

SHORT REPORT

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Toxic metal concentrations and Cu–Zn–Pb isotopic compositions in tires

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Abstract

Background: Particles from non-exhaust emissions derived from traffic activities are a dominant cause of toxic metal pollution in urban environments. Recently, studies applying multiple isotope values using the Iso-source and positive matrix factorization (PMF) models have begun to be used as useful tools to evaluate the contribution of each pollution source in urban environments. However, data on the metal concentrations and isotopic compositions of each potential source are lacking. Therefore, this study presents data on toxic metals and Cu, Zn, and Pb isotopic compositions in tires, which are one of the important non-exhaust emission sources.

Findings: Among the toxic metals, Zn had the highest concentration in all tire samples, and the mean concentrations were in the order of Zn > Cu > Pb > Sn > Sb > Ni > Cr > As > Cd. Ni, Zn, Sn, and Sb had higher concentrations in domestic tires (South Korea), and the Cu, Cd, and Pb concentrations were relatively higher in imported tires. The mean values of $\delta^{65}\text{Cu}_{\text{AE647}}$, $\delta^{66}\text{Zn}_{\text{IRMM3702}}$, and $^{206}\text{Pb}/^{207}\text{Pb}$ ranged from -1.04 to -0.22% , -0.09 to -0.03% , and 1.1242 to 1.1747 , respectively. The concentrations and isotopic compositions of Cu and Pb in the tires showed large differences depending on the product and manufacturer. However, the differences in Zn concentration and $\delta^{66}\text{Zn}_{\text{IRMM3702}}$ values were very small compared with those of Cu and Pb. The relationships of the Zn concentration and isotopic composition showed that domestic tires are clearly distinguishable from imported tires. Bi-plots of Cu, Zn, and Pb isotopic compositions indicated that tires can be clearly discriminated from natural-origin and other non-exhaust traffic emission sources.

Conclusions: The multi-isotope signatures of Cu, Zn, and Pb exhibited different isotopic values for other non-exhaust traffic emission sources than for tires, and application of the multi-isotope technique may be a powerful method for distinguishing and managing non-exhaust sources of metal contamination in urban environments.

Keywords: Cu isotope, Zn isotope, Pb isotope, Tire, Source identification

Introduction

Tires are made from natural rubber, synthetic rubber, metals, carbon black, and other compounds (Sommer et al. 2018; Halle et al. 2020). Wear particles from tires are released by traffic-related non-exhaust emissions during vehicle transportations and are one of the important sources of not only microplastic pollution (Wagner et al. 2018; Järnlskog et al. 2020) but also heavy metal pollution

in the terrestrial environments (Adachi and Tainosho 2004; Adamiec et al. 2016; Jeong and Ra 2021a).

As vehicle traffic and infrastructure such as urban roads are increasing, environmental problems such as plastic and metal pollution related to tire wear particles are also increasing worldwide. These types of pollution cause harmful effects on human health in urban environments (Khan and Strand 2018; Campanale et al. 2020; Rahman et al. 2021; Zglobicki and Telecka 2021). They are also closely related to environmental problems in the atmosphere and marine environments because particles derived from tire wear are easily resuspended by wind and transported by runoff without any treatment

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(Wagner et al. 2018; Baensch-Baltruschat et al. 2020; Jeong et al. 2020a; Tamis et al. 2021). In particular, particles from tire wear are an important contaminant that causes heavy metal pollution, especially Zn (Councell et al. 2004; Adamiec 2017; Klöckner et al. 2019; Jeong and Ra 2021b; Leifheit et al. 2021). Road dust polluted by non-exhaust traffic emission increases the concentration of toxic metals as the particle size decreases. The fine road dust particles more easily diffuse into the atmosphere than sediments from the geological origins. Toxic metals in fine urban dust can pose potentially serious health risks to residents via pathways of ingestion and inhalation (Adamiec and Jarosz-Krzeminska 2019; Kaonga et al. 2021). Many studies have reported that urban dust is severely contaminated with toxic metals, and Zn is more polluted than other metals (Skorbiłowicz et al. 2020; Jeong et al. 2020b).

The number of automobiles registered in Korea was approximately 24 million in 2021, an increase of approximately 1.3 times from the 18 million in 2011, and these include approximately 81.6% passenger cars, 3.2% vans, 14.8% trucks, and 0.4% special vehicles (KOSIS 2021). The average driving distance of automobiles in Korea is 37.9 km/vehicle, and the total annual driving distance of all vehicles is approximately 300 billion km/year (KOSIS 2021). The higher number of vehicles and greater driving distance have accelerated tire wear and the manufacturing of tires. Three billion tires were produced worldwide in 2019 (Ruwona et al. 2019; Dong et al. 2021). With increasing automobile weight, the emission factor of tire wear increases, from 45 to 57 mg/vehicle/km for passenger cars to 949 mg/vehicle/km for heavyweight trucks in Korea (Lee et al. 2020) and from 29 mg/vehicle/km for passenger cars to 2934 mg/vehicle/km for heavy duty in USA (Fiala and Hwang 2019). Lee et al. (2020) reported that the average amount of tire wear particles in Korea was 53,188 tones/year.

