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Carbon and nitrogen isotope characterization of imported coals in South Korea

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1 Introduction

Since the Industrial Revolution in the late 1700s, coal has been a major energy source widely used in transportation, industries, and electricity generation. According to recent statistics on total global coal production, the coal consumption rate has continuously increased from 4,699 Mton in 2000 to 8,025 Mton in 2022 (International Energy Agency, IEA, 2022). The increase in coal consumption is closely related to the production of electricity. In 2017, the International Energy Agency, IEA, 2019 reported that coal-fired power plants generated 40% of total electricity worldwide. Despite the necessity of coal, its use contributes to a rise in the Earth's temperature due to the emission of greenhouse gases (e.g., CO_2) into the atmosphere during combustion. Global warming, due to the use of fossil fuels, including coal, has increased the global mean surface air temperature by 0.89°C in 2022 (National Oceanic and Atmospheric Administration National Centers for Environment Information, NOAA, 2022). Recently, at the Paris Climate Conference in 2015, nearly 200 countries adopted an international agreement that aims to reduce greenhouse gas emissions to keep the global average temperature at <2°C above pre-industrial levels (UNFCCC, 2015).

China is the largest coal-producing country in the world, with >48% of global coal production (International Energy Agency, IEA, 2020). However, since 2005, China's average annual coal consumption rate has slightly exceeded the national coal production rate. Consequently, approximately 7% (300 million tons) of the total coal consumption in China has been imported from Indonesia (65.8%), Russia (17.4%), and Mongolia (3%) (International Energy Agency, IEA, 2022). However, in South Korea, the coal consumption rate (157 million tons) has largely exceeded the coal production rate (1.9 million tons) (CEIC, 2021). Therefore, the coal consumed in South Korea relies entirely on imports from other countries. In 2022, the largest amount of coal was imported from Australia (37%), followed by Russia (22%), Indonesia (20%), Canada (7%), South Africa (5%), the United States (3.7%), the Philippines (1.6%), and Colombia (1.4%) (Korea Institute of Geoscience and Mineral Resources, 2023). In contrast, imports of coal from China have gradually decreased, accounting for only 0.03% of total coal imported into South Korea in 2022.

Geographically, South Korea is located to the east of China, and air pollutants (including greenhouse gases) emitted from thermal power and industrial plants in China are transported to South Korea by the westerlies. To solve this environmental problem between the two countries, it is important to explore the scientific evidence that air pollutants move from China to South Korea. Kim (2019) assessed that the concentration of particulate matter (PM_{10}) entering Korea from China had an impact of 12%–30%, depending on the season and wind direction. Oh et al. (2020) estimated that >60% of fine particulate matter ($PM_{2.5}$) concentrations observed in South Korea over five consecutive days in January 2019 were derived from China. Park et al. (2018), based on the composition of carbon and nitrogen isotopes, found that $PM_{2.5}$ collected from Baengnyeong Island, which is geographically located between China and Korea, was predominantly derived from China. Carbon and nitrogen isotope ratios of air samples have been used to identify the origins of atmospheric pollutants (Turnbull et al., 2011; Walters et al., 2015; Pang et al., 2016; Wojtal et al., 2016). Zong et al. (2020) estimated the nitrogen isotopic composition of national NO_x ($\delta^{15}N$-NO_x) emissions by vehicle in China based on $\delta^{15}N$-NO_x values from various vehicle exhausts (n = 137). Widory and Javoy (2003) identified the contribution of CO_2 sources (e.g., vehicles, heating sources, and human respiration) in the urban atmosphere using a combination of carbon isotopes and CO_2 concentrations. However, no studies focused on whether coal-fired gases could be used to identify national-derived greenhouse gases and air pollutants from nearby countries.

Therefore, the objectives of this study were to analyze the multi-isotopic composition of coal used mainly in Korea and to preliminarily evaluate whether it is possible to judge whether greenhouse gases derived from China contribute to the atmosphere in Korea using the isotopic composition of coal. To this end, the coal samples used in coal-fired power plants in Korea, imported from eight countries (South Africa, Australia, Russia, the United States, Canada, Indonesia, Colombia, and the Philippines), were analyzed.

