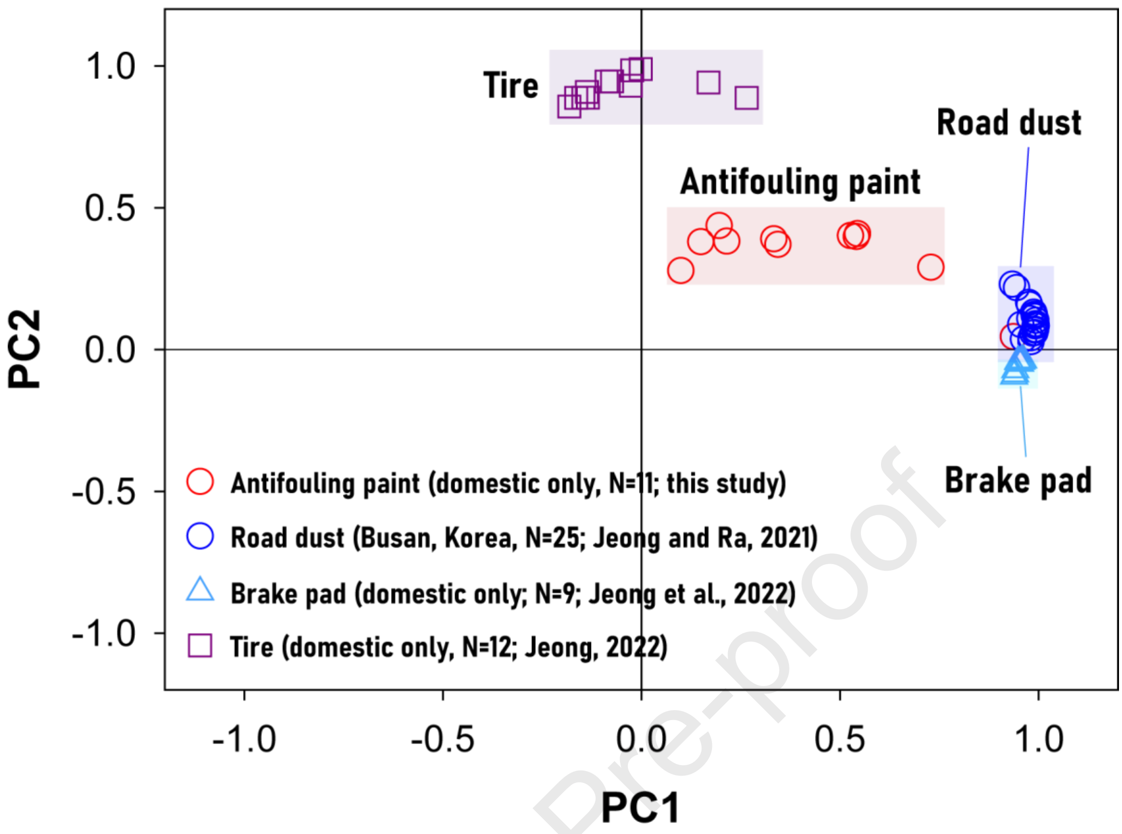


798

799 **Fig. 1**. Relationships observed in APs between Cu, Zn, and Pb concentrations and their isotopic
800 compositions. The error bars represent two standard deviations (2sd).

801



802

803 **Fig. 2.** Principal component analysis (PCA) results of metal concentrations and isotopic
804 compositions (Cu, Zn, and Pb) in antifouling paints, road dust, tires, and brake pads.