To manage metal pollution in urban environments efficiently, it is important to evaluate the relative contributions of metal pollution from various non-exhaust traffic emission sources, including tire wear. Some studies have evaluated the contributions of potential sources to PM_{2.5} and soil samples using multiple model methods based on metal concentrations (Wang et al. 2013; Chai et al. 2021; Han et al. 2021). Because metal concentrations vary significantly with time and space, multi-isotopic fingerprints (MIF) have recently been used as a powerful tool to identify and trace pollution sources more accurately and to assess their relative contributions (Kim et al. 2021; Wang et al. 2021; Souto-Oliveira et al. 2021). Positive matrix factorization (PMF) is used to determine the source contributions, and MIF has a good resolution for source discrimination (Souto-Oliveira et al. 2021). Recent

studies used a combination of PMF and isotope ratios for source identification and contributions (Souto-Oliveira et al. 2021; Wang et al. 2021). Iso-source, stable isotope analysis in R (SIAR) models, and isotope ratios were also used to evaluate the contributions (Kim et al. 2021). However, metal concentrations and multi-isotope signatures for various pollutants, particularly those of non-exhaust traffic emission sources, are lacking worldwide. To identify metal pollution sources in the environment clearly, it is necessary to establish isotope signatures for raw materials.

Therefore, this study presents the toxic metal concentrations and multi-isotopic (Cu, Zn, and Pb) signatures in domestic and imported tires produced by five different manufacturers used in Korea. There is no legislation related to non-exhaust traffic emission sources in Korea. Thus, the results of our study may aid management of metal pollution caused by tire wear and establishment of relevant regulations and environmental policies.

Materials and methods

Toxic metal analysis

Twelve tire samples produced for passenger cars in South Korea were collected from three different manufacturers (Tires A, B, and C). Tire A, B, and C accounted for the majority of tire market share in South Korea. For comparison among countries, four tire samples imported from France (Tire D) and China (Tire E) were also obtained. A portion of the surface of each tire was collected, cut into small pieces, and subjected to sonification to remove contaminants adhering to the tire surface. In May 2014, background soil (6 samples) was collected in Busan, South Korea. Information about the road dust samples was described in Jeong and Ra (2021a). Samples were digested in Teflon digestion vessels (Savillex Co., USA) with high-purity mixed acids (HNO₃: HF = 5:1) on a hot plate at 185°C. This process was repeated until the tire samples were completely decomposed. After decomposition, the samples were evaporated nearly to dryness and re-dissolved in 1% HNO₃. Toxic metals (Cr, Ni, Cu, Zn, As, Cd, Sn, Sb, and Pb) were measured using an inductively coupled plasma mass spectrometer (ICP-MS; iCAP-Q, Thermo Scientific Co., Germany). All tire samples were digested and measured in duplicate.

Cu, Zn, and Pb isotope analysis

The column separation method was used to separate and purify Cu and Zn using AG-MP1 resin (Bio-Rad, USA). To eliminate matrix effects, the purification of Cu and Zn in tire samples was performed by two-step and single-step column separation using AG-MP1 resin, respectively. Pb was separated using Pb-specific resin (Eichrom Technologies, Inc., USA). The detailed chemical

procedures and isotopic measurements have been described in Jeong et al. (2021c). The purified Cu, Zn, and Pb were evaporated nearly to dryness and re-dissolved in 3% HNO₃ for isotope analyses. All chemical experiments were performed in a clean room (Class 1000) at the Korea Ocean Institute of Science and Technology (KIOST).

The Cu, Zn, and Pb isotopic compositions were determined using a multi-collector ICP-MS (Neptune Plus, Thermo Scientific Co., Germany) at KIOST. Instrumental mass bias was corrected using a standard sample bracketing (SSB) technique (Hastuti et al. 2020). Samples and standard solutions were diluted in 3% HNO₃, and the concentrations were matched to less than ±5% at 100 ppb for Cu, 200 ppb for Zn, and 50 ppb for Pb.

The Cu and Zn isotopic data were expressed in delta (δ) notation as per mil (‰) deviations from the isotopic standard (ERM-AE647 and IRMM-3702, respectively) as follows:

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

$$\delta^{66}\text{Zn}(\text{‰}) = \left(\frac{(^{66}\text{Zn}/^{64}\text{Zn})_{\text{sample}}}{(^{66}\text{Zn}/^{64}\text{Zn})_{\text{IRMM3702}}} - 1 \right) \times 1000 \quad (2)$$

The accuracy of isotope analyses was verified by determining the isotopic composition of two in-house standard solutions for Cu (ERM AE633 and Kanto Cu solution) and Zn (IRMM-651 and Kanto Zn solution), respectively. The $\delta^{65}\text{Cu}_{\text{AE647}}$ values were $-0.21 \pm 0.00\text{‰}$ ($n=4$) for AE633 and $+0.12 \pm 0.01\text{‰}$ ($n=4$) for Kanto Cu solution. The $\delta^{66}\text{Zn}_{\text{IRMM3702}}$ values were $-11.57 \pm 0.01\text{‰}$ ($n=4$) for IRMM651 and $+0.06 \pm 0.01\text{‰}$ ($n=4$) for Kanto Zn solution. These values are consistent with those reported previously by Jeong et al. (2021c). The isotope data previously reported using NIST SRM 976 and JMC-Lyon were

converted to ERM AE647 and IRMM-3702, respectively. The $\delta^{65}\text{Cu}_{\text{AE647}}$ and $\delta^{66}\text{Zn}_{\text{IRMM3702}}$ values were -0.21‰ compared with NIST SRM 976 and -0.27‰ compared with JMC-Lyon (Moeller et al. 2012; Araújo et al. 2017). Tire samples were analyzed in duplicate for Cu, Zn, and Pb isotopic compositions. The average analytical uncertainties (1 s) of duplicate measurements for tire samples yielded range from ± 0.01 to $\pm 0.06\text{‰}$ for $\delta^{65}\text{Cu}_{\text{AE647}}$, from $\pm 0.01\text{‰}$ to $\pm 0.03\text{‰}$ for $\delta^{66}\text{Zn}_{\text{IRMM3702}}$, and from 0.0001 to 0.0003 for the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio.