2 Methodology

2.1 Coal samples

In South Korea, coal-fired power plants are located along the coastlines of the central-western (and northwestern), northeastern, and central-southern areas (Supplementary Figure S1). Most plants have been operating since the 1990s, while a few new ones are under construction. Of the coal-fired power plants, those in the western areas account for the highest electricity production (73%), followed by those in the central southern (22%), and northeastern (5%) areas (Korea Electric Power Corporation, KEPCO, 2023). A total of 68 coal samples were collected from five coal-fired power plants in western, southern, and eastern Korea (Supplementary Figure S1). Samples collected from the plants were transferred to Ziploc bags using a plastic shovel and transported to the laboratory. The samples imported from eight countries in 2021 were distributed as follows: Australia (n = 18), Indonesia (n = 21), the Russian Federation (n = 15), South Africa (n = 4), Canada (n = 2), Colombia (n = 4), the Philippines (n = 1), and the United States (n = 3). Other information, such as the location of the coal mine, was not available. The coal samples were stored in the laboratory at room temperature until analysis.

2.2 Coal sample preparation and analyses

The coal samples were dried at room temperature and pulverized using an agate mortar and pestle. To determine the carbon and nitrogen isotopic compositions ($\delta^{13}C$ and $\delta^{15}N$, respectively), approximately 50 µg and 2 mg of ground samples were enclosed in tin capsules, respectively. The packed samples were stored in a drying oven until further analysis. $\delta^{13}C$ and $\delta^{15}N$ values were measured using a VisION mass spectrometer (Isoprime, Manchester, United Kingdom) interfaced with a Vario PyroCube elemental analyzer (Elementar, Hesse, Germany). Although the elemental analyzer included a U-shaped adsorption column to separate the CO_2 and N_2 gases generated through a combustion tube maintained at 1,150°C, carbon, and nitrogen isotope ratios were separately analyzed due to the extremely high abundance of carbon than nitrogen in the samples.

$\delta^{13}C$ and $\delta^{15}N$ values were reported in the delta (δ) notation relative to VPDB and air, respectively, where δ (‰) = $(R_{sample}/R_{standard} - 1) \times 1{,}000$, and R represents $^{13}C/^{12}C$ and $^{15}N/^{14}N$, respectively. $\delta^{13}C$ values were normalized using international standards IAEA-600 (−27.8‰), NBS-22a (−29.7‰), USGS-40 (−26.4‰), and IAEA-CH6 (−10.5‰), and laboratory standard UREA (−35.46‰). $\delta^{15}N$ values were normalized using international standards USGS-40 (−4.52‰), IAEA-NO3 (4.7‰), and IAEA-600 (1.0‰), and laboratory standard UREA (20.17‰).

3 Results and discussion

The carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) contents of coal (n = 62) imported from eight countries (South Africa, Australia, Russia, the United States, Canada, Indonesia, Colombia, and the Philippines) to South Korea and the isotopic compositions of each element are listed in Supplementary Tables S1, S2, respectively.

3.1 Major elements in imported coal samples

Carbon contents in coal (n = 62) were predominantly high at 47.3%–75.5% (68.3% ± 4.9%), followed by H at 3.0%–6.1% (4.9% ± 0.6%), N at 0.7%–2.5% (1.4% ± 0.5%), and S at 0.1%–1.6% (0.4% ± 0.3%). There were no correlations between the elemental contents or even between those from the same country. Additionally, no correlation was observed between $\delta^{13}C$ and any other element (not shown). When the C content in coal is entirely determined by coalification processes, their $\delta^{13}C$ values increase together with the C content due to the loss of methane during the process, which is typically a ^{13}C-depleted carbon (Whiticar, 1996; Thomas et al., 2022). Due to the lack of correlation between $\delta^{13}C$ values and C content in coal, Suto and Kawashima (2016) suggested other factors besides coalification processes, such as photosynthetic fractionation associated with geological time. Thus, the C isotopic composition