805

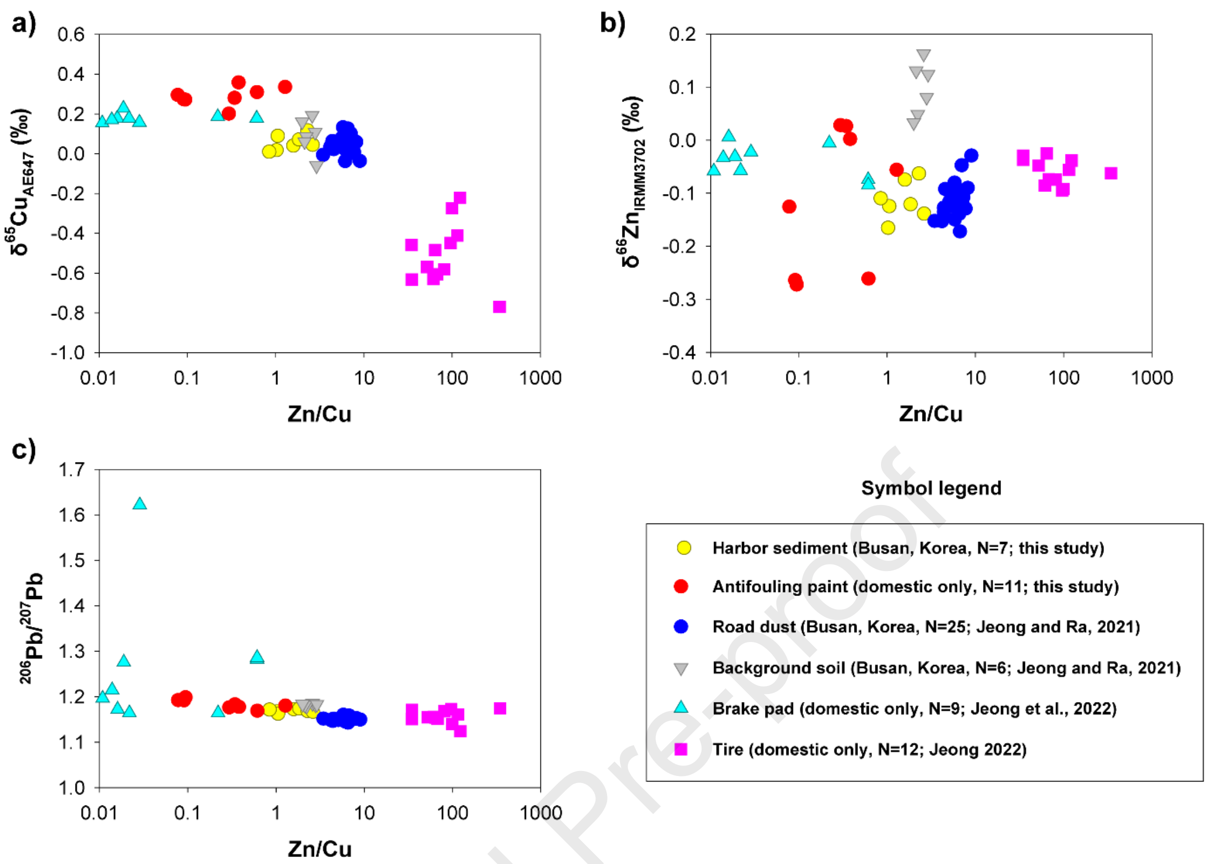


Fig. 3. Relationship between Zn/Cu ratios and isotopic compositions of Cu, Zn, and Pb in this study.