Results and discussion

Toxic metal concentrations

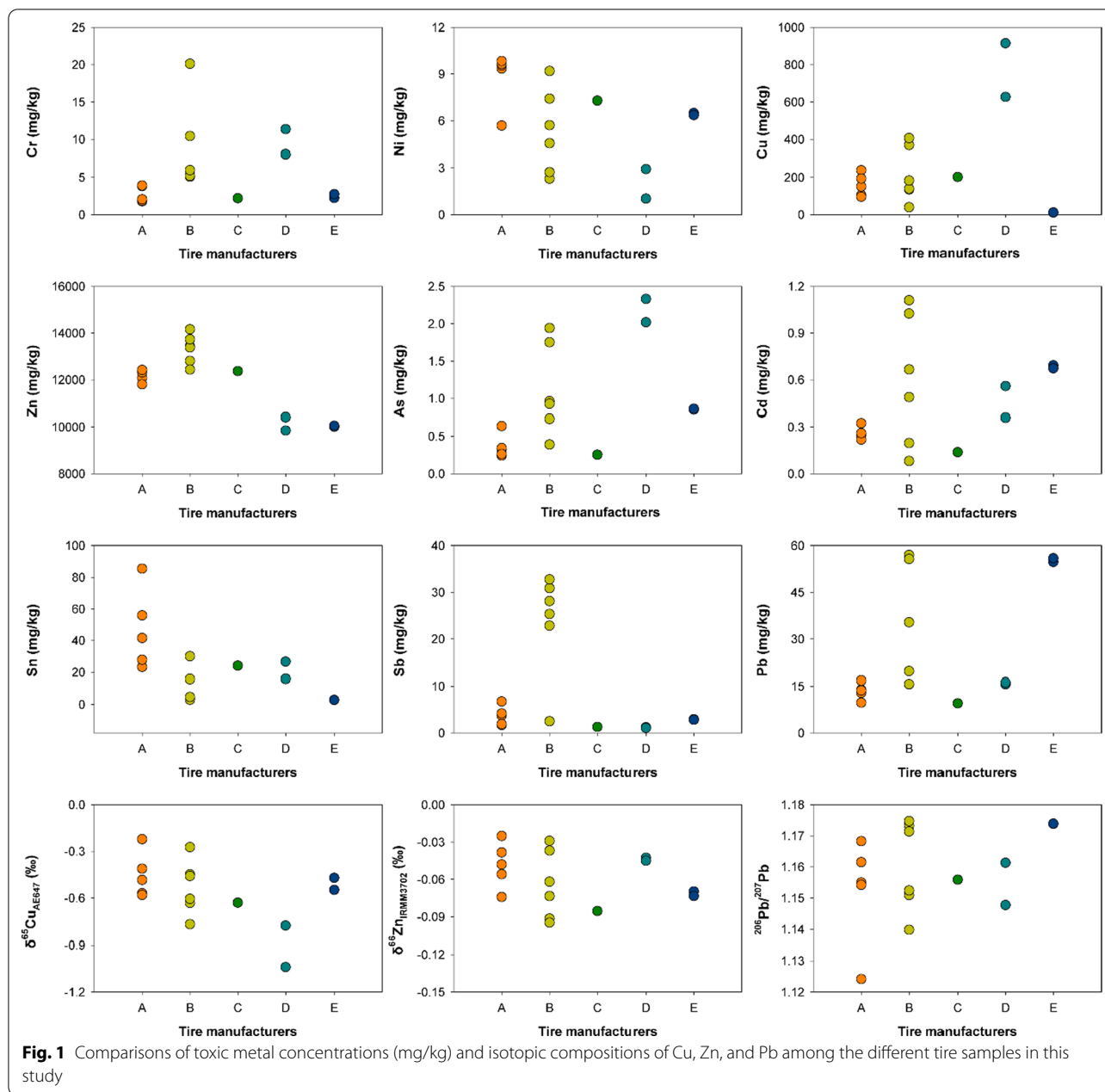
The mean concentrations of toxic metals in all tire samples (Tire A, B, C, D, and E) were in the order of Zn > Cu > Pb > Sn > Sb > Ni > Cr > As > Cd (Table 1 and Fig. 1). Zn had the highest concentration among the toxic metals, with mean values of 10,128–13,322 mg/kg. Zn showed a relatively small difference (1.4 times) in concentration among tire samples compared with the other toxic metals. The Zn concentration of domestic tires (Tires A, B, and C) was higher than that of imported tires (Tires D and E) and was similar to those of tires used in the UK (9500 mg/kg; Dong et al. 2017) and USA (12,980 mg/kg; Thapalia et al. 2010).