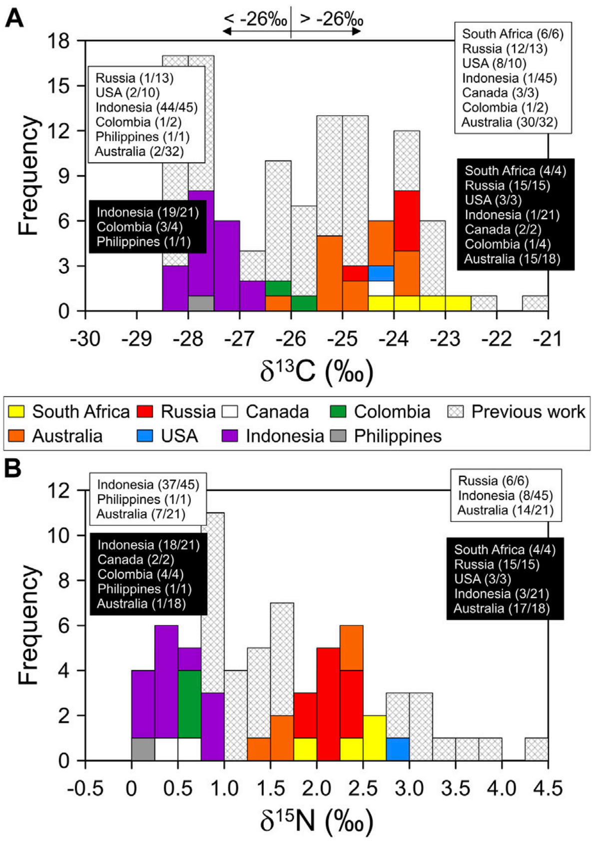

FIGURE 1
Distributions of δ^{13}C and δ^{15}N values for coals imported in South Korea from eight coal-producing countries in this study (colored bars) and in previous studies (hatched bars). The bars represent bimodal distributions at approximately −26‰ and 1.3‰ for δ^{13}C and δ^{15}N values, respectively. Coal-producing countries corresponding to the colored and hatched bars are listed in black and white squares, respectively. The fraction represents the ratio of the number of samples with **(A)** <−26‰ or >−26‰ and **(B)** <1.3‰ or >1.3‰ to the number of samples analyzed for coals from different countries.

of the coal in this study was assumed to be determined by the factors suggested by Suto and Kawashima (2016).

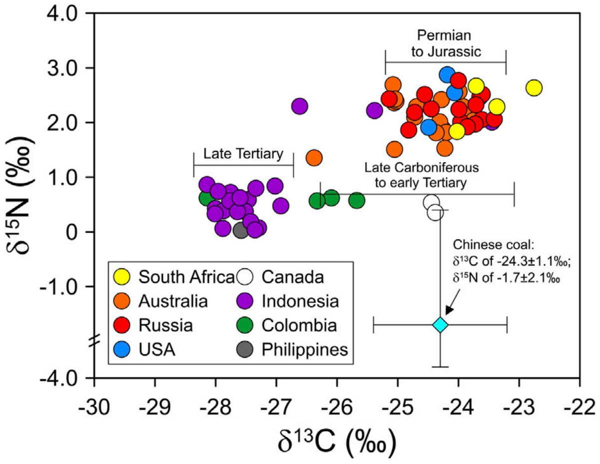

FIGURE 2
Plot of δ^{13}C and δ^{15}N values of coals imported in South Korea from eight coal-producing countries: South Africa, Australia, Russia, the United States, Canada, Indonesia, Colombia, and the Philippines. The isotope compositions representative of Chinese coal (blue color diamond) are from previous studies (Xiao and Liu, 2011). The carbon isotope compositions of the coal correspond to the geological time suggested by Suto and Kawashima (2016).

3.2 Carbon isotopic compositions in imported coal samples

The δ^{13}C values ranged from −28.1‰ to −22.8‰ (average −25.4 ± 1.6‰, n = 68) (Supplementary Figure S2; Supplementary Table S2). On average, Indonesian and South African coal samples showed the lowest (average −27.3 ± 1.1‰, n = 21) and highest (average −23.5 ± 0.5‰, n = 4) δ^{13}C values, respectively. Two samples of Indonesian coal significantly exceeded the Grubbs test value ($G_{critical}$ 2.73; $G_{observed}$ 3.22-3.58; $p > 0.0001$). With the two samples excluded, the Indonesian and South African coal samples could be completely discriminated. Although the numbers of coal samples from the Philippines and Colombia were low, their δ^{13}C values were similar to those of Indonesian coal. The samples from the other countries (such as Russia, Australia, Canada, and the United States) included δ^{13}C values closer toward South African coal; i.e., the average values of Russian and Australian coals were −24.1 ± 0.5‰ and −24.6 ± 0.6‰, respectively. These results were consistent with previously reported δ^{13}C values. Suto and Kawashima (2016) reported δ^{13}C values of −24.4 ± 1.1‰ for Russian coal and −24.5 ± 0.6‰ for Australian coal.