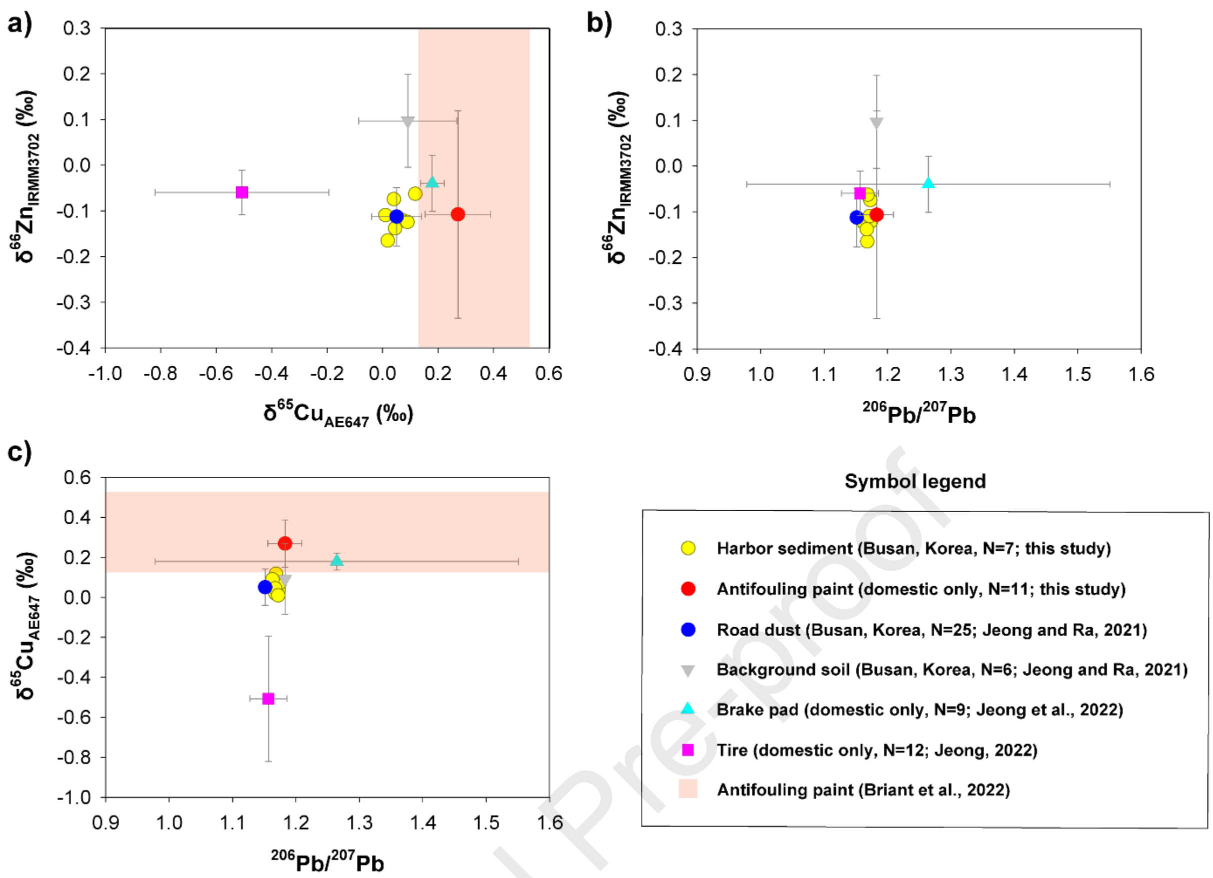


Fig. 4. Comparison between Korean harbor sediments and various pollution sources including APs using these and previously published Cu, Zn, and Pb isotopic compositions.

Table 1. Cu and Zn isotopic compositions of in-house standard solutions and reference materials in this study with previously reported values.

	$\delta^{65}Cu_{AE647}$ (‰)	**2sd**	**n**	**$\delta^{66}Zn_{IRMM3702}$ (‰)**	**2sd**	**n**	**References**
ERM-AE633	–0.21	0.03	8				This study
Kanto Cu	0.12	0.01	8				This study
IRMM-651				–11.59	0.01	4	This study
Kanto Zn				–0.07	0.02	5	This study
BHVO-2	–0.08	0.03	3	–0.05	0.09	3	This study
BHVO-2				0.00	0.12		Sossi et al., 2015
BHVO-2	–0.08	0.10					Wang et al., 2020
BHVO-2	–0.06	0.16	4	–0.07	0.14	4	Jeong et al., 2021

Table 2. Comparison of mean, and standard deviation values for metal concentrations in antifouling paints used in Korea.