The mean concentrations of Ni (8.81 mg/kg), Sn (46.8 mg/kg), and Sb (23.7 mg/kg) were relatively high in the domestic tires, whereas those of Cr, Cu, Cd, and Pb were higher in the imported products. Tire D had the highest mean concentrations of Cr (9.70 mg/kg) and Cu (770.7 mg/kg), and Tire E had the highest concentrations of Cd (0.68 mg/kg) and Pb (55.4 mg/kg).

The differences in the mean concentrations among all tire samples were 11-fold for Cr, tenfold for Ni and As, 81-fold for Cu, 14-fold for Cd, 30-fold for Sn and Sb, and sixfold for Pb, which were significantly higher than the difference in the Zn concentration. This difference in

Table 1 Mean (standard deviation in parentheses) of toxic metal concentrations (mg/kg) in tires from different manufacturers and comparisons with published data

Samples	Cr	Ni	Cu	Zn	As	Cd	Sn	Sb	Pb
Tire-A ($n=5$)	2.68 (1.08)	8.81 (1.76)	156.7 (59.9)	12,194 (259)	0.36 (0.16)	0.26 (0.04)	46.8 (25.1)	3.6 (2.0)	13.4 (2.5)
Tire-B ($n=6$)	8.67 (5.97)	5.32 (2.68)	212.1 (144.5)	13,322 (623)	1.12 (0.60)	0.59 (0.42)	10.2 (10.9)	23.7 (11.0)	33.2 (19.4)
Tire-C ($n=1$)	2.20	7.28	202.0	12,367	0.25	0.14	24.1	1.3	9.5
Tire-D ($n=2$)	9.70 (2.35)	1.98 (0.01)	770.7 (203.4)	10,128 (395)	2.18 (0.22)	0.46 (0.14)	21.3 (7.6)	1.1 (0.1)	15.9 (0.4)
Tire-E ($n=2$)	2.49 (0.36)	6.42 (0.01)	11.6 (0.4)	10,032 (31)	0.86 (0.01)	0.68 (0.01)	2.8 (0.02)	2.9 (0.1)	55.4 (0.8)
Tire (Dong et al. 2017)	–	–	36.7	9,500	–	–	–	–	–
Tire (Thapalia et al. 2010)	–	–	–	12,980	–	–	–	–	–
Background soil (unpublished data)	–	–	36.4	96.9	–	–	–	–	33.9
Road dust (< 10 μm) (Jeong and Ra 2021a)	300	75.6	513	3,007	17.0	5.6	–	61.6	480



toxic metal concentrations in tires reflects differences in the raw materials used by different manufacturers. The difference in the mean concentration of toxic metals in tires produced by the same manufacturer (Tire A) were 1.1- (Zn) to 4.0 (Sb)-fold. Among non-exhaust traffic emission sources, brake pads also were made by the same manufacturer but there was a large difference in concentration depending on the product (Jeong et al. 2022), even the same manufacturer may have used different raw materials depending on the tire product or production period.

Many studies have reported that the pollution level of Zn in road dust or road-deposited sediments is higher than the levels of other metals such as Cu, Pb, Ni, Cd, and Sb (Cai and Li 2019; Faiz et al. 2009; Jeong et al. 2020a, 2020b; Miazgowicz et al. 2020). Particles released by tire wear are widely considered to be important pollutants providing a source of Zn, especially in urban environments (Adachi and Tainosho 2004; Apeageyi et al. 2011; Skorbilowicz et al. 2020). The Cr, Ni, Cu, As, Cd, Sb, and Pb concentrations in domestic tire samples were lower than those in the finest road dust in metropolitan

city of Korea (Jeong and Ra 2021a). However, the mean Zn concentration was up to 4.4 times higher in the tires of this study than in road dust (3007 mg/kg; Jeong and Ra 2021a), indicating that the Zn contamination in road dust has a greater effect from tire wear than other non-exhaust emission sources such as brake pad and asphalt wear.

Cu isotopic composition

The $\delta^{65}\text{Cu}_{\text{AE647}}$ values of the different types of tires in this study are listed in Table 2. The $\delta^{65}\text{Cu}_{\text{AE647}}$ values were all negative, ranging from -1.04 to -0.22 ‰ and the overall variation in $\delta^{65}\text{Cu}_{\text{AE647}}$ was 0.82 ‰. The mean $\delta^{65}\text{Cu}_{\text{AE647}}$ values were -0.45 ‰ (Tire A), -0.53 ‰ (Tire B), -0.63 ‰ (Tire C), -0.91 ‰ (Tire D), and -0.51 ‰ (Tire E) (Table 2). The difference in $\delta^{65}\text{Cu}_{\text{AE647}}$ values among different tire products from the same manufacturer was larger than the difference among manufacturers (Fig. 2). The mean $\delta^{65}\text{Cu}_{\text{AE647}}$ value in domestic

tires was -0.54 ‰. Among the various manufacturers, Tire D had the lightest isotopic composition of Cu (-0.91 ‰). The $\delta^{65}\text{Cu}_{\text{AE647}}$ value of Tire E (imported tires) was in the range of that of domestic tires. The $\delta^{65}\text{Cu}_{\text{AE647}}$ of the tires in this study were different from those of tires from the UK ($\delta^{65}\text{Cu}_{\text{AE647}}$: $+0.05$ ‰; Dong et al. 2017). The mean $\delta^{65}\text{Cu}_{\text{AE647}}$ value in brake dust (Busan, South Korea; Jeong et al. 2022), which contributes significantly to metal contamination in road dust, was $+0.05$ ‰. The isotopic values were lower in the tires of this study compared with brake dust.