The carbon isotope ratios obtained in this study were classified into two groups with a bimodal distribution in the histogram (Figure 1). The δ^{13}C values of approximately <−26‰ were observed in the samples from Indonesia, Colombia, and the Philippines, whereas those of others were >−26‰. This phenomenon has also been observed in previously reported δ^{13}C values (Rigby and Batts, 1986; Suto and Kawashima, 2016; Feng et al., 2020). Specifically, most δ^{13}C values for Indonesian coals (−27.7 ± 0.7‰, n = 45) were lighter than −26‰, whereas those from Australia (−24.7 ± 0.8‰, n = 32) and Russia (−23.9 ± 1.3‰, n = 13) were heavier (Figure 1). According to Suto and Kawashima (2016), coal samples (mainly produced by conversion by C3 plants) characterized by a relatively young coal-production age, such as the Cenozoic Tertiary, had lighter δ^{13}C values, whereas coals with heavier δ^{13}C values were produced from the Paleozoic Permian to Mesozoic Jurassic periods (Figure 2). Likewise, different CO_2 concentrations and O_2/CO_2 ratios in the atmosphere over geologic time led to photosynthetic fractionation of −24‰ during the Carboniferous and Permian times and −18‰ during the Cretaceous times (Beerling et al., 2002; Strauss and Peters-Kottig, 2003), producing a wide range of δ^{13}C values for coal. These results implied that the same coal-producing countries export coal with similar δ^{13}C values to South Korea and that δ^{13}C values of coal used in South Korea can be subdivided into ca. −28‰–−27‰ and the other group of ca. −25‰–−24‰. For differences in the carbon isotope between the two groups, conversion by C4 plants into coal would not be dominant. Coal was mostly formed between the

Mesozoic and Paleozoic periods (Suto and Kawashima, 2016), and the C4 plant appeared in the Cenozoic period (Osborne and Beerling, 2006). Of the samples, only Indonesian coal was formed in the Cenozoic period (Suto and Kawashima, 2016) and might be from the C4 plants. If so, their carbon isotope compositions theoretically should be characterized by higher δ^{13}C values than those in this study due to the typical δ^{13}C value of the C4 plants. However, Indonesian coal samples in this study showed lower δ^{13}C values compared to other coal samples (Figures 1, 2). Thus, we excluded the potential influence of plant types (i.e., C3 and C4 plants) on the difference in δ^{13}C values.

3.3 Nitrogen isotopic compositions in imported coal samples

The δ^{15}N values of coal samples ranged from 0.03‰ to 2.87‰ (average 1.56 ± 0.89‰, $n = 68$) (Supplementary Table S2), which is a trend similar to the classification of carbon isotopic compositions related to producing countries. On average, coal samples from Indonesia, Canada, Colombia, and the Philippines showed the lowest δ^{15}N values (average 0.65 ± 0.59‰, $n = 28$), which had the lower values by excluding three samples with δ^{15}N values of >2.0‰ (0.47 ± 0.25‰, $n = 25$); the Grubbs test values (G_{critical} 2.71) were significantly high for the three samples (G_{observed} 2.80–3.73; $p > 0.0001$). The samples from other countries (South Africa, Russia, the United States, and Australia) showed relatively ^{15}N-enriched isotope values of 1.35‰–2.87‰ (average 2.20 ± 0.35‰, $n = 40$). The difference in the average of δ^{15}N values was statistically significant (*t*-test, $p < 0.0001$). These results were similar to those reported previously for δ^{15}N values. That is, the δ^{15}N values for Russian and Australian coal samples were higher (average 2.13 ± 1.15‰, $n = 27$) than those of Indonesia and the Philippines (1.23 ± 0.52‰, $n = 27$) (Rigby and Batts, 1986; Feng et al., 2020). Canadian coal mostly exhibited δ^{15}N values of 0‰–1‰ (Whiticar, 1996). Based on previous studies, the geographical deviations in δ^{15}N values are attributed to organic matter sources and peat-forming vegetation (Xie et al., 2021). The variations in coal rank values from bituminous to anthracite coal were independent of δ^{15}N values (Xie et al., 2021), and all coal samples used in this study were anthracite. These results support the fact that the δ^{15}N values of coal in this study were mainly determined by the organic source materials and coal-forming environment.