		Al	Fe	Ti	Mn	V	Cr	Co	Ni	Cu	Zn	As	Mo	Cd	Sn	Sb	Pb
	(unit)	%	%	%	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	%	%	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Domestic antifouling paint makers (n=11)																	
A (n=3)	mean	0.16	2.93	3.49	29.2	0.91	59.1	0.77	41.7	23.87	8.03	1.41	2.62	0.65	212.7	5.50	140.3
	std	0.09	5.03	3.32	44.7	0.54	21.7	0.73	19.6	2.00	0.52	1.05	0.89	0.33	47.2	4.17	52.2
B (n=2)	mean	0.54	0.14	0.65	79.0	1.53	87.6	4.65	11.0	22.14	0.02	0.55	1.23	0.13	288.6	5.91	208.5
	std	0.06	0.00	0.71	10.8	0.40	20.5	1.54	0.02	0.97	0.00	0.03	1.04	0.00	8.4	0.56	36.2
C (n=3)	mean	0.19	0.97	0.76	21.1	6.01	57.8	1.85	211.5	48.35	2.56	1.94	5.65	1.97	638.3	6.33	185.4
	std	0.03	1.57	1.23	21.2	9.63	19.3	1.36	94.1	9.92	2.17	1.14	2.97	1.32	199.4	1.66	17.4
D (n=2)	mean	0.20	2.15	1.98	91.8	4.70	8.5	2.84	37.0	27.09	7.55	8.25	4.70	0.74	400.9	5.75	45.3
	std	0.05	2.91	2.76	62.4	4.12	4.0	3.21	9.4	11.04	6.04	9.53	2.48	0.42	266.0	5.85	11.1
E (n=1)	mean	0.11	5.39	0.01	22.8	1.39	26.1	0.95	57.1	19.95	25.46	1.97	2.73	0.56	190.5	2.93	92.1
Domestic	**mean**	**0.24**	**1.97**	**1.64**	**46.8**	**3.15**	**51.7**	**2.16**	**83.0**	**30.46**	**6.58**	**2.69**	**3.58**	**0.93**	**374.8**	**5.61**	**143.4**
	min	0.07	0.03	0.001	2.8	0.44	5.7	0.31	10.9	19.28	0.01	0.53	0.50	0.13	162.1	1.61	37.5
	max	0.58	8.74	6.62	135.9	17.13	102.1	5.74	318.2	54.44	25.46	14.99	8.99	3.49	851.5	10.11	234.1
	std	0.16	2.97	2.25	43.0	5.06	30.6	1.96	94.1	13.00	7.39	4.17	2.37	0.94	221.8	2.89	65.7
Imported antifouling paint makers (n=14)																	
F (n=7)	mean	0.23	0.45	1.66	9.0	1.06	30.3	0.78	91.5	45.10	8.89	1.30	2.69	1.14	396.3	4.88	195.7
	std	0.08	1.04	3.35	7.3	0.54	22.3	0.43	71.4	4.77	1.50	1.27	1.85	0.38	181.0	1.65	88.6
G (n=4)	mean	0.17	2.40	2.96	27.7	2.08	29.5	1.17	83.5	29.86	7.99	1.23	5.37	1.16	248.9	2.74	70.9
	std	0.10	3.03	4.15	27.2	1.96	28.2	0.99	57.1	9.26	1.85	0.79	5.21	0.97	203.1	1.81	51.3
H (n=2)	mean	0.06	0.88	0.18	10.4	0.40	11.0	1.21	30.8	45.59	6.81	7.23	3.95	10.10	127.4	3.45	212.8
	std	0.01	1.23	0.21	11.4	0.22	1.5	0.29	9.7	5.61	9.38	7.04	2.33	11.92	10.2	2.13	62.9
I (n=1)	mean	0.86	6.22	0.01	110.7	7.34	36.3	1.03	88.8	27.32	13.77	16.78	3.03	1.53	424.3	11.79	121.1
Imported	**mean**	**0.23**	**1.48**	**1.70**	**21.8**	**1.71**	**27.7**	**0.97**	**80.3**	**39.54**	**8.68**	**3.23**	**3.66**	**2.45**	**317.8**	**4.56**	**157.1**
	min	0.06	0.01	0.002	2.35	0.24	0.49	0.15	1.7	17.33	0.17	0.36	0.36	0.42	3.4	0.05	12.1
	max	0.86	6.35	9.13	110.66	7.34	76.32	2.39	235.91	52.12	13.77	16.78	12.24	18.52	755.4	11.79	320.2
	std	0.20	2.31	3.20	30.5	2.00	21.6	0.60	59.7	9.76	3.36	4.95	3.12	4.66	189.4	2.77	90.6
Harbor sediments (n=7)																	
Busan harbor sediment	**mean**	**8.01**	**4.06**	**0.40**	**515.9**	**90.55**	**74.1**	**11.81**	**27.9**	**196.2**[a]	**280.8**[a]	**11.28**	**1.62**	**0.36**	**7.1**	**1.37**	**60.1**
	min	6.83	3.20	0.34	473.2	69.05	55.9	8.07	17.2	115.1[a]	194.6[a]	9.78	0.92	0.17	4.7	1.02	41.6
	max	8.71	4.65	0.45	576.0	107.25	90.9	13.95	33.6	288.3[a]	464.7[a]	13.90	3.30	0.72	11.4	1.91	90.4
	std	0.59	0.48	0.04	47.0	11.90	11.3	1.97	5.4	77.9[a]	87.0[a]	1.47	0.80	0.19	2.8	0.35	20.9

[a]unit: mg/kg

820 **Table 3.** Comparison of mean, and standard deviation values for Cu, Zn, and Pb isotopic
821 composition of the present study.