Figure 2a illustrates the relationship between the concentration and isotopic composition of Cu in the tire samples. Both the Cu concentration and $\delta^{65}\text{Cu}_{\text{AE647}}$ values in the tire samples showed large differences depending on the manufacturer and seemed to differ between the domestic tires and imported Tire D but were indistinguishable between domestic and Tire E.

Table 2 Comparisons of the mean, minimum, and maximum values of the Cu, Zn, and Pb isotopic compositions in this study with results in the literature

Samples	$\delta^{65}\text{Cu}_{\text{AE647}}(\text{‰})$	$\delta^{66}\text{Zn}_{\text{IRMM3702}}(\text{‰})$	$^{206}\text{Pb}/^{207}\text{Pb}$	References
Tire-A	-0.45 (-0.58 to -0.22)	-0.05 (-0.07 to -0.03)	1.1526 (1.1242 to 1.1683)	This study ($n=5$)
Tire-B	-0.53 (-0.77 to -0.27)	-0.06 (-0.09 to -0.03)	1.1604 (1.1398 to 1.1747)	This study ($n=6$)
Tire-C	-0.63	-0.09	1.1559	This study ($n=1$)
Tire-D	-0.91 (-1.04 and -0.78)	-0.04 (-0.05 and -0.04)	1.1545 (1.1477 and 1.1613)	This study ($n=2$)
Tire-E	-0.51 (-0.55 and -0.47)	-0.07 (-0.073 and -0.070)	1.1739 (1.1738 and 1.1739)	This study ($n=2$)
Tire (UK)	0.05 (-0.04 to 0.12)	-0.07 (-0.08 to -0.06)	–	Dong et al. (2017)
Tire (USA)	–	-0.23 (-0.37 to -0.13)	–	Thapalia et al. (2010)
Background soil	0.09 (-0.06 to 0.19)	0.10 (0.03 to 0.16)	1.1827 (1.1792 to 1.1854)	unpublished data
Road dust	0.05 (-0.04 to 0.13)	-0.11 (-0.17 to -0.03)	1.1514 (1.1432 to 1.1606)	Jeong and Ra (2021a)
Brake dust	0.19 (0.16 to 0.21)	-0.17 (-0.19 to -0.16)	1.1967 (1.1966 to 1.1968)	Jeong et al. (2022)

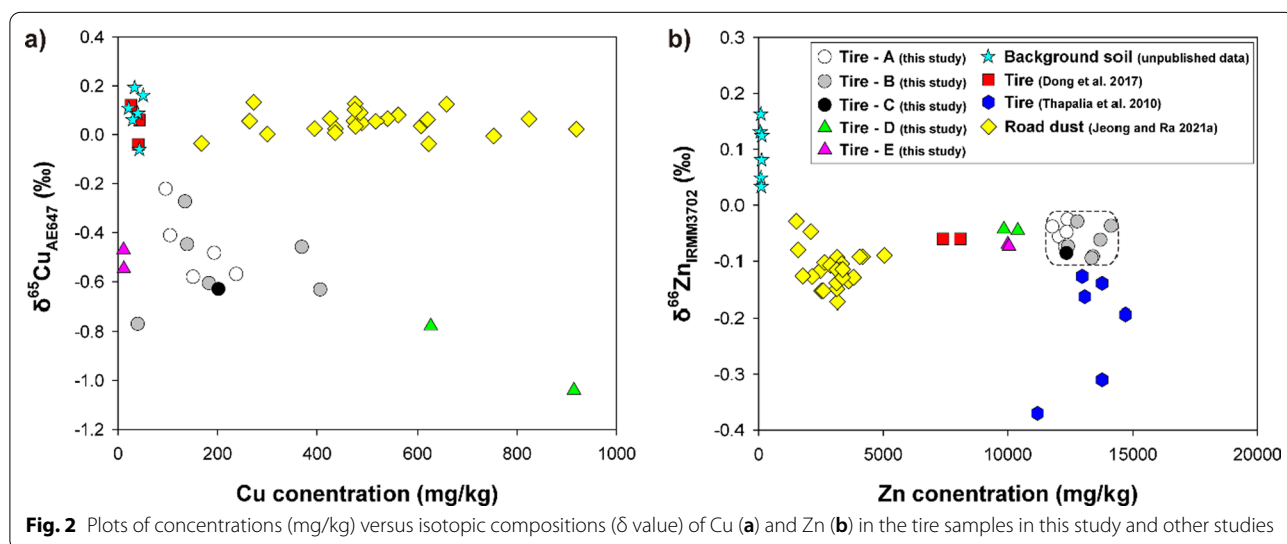


Fig. 2 Plots of concentrations (mg/kg) versus isotopic compositions (δ value) of Cu (a) and Zn (b) in the tire samples in this study and other studies

Similar to the tires, there was a large difference in the Cu concentration in road dust in Korea, but the difference in $\delta^{65}\text{Cu}_{\text{AE647}}$ values was very small. As shown in Fig. 2a, the results from the tires in this study are clearly distinguished from those from road dust (Jeong and Ra 2021a) and background soils in Korea (unpublished data).

Zn isotopic composition

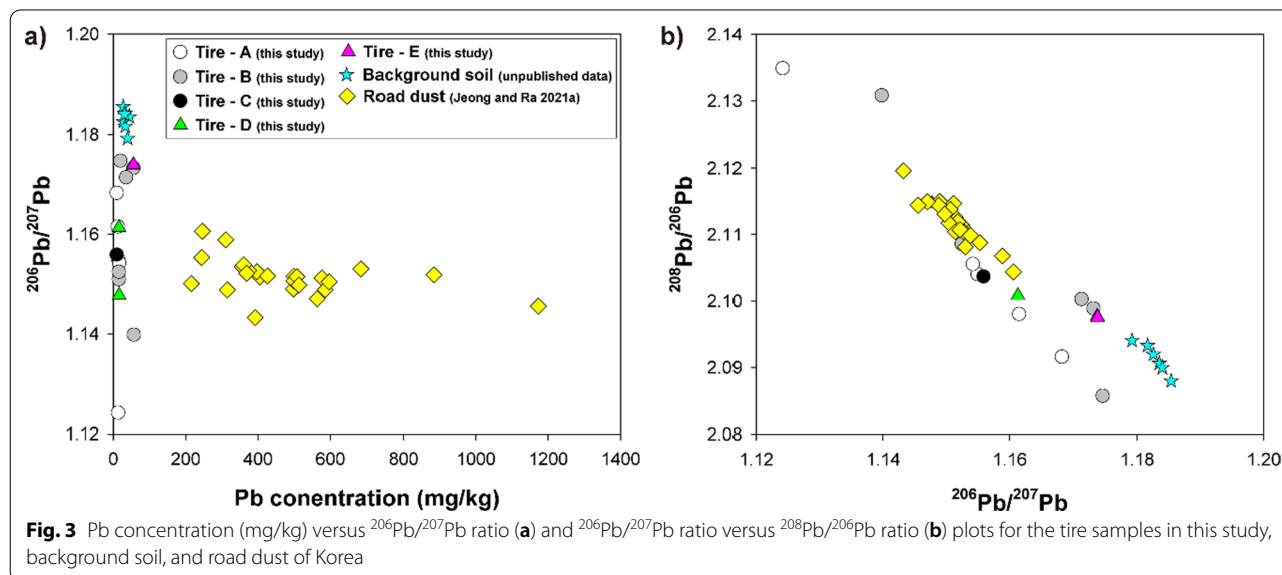
The Zn isotopic composition ($\delta^{66}\text{Zn}_{\text{IRMM3702}}$) in all tires varied between -0.09 and -0.03‰ . The overall variation in the $\delta^{66}\text{Zn}_{\text{IRMM3702}}$ of this study was $\sim 0.06\text{‰}$, indicating a smaller variation of isotopic composition among tire samples compared with $\delta^{65}\text{Cu}_{\text{AE647}}$ (Table 2). The $\delta^{66}\text{Zn}_{\text{IRMM3702}}$ was similar between the domestic tires (-0.09 to -0.03‰) and imported tires. Results in this study were similar to the $\delta^{66}\text{Zn}_{\text{IRMM3702}}$ value of tires from the UK (-0.07‰ ; Dong et al. 2017), but heavier than that of tires from the USA (-0.23‰ ; Thapalia et al. 2010). Similar to the case of Cu, there was a larger difference in $\delta^{66}\text{Zn}_{\text{IRMM3702}}$ in tire products from the same manufacturer than in those from different manufacturers. The tires also showed a slightly higher $\delta^{66}\text{Zn}_{\text{IRMM3702}}$ value than those of road dust (-0.11‰ ; Jeong and Ra 2021a) and brake dust (-0.17‰ ; Jeong et al. 2022) (Table 2).

As shown in Fig. 2b, the tires in this study had a higher Zn concentration and lower $\delta^{66}\text{Zn}_{\text{IRMM3702}}$ value compared with background soils. The mean $\delta^{66}\text{Zn}_{\text{IRMM3702}}$ value did not differ between domestic tires and road dust, but the Zn concentration was 4 times higher in tires than that of road dust, showing a clear distinction between the tires and road dust (Fig. 2b).

Although the difference in $\delta^{66}\text{Zn}_{\text{IRMM3702}}$ values among the different types of tires was quite small compared with the difference in $\delta^{65}\text{Cu}_{\text{AE647}}$ values, it appears to discriminate the various tire manufacturers due to the large differences in the Zn concentration. In particular, results in this study showed that domestic tires were clearly distinguishable from imported tires, background soil, and road dust (Fig. 2b), suggesting that the Zn isotopic composition is useful tool for classifying various pollution sources related to traffic activities.

Pb isotopic composition

The $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the tires of this study are also summarized in Table 2. The Pb isotopic composition in the tires ranged from 1.1242 to 1.1747. The mean $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in Tire A, B, C, D, and E tires were 1.1526, 1.1604, 1.1559, 1.1545, and 1.1739, respectively. The $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in Tire D (imported tires) was closer to that of domestic tires, and Tire E (imported tires) had the highest $^{206}\text{Pb}/^{207}\text{Pb}$ ratio among the five manufacturers (Fig. 2). The differences in the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio among products from the same manufacturer were 0.0441 for Tire A and 0.0349 for Tire B, and these values were larger than the mean difference (0.0213) among manufacturers (Fig. 2). The Pb isotopic composition ($^{206}\text{Pb}/^{207}\text{Pb}$) in the tires was similar that in road dust (mean: 1.1514; Jeong and Ra 2021a) (Table 2). Figure 3 shows the relationship between the Pb concentration and $^{206}\text{Pb}/^{207}\text{Pb}$ ratio and between $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios. There was no difference in the mean $^{206}\text{Pb}/^{207}\text{Pb}$ ratio between tires of this study and road dust (Jeong and Ra 2021a), but the Pb concentration in the tires was lower than that in road dust.



Because tires had a lower $^{206}\text{Pb}/^{207}\text{Pb}$ ratio than that in background soil of Korea (mean: 1.1827; unpublished data), tires were distinguished from road dust and background soil in the plot of Pb concentration versus $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (Fig. 3a). As shown in Fig. 3b, differences in the Pb isotopic ratios ($^{206}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$) were observed. The background soils of Korea had a low $^{206}\text{Pb}/^{208}\text{Pb}$ ratio and high $^{206}\text{Pb}/^{207}\text{Pb}$ ratio, but the tires had a relatively high $^{206}\text{Pb}/^{208}\text{Pb}$ ratio and low $^{206}\text{Pb}/^{207}\text{Pb}$ ratio. Although the Pb isotopic ratios of tires and road dust overlapped, the Pb concentration of road dust was approximately 19 times higher than that of tires. Therefore, in the case of Pb, road dust appears to be contaminated by different non-exhaust traffic emission sources compared with the tires and background soils.

Application of multi-isotopes as a useful tool for source identification in urban environments

Many researchers have investigated single stable isotopes such as Cu (Babcsányi et al. 2014; Li et al. 2015), Zn (Desaulty et al. 2020; Tu et al. 2020), and Pb (Rosca et al. 2018; Dietrich et al. 2021) to trace pollution sources or understand their behavior in various environments. However, because most environments are contaminated with a variety of toxic metals, a single isotope study can be applied only where the metal pollution source is simple and limited. Thus, the multi-isotope approach [e.g., Cu and Zn (Fekiacova et al. 2015; Araújo et al. 2019a), Cu and Pb (Jeong et al. 2020c), Zn and Pb (Souto-Oliveira et al. 2021), Cu, Zn, and Pb (Araújo et al. 2019b; Souto-Oliveira et al. 2019; Jeong and Ra 2021a, 2021b)] is effective for tracing pollution sources accurately compared with the single-isotope approach.

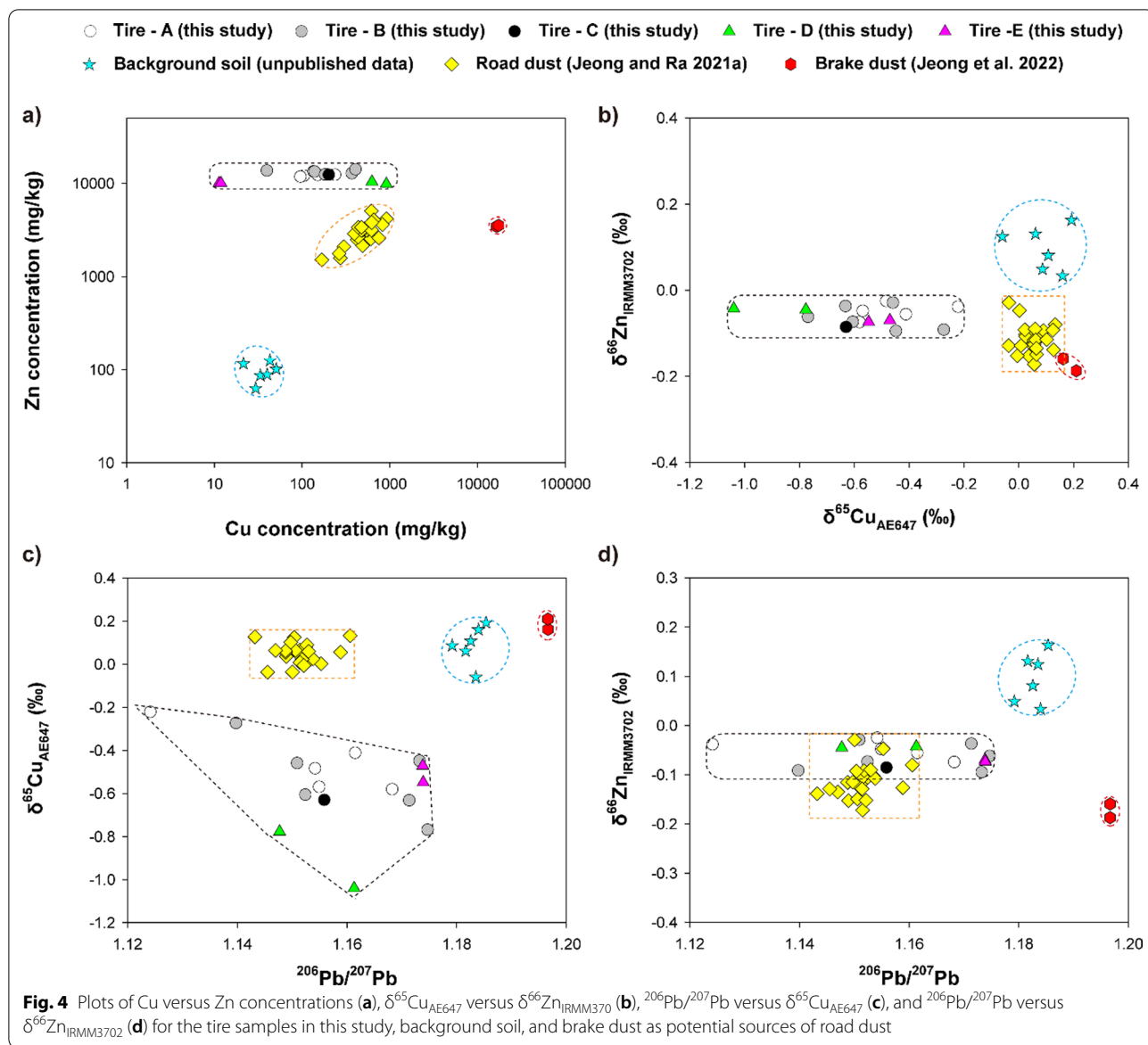
The relationships between Cu and Zn concentrations and between Cu, Zn, and Pb isotopic compositions are shown in Fig. 4. Because tire and brake dust samples have significantly higher concentrations of Zn and Cu than other pollutants, tire and brake dust, the dominant anthropogenic sources of road dust, are clearly distinguished from natural origin (background soil) (Fig. 4a). The tires had a wide range of $\delta^{65}\text{Cu}_{\text{AE647}}$ values and a narrow range of $\delta^{66}\text{Zn}_{\text{IRMM3702}}$ values. The bi-plot of $\delta^{65}\text{Cu}_{\text{AE647}}$ versus $\delta^{66}\text{Zn}_{\text{IRMM3702}}$ showed that it is possible to differentiate among potential sources such as background soil, tire and brake dust (Fig. 4b). The bi-plots of Cu or Zn versus Pb isotopic compositions in Fig. 4c and Fig. 4d indicate that Cu and Zn isotopic compositions are difficult to distinguish among road dust, background soil, and brake dust, but these pollution sources have different Pb isotopic compositions. These results suggest that Cu and Zn contamination in road dust is caused mainly by brake dust and tires, but that Pb contamination in road dust is likely affected by other pollution sources.

This study focused on presenting information on the concentration and isotopes of tires used in passenger cars since light-duty vehicles (passenger cars) account for 81.6% of registered automobiles in Korea. The isotope values in tires of passenger cars showed little difference among manufacturers compared to metal concentrations. In Korea, heavy-duty vehicles (including vans and trucks) account for 18% as of 2021 (KOSIS 2021). It has been reported that tire and brake wear on heavy-duty vehicles is higher than on light-duty vehicles (Fiala and Hwang 2019). Therefore, it is needed to produce isotope data on tires used in heavy-duty vehicles. Tire particles released into the urban environment by traffic activity can also be closely related to the weight and speed of the vehicles. Therefore, in order to accurately evaluate the impact of tire wear particles on road dust and the pollution contribution rate, it is necessary to perform concentration and isotope analysis after developing a separation technology for tire wear particles contained in road dust.

Recently, some researchers have begun to discriminate accurately and estimate the relative contribution of each pollution source by applying the positive matrix factorization (PMF) (Chai et al. 2021; 2021; Liu et al. 2021; Souto-Oliveira et al. 2021) and the Iso-source and stable isotope analysis in R (SIAR) models (Kim et al. 2021). As the concentrations of toxic metals vary greatly depending on sampling site and the various contamination sources in comparison with isotope signatures, multi-isotope data are more appropriate for precise evaluation of the contribution of each potential source. To reduce metal contamination levels in the environment and their harmful effects on organisms and human health, pollutants that contribute significantly to metal contamination must be managed first. Therefore, it is very important to construct various isotope signatures for as many potential contamination sources as possible in a systematic manner, but these data are very insufficient both in Korea and worldwide. Results in this study indicated that combinations of Cu, Zn, and Pb isotopes are useful tools for discriminating their sources. Such multi-isotope studies and database construction of pollution sources will play an important role in tracking and efficiently managing sources of metal contamination in urban environments, especially road dust, which is becoming more polluted by metals worldwide.

Conclusions

This study provided the toxic metal concentrations and Cu, Zn, and Pb isotopic compositions in tires, which are important sources of metal contamination. Also, this study evaluated how multi-isotope signatures can be useful tools for classifying traffic-related pollutants in urban environments. The Zn concentration was the



highest toxic metal concentration in all tire samples. The mean concentrations of Ni, Zn, Sn, and Sb were higher in the domestic tires than imported tires, and there were large differences in metal concentrations depending on the product and manufacturer. The isotopic difference in $\delta^{66}\text{Zn}_{\text{IRMM3702}}$ values was smaller than the difference in $\delta^{65}\text{Cu}_{\text{AE647}}$ values. These results indicated that multi-isotope signatures and their combinations can be useful tools for discriminating various non-exhaust traffic sources and background soil. The establishment of such multi-isotope data will play an important role in estimating the relative contributions of metal pollution in environments and managing the potential sources from non-exhaust traffic-related emissions.

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Authors' contributions

HJ: Conceptualization, Methodology, Investigation, Visualization, Writing-original draft, Writing-review & editing, Funding acquisition. The author read and approved the final manuscript.

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Availability of data and materials

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

Declarations

Competing interests

The author declares no competing interests in relation to the work described.

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