3.4 Comparison with carbon and nitrogen isotopes in Chinese coals and implications

Chinese coal represents the wide range of δ^{13}C values from −29.3‰ to −22.1‰ (average −24.3 ± 1.1‰, $n = 351$) (Supplementary Figure S2), and those from 25th to 75th percentiles are from −24.8‰ to −23.5‰ (Duan, 1995; Zhang et al., 1999; Suto and Kawashima, 2016; Xu et al., 2017; Ding et al., 2018; Guo et al., 2020; Zheng et al., 2020; Wang et al., 2022). The δ^{15}N values of Chinese coal (for anthracite only) range from ca. −4.0‰ to +1.5‰ with a median of −2.0‰, and those from the 25th to 75th percentiles range from approximately −3.0‰ to −0.5‰ (Xiao and Liu, 2011). Both δ^{13}C and δ^{15}N values of Chinese coal were lower than those of the coal used in South Korea, and thereby, were precisely discriminated from the others, especially by δ^{15}N values (Figure 2). Nonetheless, judging whether Chinese coal combustion affects the air quality in South Korea is challenging using the discrimination of the multi-isotopic compositions of coal due to the following reasons:

According to previous studies (Widory, 2006; Warwick and Ruppert, 2016), the carbon isotope fractionation between CO_2 derived from coal and its combustion is approximately ~2‰, and no one of them has consistently higher (or lower) δ^{13}C value. Considering this isotope fractionation, δ^{13}C values of Chinese coal were similar to those of the imported coal in South Korea. In contrast, NO_x derived from coal combustion has δ^{15}N values greatly different from those of the coal itself because of the isotopic fractionation occurring in fuel NO_x production and NO_x reduction technologies (Felix et al., 2012). In South Korea, for NO_x released from coal-fired plants operating with the selective catalytic reduction (SCR) (with NO_x removal process) and flue gas desulfurization (without NO_x removal process) systems, the δ^{15}N values have been reported to be 17.6 ± 0.4‰ and 10.4 ± 0.2‰, respectively (Park et al., 2019). Similarly, Zong et al. (2022) estimated the δ^{15}N value of 17.9‰ for NO_x from industrial coal combustion when NO_x removal systems reached 79% in China. In Korea, SCR systems operate in most coal-fired plants (Kim et al., 2020); therefore, the NO_x derived from coal-fired plants in both countries represents similar δ^{15}N values, although Chinese coals are different from those used in Korea. Moreover, considering NO_x is highly reactive and is eliminated within 2 days of emission into the atmosphere (Kenagy et al., 2018) and fine dust originating from China takes approximately one to 7 days to move to South Korea (Kim, 2019), it might be useless to assess whether atmospheric pollutant from China moves to South Korea using nitrogen isotope of NO_x. Non-fossil fuel emissions (e.g., biomass burning and microbial N cycle) account for >50% of the total NO_x emissions in East Asia (Song et al., 2021). Isotope fractionation occurs during transformation processes into other N-bearing compounds (e.g., HNO_3, NO_3^-, NH_3, and particulate nitrate) and preferential wet scavenging (Chen et al., 2022); the δ^{15}N value of 3.9 ± 1.8‰ deviated between precipitation NO_3^- and the initial NO_x mixture. Thus, instead of intercontinental source tracking of air pollutants, it can be used as a powerful tool to assess the sources impacting domestic air quality because NO_x emitted from coal-fired power plants represents the distinct δ^{15}N values compared to those of other sources (please see the following paragraph for more details). Nonetheless, the possibility of intercontinental transport of pollutants between China and South Korea may exist because pollution transport occurring as plumes is horizontally spread over ~1,000 km scale in the free troposphere for ~2 weeks (English, 2011; Zhuang et al., 2018).

Meanwhile, vehicle emission, with coal-fired emission, is a major anthropogenic source releasing NO_x into the atmosphere. According to previous studies, NO_x derived from vehicle emission has a wide range of δ^{15}N values. In general, gasoline-derived NO_x shows higher δ^{15}N values (−15.1‰ ~ +10.5‰) than those from diesel vehicles (−23.3‰ ~ +5.4‰) due to the isotope fractionation occurring during NO production and reduction in vehicle engines (Widory, 2007; Walters et al., 2015). Recently, Zong et al. (2020) reported δ^{15}N values of −18.8‰ to +6.4‰ for vehicle-derived NO_x with consideration for differences in structure, performance, and operation between gasoline and diesel engines. Consequently, vehicle-derived NO_x represents $\delta^{15}N$ values different from those of coal-fired plants. Non-fossil fuel NO_x has $\delta^{15}N$ values of −30.3 ± 9.4‰ for microbial N cycle and 1.0 ± 4.1‰ for biomass burning (Chen et al., 2022). According to the OPEC's statistics, crude oil used in China and South Korea is dominantly imported from Middle East countries (Saudi Arabia, UAE, Kuwait, and Iraq). Thus, combustions of the oil may emit CO_2 gas with similar $\delta^{13}C$ values to the atmosphere. It would be difficult to estimate the contribution of CO_2 from China to the atmosphere in South Korea. Based on the analytical data in this study and literature review (Semmens et al., 2014; Suto and Kawashima, 2016; Wang et al., 2022), $\delta^{13}C$ values for gasoline- and diesel-derived CO_2 are discriminated from coal-derived CO_2. Note that their intrinsic isotopic signals can be disturbed by both natural and anthropogenic sources with distinct isotopic values. For example, the $\delta^{13}C$ values of soil CO_2 range from −31‰ to −24‰ (Jasek et al., 2014), similar to the $\delta^{13}C$ values of CO_2 from vehicle emissions of −29.3‰ to −27.6‰, while those of CO_2 from the combustion of natural gas (heating source) have a low range of −40.5‰ to −37.7‰ (Widory and Javoy, 2003). Recently, the relationship between CO_2 concentration and its carbon isotope compositions has been used to trace sources in a local area (Clark-Thorne and Yapp, 2003; Widory and Javoy, 2003). These results suggest that vehicle derived NO_x and CO_2 have the distinct multi-isotope values and can be discriminated those from coal-fired power plants, implying that the multi-isotopes for coal- and fuel-derived gases can be used to identify atmospheric sources in local scale.

4 Conclusion

The coal samples (n = 68) imported from eight countries (Australia, Colombia, Indonesia, Russia, the United States, Canada, South Africa, and the Philippines) to Korea were collected for comparison with Chinese coal using multi-isotopic compositions and to determine whether it is possible to evaluate the contribution of air pollutants in Korea from coal combustion derived from nearby countries. Coals used in coal-fired power plants in South Korea showed two ranges from −28‰ to −27‰ and from −25‰ to −24‰ for $\delta^{13}C$ values and from 0‰ to 1‰ and from 1.8‰ to 2.8‰ for $\delta^{15}N$ values. By comparison, Chinese coals showed −24.3‰ for $\delta^{13}C$ values and −1.7‰ for $\delta^{15}N$ values. Thus, on a plot of $\delta^{13}C$ and $\delta^{15}N$ values, coals imported in South Korea were discriminated from Chinese coals, especially by $\delta^{15}N$ value. These results suggest that a database for multi-isotopic compositions of coals produced in various countries can play a role in identifying Chinese coals. The similar $\delta^{13}C$ values of coal used in both countries were preserved after coal combustion with a small isotope fractionation. However, the $\delta^{15}N$ value for NO_x emitted from coal-fired power plants in both countries can be similar, owing to isotopic fractionation occurring in the fuel NO_x production and NO_x reduction processes. Complex chemical reactions occurring between NO_x and other N-bearing compounds in the atmosphere did not allow us to use multi-isotope compositions as tracers for discriminating intercontinental air pollutant sources. Therefore, the results of this study suggest that more information on air pollutant sources and other analytical tools are required to quantitatively estimate whether emissions from coal combustion in China contribute to air quality in South Korea. In addition, coal derived gases have distinct isotope values discriminated from vehicle emissions, implying that multi-isotopes for gas samples can be used to quantitatively estimate anthropogenic sources in atmosphere in local scale.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

Author contributions

E-KJ: Conceptualization, Data curation, Methodology, Visualization, Writing–original draft. YK: Formal Analysis, Investigation, Writing–review and editing. Y-YJ: Writing–review and editing. K-SL: Writing–review and editing. S-HC: Writing–review and editing, Formal Analysis. Y-SB: Formal Analysis, Writing–review and editing. W-JS: Conceptualization, Funding acquisition, Methodology, Project administration, Supervision, Writing–review and editing.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's note

Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fenvs.2023.1279004/full#supplementary-material

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