		$\delta^{65}Cu_{AE647}$	$\delta^{66}Zn_{IRMM3702}$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{208}Pb/^{206}Pb$	$^{206}Pb/^{207}Pb$
	(unit)	‰	‰					
Domestic antifouling paint makers (n=11)								
A (n=3)	mean	0.28	0.02	18.4329	15.6298	38.1938	2.0720	1.1794
	std	0.08	0.01	0.0604	0.0052	0.0455	0.0043	0.0035
B (n=2)	mean	0.18	–0.08	18.2198	15.6207	38.0499	2.0884	1.1664
	std	0.005	0.02	0.0359	0.0024	0.0301	0.0024	0.0021
C (n=3)	mean	0.28	–0.16	18.7412	15.6550	38.4026	2.0492	1.1971
	std	0.01	0.09	0.1401	0.0128	0.1053	0.0097	0.0080
D (n=2)	mean	0.29	–0.27	18.5232	15.6412	38.2786	2.0668	1.1842
	std	0.03	0.01	0.3606	0.0309	0.1839	0.0304	0.0208
E (n=1)	mean	0.34	–0.06	18.4594	15.6333	38.1801	2.0683	1.1808
Domestic	**mean**	**0.27**	**–0.11**	**18.4971**	**15.6374**	**38.2387**	**2.0675**	**1.1829**
	min	0.18	–0.27	18.1944	15.6190	38.0286	2.0380	1.1649
	max	0.36	0.03	18.9027	15.6693	38.5242	2.0901	1.2063
	std	0.06	0.11	0.2292	0.0175	0.1502	0.0176	0.0134
Imported antifouling paint makers (n=14)								
F (n=7)	mean	0.25	–0.08	18.8081	15.6621	38.4439	2.0441	1.2009
	std	0.04	0.07	0.1730	0.0192	0.1382	0.0127	0.0096
G (n=4)	mean	0.20	–0.15	18.6768	15.6560	38.3278	2.0525	1.1929
	std	0.16	0.13	0.3279	0.0234	0.2223	0.0243	0.0192
H (n=2)	mean	–0.13	–0.06	17.5905	15.5718	37.4421	2.1288	1.1296
	std	0.04	0.03	0.3290	0.0219	0.3036	0.0226	0.0195
I (n=1)	mean	0.30	–0.04	18.4462	15.6364	38.2379	2.0707	1.1810
Imported	**mean**	**0.18**	**–0.09**	**18.5722**	**15.6456**	**38.2529**	**2.0605**	**1.1870**
	min	–0.16	–0.34	17.3579	15.5563	37.2274	2.0261	1.1158
	max	0.32	–0.01	19.0440	15.6864	38.6538	2.1447	1.2140
	std	0.16	0.09	0.4790	0.0368	0.3871	0.0338	0.0279
Harbor sediments (n=7)								
Busan harbor sediment	**mean**	**0.06**	**–0.11**	**18.2739**	**15.6263**	**38.3801**	**2.1003**	**1.1694**
	min	0.01	–0.17	18.1681	15.6166	38.2353	2.0977	1.1630
	max	0.12	–0.06	18.3619	15.6347	38.5190	2.1046	1.1744
	std	0.04	0.04	0.0677	0.0068	0.1185	0.0025	0.0039

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Highlights

- First multi-isotopic and elemental fingerprints of antifouling paints (APs).
- APs isotopic compositions vary depending on manufacturer and color.
- Unique chemical fingerprint of APs differentiates them from other pollutants.
- Major contribution of harbor sediments in Korea indicated urban sources than APs.
- Metal isotopic signatures may enable source discrimination in forensic studies.

CRediT authorship contribution statement

Hyeryeong Jeong: Conceptualization, Investigation, Metal and Isotope analysis, Visualization, Validation, Writing-original draft. **Daniel F. Araújo:** Validation, Writing-Review & Editing. **Joël Knœry:** Validation, Writing-Review & Editing. **Nicolas Briant:** Validation, Writing-Review & Editing. **Kongtae Ra:** Methodology, Sampling, Metal and Isotope analysis, Visualization, Funding acquisition, Writing-Review & Editing.

Declaration of interests

☒ 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.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: