



# Assessment of Pollution Sources and Contribution in Urban Dust Using Metal Concentrations and Multi-Isotope Ratios (<sup>13</sup>C, <sup>207/206</sup>Pb) in a Complex Industrial Port Area, Korea

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Article

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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Abstract: The metal concentrations and isotopic compositions (<sup>13</sup>C, <sup>207/206</sup>Pb) of urban dust, topsoil, and PM<sub>10</sub> samples were analyzed in a residential area near Donghae port, Korea, which is surrounded by various types of industrial factories and raw material stockpiled on empty land, to determine the contributions of the main pollution sources (i.e., Mn ore, Zn ore, cement, coal, coke, and topsoil). The metal concentrations of urban dust in the port and residential area were approximately 85~112 times higher (EF > 100) in comparison with the control area (EF < 2), especially the Mn and Zn ions, indicating they were mainly derived from anthropogenic source. These ions have been accumulating in urban dust for decades; furthermore, the concentration of  $PM_{10}$  is seven times higher than that of the control area, which means that contamination is even present. The isotopic (<sup>13</sup>C, <sup>207/206</sup>Pb) values of the pollution sources were highly different, depending on the characteristics of each source: cement (-19.6‰, 0.8594‰), Zn ore (-24.3‰, 0.9175‰), coal (-23.6‰, 0.8369‰), coke (-27.0‰, 0.8739‰), Mn ore (-24.9%, 0.9117%), soil (-25.2%, 0.7743%). As a result of the evaluated contributions of pollution source on urban dust through the Iso-source and SIAR models using stable isotope ratios (<sup>13</sup>C, <sup>207/206</sup>Pb), we found that the largest contribution of Mn (20.4%) and Zn (20.3%) ions are derived from industrial factories and ore stockpiles on empty land (Mn and Zn). It is suggested that there is a significant influence of dust scattered by wind from raw material stockpiles, which are stacked near ports or factories. Therefore, there is evidence to support the idea that port activities affect the air quality of residence areas in a city. Our results may indicate that metal concentrations and their stable isotope compositions can predict environmental changes and act as a powerful tool to trace the past and present pollution history in complex contexts associated with peri-urban regions.

**Keywords:** urban dust; metal concentration; multi-stable isotopes (<sup>13</sup>C, <sup>207/206</sup>Pb); contamination assessment; source identification

# 1. Introduction

Rapid urban development, explosive population growth, industrial activities, and increases in automobile exhaust have caused widespread pollution in the surrounding environment [1–4]. Pollutants steadily accumulate in urban areas, and toxic substances, especially heavy metals, are excessively concentrated [4]. Urban dust (house and road) and topsoil are environmental key indicators due to the fact that they contain complex particle mixtures and heavy metal ions from atmospheric deposition [5–7]. Therefore, studies on metal enrichment in urban dust and surface topsoil has been reported in the numerous scientific literature [8–16]. It is generally derived from several sources, such as crustal material, atmospheric sediment, industrial activity, coal combustion, biomass burning, and traffic activity (emissions, tire wear, brake wear, and road wear) [13], and

can be easily transported by runoff or resuspended by wind [14]. These pollutants in industrial complexes and ports, and frequent exposure to residents in adjacent living areas, can cause various health problems, such as respiratory disease, lung disease, heart disease, and rhinitis [17–25]. Thus, tracking the source of heavy metal ions and investigating the quantitative contribution of pollutants as an environmental forensic science is critical to understanding their environmental behavior and controlling exposure risk [26,27].

Previous studies have developed numerous methods to trace various types of environmental pollutions that are often difficult to identify. Metal concentrations and statistical analyses, such as clustering analysis, principal component analysis (PCA), and multivariate and geostatistical analysis, are frequently used to identify environmental pollution sources and the routes of metal contamination [3,28-37]. These methods are easy to use, but typically only offer general information on the sources. Another approach is the use of metal ratios of some crustal elements, such as Al and Fe (Enrichment Factor, [3]). These methods may provide useful information on potential enrichments, but the determination of sources based on these measurements is often uncertain. Isotopic fingerprinting, which is based on stable isotopic ratios, is a superior and in-depth method used to identify the origins of various contaminants because isotopic ratios are highly sensitive tracers, as different pollutant sources have difference isotopic values [38–43]. The stable C isotope ratio  $(\delta^{13}C)$  of various types of environmental samples reflects the isotope ratio of their source material and isotopic fractionations related to their generation processes. Samples (e.g., urban dust, topsoil, and atmospheric PM) with C derived from different plant materials  $(C_3 \text{ and } C_4 \text{ plants})$ , different fossil fuels (coal, diesel, gasoline, natural gas, and crude oil), different combustion conditions, and different degrees of post-emission transformation can be differentiated using their  $\delta^{13}$ C compositions. Therefore, the  $\delta^{13}$ C values of samples have been determined in various studies and used for source apportionment [25,42,44–46]. A number of studies have used Pb isotope ratios to identify the sources and transport pathways of Pb in atmospheric PM because the Pb isotope ratio does not change during industrial or environmental processing, retaining its characteristic ratio inherited at its source [47,48]. Kelepertzis (2016) analyzed the origin of natural Pb originating from soil and Pb from concrete, asphalt, automobile exhaust gas, and various types of plants [49]. Han (2016) examined the contribution from external sources using the <sup>206</sup>Pb/<sup>207</sup>Pb isotope ratios of road dust (anthropogenic source) and crust (natural source) [50]. Li (2018) used Pb isotope consumption to reveal that residential dust originates from coal combustion, while road dust is an automobile exhaust gas emission [3]; Kumar (2013) found that road dust in residential areas and adjacent highway dust have different origins [51]. Identifying a definite source with this information, however, is sometimes difficult due to the uncertainty associated with the isotope composition of the source (distributed over a wide range) or occasionally overlapping sources. Because the use of the single isotope ratio has some limitations in pollution research, better results can be obtained by multiple isotope systems [3,12,52,53]. Therefore, presents studies have now proposed a new paradigm based on the understanding of pollution sources of urban dust and topsoil, which indicate that the combination of multiple approaches should provide more detailed information rather than the application of only one method. In this study, C and Pb isotopic fingerprints were determined in main urban pollutant sources such as stockpiles of Mn and Zn ore, cement, coal, cokes, and topsoil collected from the industrial and residential areas of Donghae port. This port is one of five major trading ports in Korea, is characterized by international trade exchanges, and has serious problems with air quality.

Here, the objectives of this study are to (1) determine the metal concentrations in urban dust (house and road) topsoil, and  $PM_{10}$  samples in industrial, residential, and port areas; (2) evaluate the spatial distribution of metal concentrations; (3) asses the metal pollution level; and (4) reveal the potential sources and their contribution through multi isotopic (C, Pb) compositions. To the best of our knowledge, this is the first study that combines metal concentrations and multi stable isotope (C and Pb) approaches to address the behavior of urban dust and the contributions of anthropogenic pollution sources in a

complex industrial area near an international shipping port. Our results should provide an improved understanding of the metal behavior in urban dusts and the ability to effectively manage human and environmental exposure risks.

# 2. Materials and Methods

# 2.1. Site Information

Donghae port  $(37.4^{\circ} \text{ S}, 129.12^{\circ} \text{ N})$  is an artificial port that was built in 1974, with an area of 13,542 thousand m<sup>2</sup>. The port is characterized by a small difference in tides, and is the largest trading port of the East Sea, which allows entry and departure at all times. The world's largest cement plant, Korea's largest ferroalloy production plant, a steel plant, a small-scale industrial complex, and a thermal power plant are located adjacent to Donghae port. Logistics warehousing and stevedoring businesses are prospering at the port, with a total annual cargo volume of 30,000 tons and a maximum simultaneous berthing capacity of 16 thousand tons (50,000 tons, class 8 ships) for a total of 3000 ships. By cargo type, the port stores ore products (12,400 thousand tons) and cement and coal (11,645 thousand tons and 4290 thousand tons, respectively) [54]. However, due to a lack of warehouses and logistical planning, raw materials (Mn and Zn ore, cement, zinc, coke, and briquettes, among others) shipped to the port have been stacked as a stockpile in surrounding empty land and have been left unattended for decades. There is no minimum cover facility at the port. Ore materials, transported by means of trucks, are also stacked uncovered in the ore processing area and are scattered to adjacent areas via wind, such that the constant exposure of residential areas or adjacent soil is a substantial problem that has been causing numerous diseases for decades. In addition because the residential area is located between the port and an industrial complex, residents have been exposed to various pollutants for an extended period (more than 30 years), resulting in lung diseases (pneumonia, lung nodules, atelectasis, and calcification), respiratory disorders, and other chronic health damage. Currently, 16,000 people live in adjacent residential areas; however, this population decreases every year.

# 2.2. Sampling

Urban dust (road and house), topsoil, PM<sub>10</sub>, and pollution source (Mn and Zn ore, coal, cokes, and cement) samples were collected in June 2016. All samples were taken in duplicate. The sampling sites were located in different functional areas, including port, industrial, and residential areas, as shown in Figure 1. In order to compare with the study area, rural topsoil from 30 km away, in an area that is not affected by industrial complexes, was selected as a control. Pollution source samples were collected directly at the stockpiles using a plastic seedling shovel and transferred to 200 mL glass vials for storage. Urban dust samples were collected from the rooftops and windows of houses in residential areas, and road dust samples were collected from roads adjacent to the port, using a brush and plastic dustpan at least three times within 0.5 m. Repeatedly, the total weight was carefully swept over 300 g. Collected samples were stored in sealed plastic bags and immediately transferred to the laboratory. Sample were air-dried in the laboratory for 15 days, then sieved through a 500  $\mu$ m nylon sieve to remove small stones and bricks, leaves, cigarette butts, and other debris, and were finally stored in a refrigerator at 4 °C. Topsoil samples were taken three times from the surface to a depth of 1 cm within the upper 1  $m^2$  range using a stainless steel shovel at the site. The samples were then sealed in a clean polyethylene plastic bag and transferred to the laboratory. After drying the sample for weeks, foreign substances, such as leaves and large stones, were removed with a 500 µm nylon sieve, and the samples were pulverized into particles using a mortar and pestle. The pulverized sample was stored in a refrigerator at 4 °C.  $PM_{10}$  sample collectors were installed on the rooftops of schools, buildings, and houses in residential, urban, and control areas. PM<sub>10</sub> samples were collected for 72 h once a week from Monday to Wednesday using a high-volume air sampler (HV-1000R, Sibata, Japan), adapted with a PM<sub>10</sub> impactor (Sibata, Japan). PM<sub>10</sub> were sampled in quartz microfiber

filters (254 mm  $\times$  203 mm  $\times$  2.2 mm) that were pre-combusted to 700 °C for 2 h to remove any volatile organic compound before sampling.



Figure 1. Map showing the location of the sampling sites in Donghae port, Korea.

# 2.3. Trace Elemental Analysis

All samples were processed and analyzed in a trace metal clean HEPA filtered laboratory, using high purity acids and milliQ water. The ground samples (10 g, minimum) and quartz filters were digested in a Teflon tube with 50 mL of high-purity mixture acids (HF/HCl/HNO<sub>3</sub>, 1:6:2), sonicated for 2 h, and heated on a hot-block at 100 °C for 4 h. The obtained solutions were cooled, filtered through Whatman No. 40 filter paper, and diluted in 10 mL of 2% HNO<sub>3</sub> for subsequent analysis [55]. This digestion procedure was repeated twice. The solution samples were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 5300 DV, Perkin Elmer, Wellesley, MA, USA) for Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Pb, Sr, Ba, and Ni.

#### 2.4. Stable Isotope Analysis

For Pb isotope ratio determination, the extracted solutions were purified with exchange resin (AG1x8, anionic resin), and were adjusted to a Pb concentration of  $20 \ \mu g \ L^{-1}$  using 2% HNO<sub>3</sub> to monitor the performance of the instrument. The <sup>206</sup>Pb/<sup>204</sup>Pb, <sup>207</sup>Pb/<sup>204</sup>Pb, <sup>208</sup>Pb/<sup>204</sup>Pb, <sup>208</sup>Pb/<sup>206</sup>Pb, and <sup>207</sup>Pb/<sup>206</sup>Pb ratio analyses were carried out on an MC-ICP-MS (Nu plasma II, Nu). To inject the samples into the MC-ICP-MS, a DSN-100 desolvating system equipped with a micromist nebulizer was employed.

Thallium (T1, NIST 997), as an internal standard material, was added to all samples to correct for instrumental drift and Pb mass fractionation, which improved the reproducibility of the isotope value. In addition, Pb isotope ratios were corrected using a standard reference material (NIST 981, National Institute of Standards and Technology, USA) through the standard bracketing method. The NIST SRM 981 standard was separately run after every five samples to compensate for any mass bias and to assess precision. The combination of T1 normalization and the classic bracketing method provided an analytical precision of 0.0021, 0.0005, and 0.0002 for  $^{208}$ Pb/ $^{206}$ Pb,  $^{207}$ Pb/ $^{206}$ Pb, and  $^{206}$ Pb/ $^{204}$ Pb, respectively.

To analyze the C isotope ratios of the dust, pollution source, and soil samples, carbonate was removed using concentrated 1 N HCl for 6 h [56]. Triplicate samples placed in acid with an HCl fume were compared with samples that were not placed in acid with an HCl fume. This test showed no differences in the  $\delta^{13}$ C isotope values at less than 0.2‰. Therefore, no pre-treatment was necessary for the isotope analysis. The stable C isotopic ratios  $(\delta^{13}C)$  in all samples were measured by an isotope ratio mass spectrometer (IRMS) with an elemental analyzer (Vario MicroCube-Isoprime 100; Elementar-GV Instruments, UK).

The  $\delta$  values (‰) were calculated using the following equation:

$$\delta(\%) = \left[ (R_{\text{sample}}) / (R_{\text{standard}}) - 1 \right] \times 1000 \tag{1}$$

where R =  $({}^{13}C/{}^{12}C)$ . The international reference standard materials for the stable isotope analysis of  $\delta^{13}C$ , i.e., Vienna Pee Dee Belemnite (VPDB), were used. The reference materials were procured from the International Atomic Energy Agency, Vienna, Austria. The  $\delta^{13}C$ value was standardized using IAEA-CH-6 (Sucrose) and USGS24 (Graphite). The analytical precision for the standardization of the reference materials was 0.1‰.

# 2.5. Assessment of Heavy Metal Pollution

To assess the heavy metal contamination of urban dust, the enrichment factor (EF) was used:

$$EF = (Metal/Li)sample/(Metal/Li)background$$
 (2)

where  $(Metal/Li)_{sample}$  is the concentration of the heavy metal and Li in the sample and  $(Metal/Li)_{background}$  is the concentration of the heavy metal and Li in the control area. For the background concentration, the average perceptual concentration reported in Rudnick and Gao (2003) was used [57]. Al, Fe, and Li are generally used as normalizing elements [58,59]. Because Al and Fe hydroxides can precipitate when the salinity is changed in the estuary environment, Li can be more suitable for normalizing element [4,12,15,17]. The EF is divided into five classes according to each heavy metal type as follows: EF < 2, minimal enrichment; 5 < EF > 2, moderate enrichment; 20 < EF > 5, significant enrichment; 40 < EF > 20, very high enrichment; and EF > 40, extremely high enrichment [60,61].

#### 2.6. Mixing Model

Statistical analyses were performed using the SIAR (Stable Isotope Analysis) Bayesian mixing model in R (version 3.1.10, [62]). Before the analysis, all data were verified for normality and homogeneity of variances. Correlations between variables were valuated using Pearson correlation coefficients.

#### 3. Results and Discussion

# 3.1. Heavy Metals in Urban Dust, Topsoil and PM<sub>10</sub>

The concentrations of Co, Sr, and Ba in urban dust (house and road) and topsoil are similar to the concentration of topsoil in the control area, whereas the concentrations of Mn, Ni, Cu, Cr, Zn, As, Cd, and Pb are significantly higher than those in the control topsoil (Table 1). This suggests that Co, Sr, and Ba in urban dust and topsoil are likely predominantly derived from natural sources; however, Mn, Ni, Cu, Cr, Zn, As, Cd, and Pb may be influenced by anthropogenic sources. The average concentrations of Mn, Zn, Pb, and Cd in urban dust are 84-, 111-, 25-, and 56-fold higher and are 241-, 43-, 17-, and 18-fold higher in topsoil compared with those of topsoil in the control area, respectively. In addition, the average concentrations for those of  $PM_{10}$  in urban area are also approximately 1.3–7.0 times higher compared with the control area, which means that contamination is even present (Table 2). When compared with the metal concentrations and enrichment factors of urban dust in other environments worldwide, the levels of Mn, Zn, and Cd were dozens of time higher; Pb also shows high concentrations, except for in a few studies (Tables 1 and 3). It is indicated that the study area exhibited severe Mn, Zn, Cd, and Pb pollution. Therefore, we focused on metals of environmental concern: Mn, Zn, Cd, and Pb

Location	Туре				Metal Ion (mg/kg)										Reference
				Cr	Mn	Со	Ni	Cu	Zn	As	Cd	Pb	Sr	Ba	
			Minimum	24.6	2537	7.2	14.8	50.8	364	11.5	2.5	15.9	120	17.5	-
	urba	urban dust (Port area, n = 5) Max Me		56.0	38,583	35.9	29.2	866	57,584	127	192	680	286	213	
	(Port a			35.5	13,736	15.1	19.6	244	13,860	36.7	47.7	209	164	95.7	
				33.1	10,988	10.8	18.3	110	1469	12.9	9.0	37.7	127	77.6	
			SD	11.9	14,794	11.7	5.6	350	24,677	50.8	81.6	286	70.3	71.7	
	urban dust (Residence area, n = 6) Minimum Maximum Mean Median SD		59.9	19,139	18.5	29.9	103	5255	11.4	5.5	19.2	101	29.0	-	
			Maximum	496	157,119	46.0	136	439	35,570	85.9	119	3389	250	181	
			Mean	232	68,793	28.4	84.0	276	12,114	42.5	41.2	794	154	86.3	
			Median	221	52,293	23.4	81.9	257	6400	27.0	14.9	242	149	69.6	
			SD	164	52,374	11.7	42.4	125	12,799	31.2	48.2	1295	54.8	64.2	
Donghae, Korea	topsoil (Residence area, n = 3) (Residence area, n = 3) (Mean (Median SD		105	86,525	30.5	49.3	131	2620	12.2	9.8	33.6	190	92	This study	
U U			Maximum	583	144,214	37.7	97.3	241	7366	29.3	24.2	751.1	384	1444	
			Mean	329	117,798	34.7	74.0	177	5080	22.4	14.9	338	277	557	
			Median	198	122,753	35.8	75.4	158	5256	25.7	10.5	227	256	135	
			SD	241	29,211	3.7	24.0	57.1	2378	9.0	8.1	371.1	98.5	768.4	
		Mn Ore	Mean	1.4	411,439	54	14	5	101	5.4	0.6	1.2	56	124	-
	Pollution	Coal	Mean	25	75	3.8	5.1	26	37	7.3	0.7	5.3	136	64	
	source	Cokes	Mean	10	17	2.5	360	3	37	1.8	0.7	0.7	3.6	5.8	
		Cement	Mean	6.8	895	17	68	140	337	30	0.9	34	242	144	
		Zn ore	Mean	21	15,419	658	35	9398	450,428	22	925	210	3.2	3.8	-
	topsoil (Control, rural area)			51	488	9.6	11	39	116	5.8	0.8	20	71	309	-

Table 1. Results of metal concentration in pollution source, control soil, and urban dust samples of this study and other literature values.

Tantan	Tuno		Metal Ion (mg/kg)											
Location	Type		Cr	Mn	Со	Ni	Cu	Zn	As	Cd	Pb	Sr	Ba	
Seoul, Korea	dust (urban)	Mean	58			20	70	179		1.0	35			[63]
Ulsan, Korea	dust (industry)	Mean				18	119	136		1.4	82			[64]
Shihwa, Korea	dust (industry)	Mean	468	660	17	181	1034	1261	21	16	1.9	1418		[4]
Gary, USA	dust (industry)	Mean	153	2668			30	202				207	302	[65]
Stratoni, Greece	dust (mining)	Mean		1250			446	2720		10	1660			[66]
Volos, Greece	dust (industry)	Mean	745	3021		93.5	154	2169	57.3	6.2	300			[11]
Beijing, China	dust (urban)	Mean	114.3	685	12.3	30.4	62.3	318	5.6	0.9	85.3	349	754	[67]
Hangzhou, China	dust (urban)	Mean		616						0.6	1165			[3]
Huludao, China	dust (industry)						264	5271		72.8	533			[68]
Sonora, Mexico	dust (urban)	Mean	11.1		2.2	4.7	26.3	387.9		4.2	36.1			[69]
Hong Kong	dust (industry)	Mean	124			29	110	3840	67		120			[70]
Hamilton, USA	dust (urban)	Mean	34	793		38	245	611	4		468	128		[71]
Newcastle, UK	dust (urban)					26	132	421	6.4	1.0	992			[72]
Baghdad, Iraq	dust (urban)		32	322		80	24	94		0.9	156			[73]

Table 1. Cont.

Location	Tuno		Metal Ion (ng/m <sup>3</sup> )											
	Type		Cr	Mn	Со	Ni	Cu	Zn	As	Cd	Pb	Sr	Ba	
Donghae, Korea	PM <sub>10</sub> (Urban area, n = 15)	Minimum	48.3	136.3	1.9	9.7	11.7	97.6	11.9	0.8	15.1	43.5	386.5	
		Maximum	54.3	781.4	2.4	12.9	902.5	360.0	14.3	2.0	38.0	57.0	539.1	
		Mean	50.6	452.6	2.1	11.1	222.7	161.6	13.3	1.0	21.3	50.7	456.3	
		Median	2.7	253.1	0.2	1.2	381.8	111.5	1.0	0.5	9.5	4.9	57.5	
		SD	49.4	379.2	2.2	11.2	51.9	120.6	13.5	0.8	16.9	51.0	461.8	
	PM <sub>10</sub> (Control	Minimum	20.0	53.8	1.4	7.9	6.6	75.6	9.8	0.6	11.7	0.6	284.8	
		Maximum	58.8	72.3	2.7	11.5	13.3	167.6	21.5	0.7	20.7	0.7	502.4	
		Mean	43.8	64.3	1.9	9.4	9.8	112.7	13.9	0.7	15.7	0.7	358.3	
	area, $n = 3$ )	Median	20.9	9.5	0.8	1.8	3.3	48.5	6.6	0.1	4.6	0.1	124.9	
		SD	52.7	66.8	1.4	8.8	9.4	95.0	10.4	0.7	14.8	0.7	287.6	

**Table 2.** The concentration of metal ion of  $PM_{10}$  samples in the study area.

Specifically, the concentrations of Zn in urban dust (max = 57,584 mg/kg, mean = 12,987mg/kg) and topsoil (max = 7366 mg/kg, mean = 5080 mg/kg) around residence and port areas are significantly higher than those of topsoil in the control area (116 mg/kg). Zinc can provide parts made of ferrous metal with very efficient anti-corrosion protection in the long run. It is used as a protective coating for steel products and can be galvanized, sheradized, or electroplated; it is also a component of zinc rich paint and printing ink for corrosion protection [4,74,75]. Because there is a Zn smelting plant and steel-related and autoparts manufactures located in the study area, it is estimated that the particles generated from them contributed to the dust in urban area. In addition, frequent transportation by automobile from the port to the ferroalloy and steel production plants would have affected urban dust, because Zn is closely related to traffic activities such as tire and brake pad wear [76]. A comparison of the metal concentration in urban dust with scientific reports are shown in Table 1. Our results were dozens of times higher compared to those in domestic industrial complexes [4,12] and other regions of worldwide: Yeung et al. (2003) in Hong Kong [70], Argyraki (2014) in Greece [66], Yu et al. (2016) in China [8], and Dietrich et al. (2019) in the USA [65]. The reasons for this trend could be due to the possibility that there are other major pollutants except for the known Zn sources previously described. It may result that the particles scattered by the wind from the Zn ore stockpile containing a high Zn concentration have accumulated in urban dust. Therefore, stockpiles of raw materials could have a greater impact in urban dust than traffic activities or steel-related factory operation.

The concentration of Mn in urban dust (max = 157,119 mg/kg, mean = 41,265 mg/kg) and topsoil (max = 144,214 mg/kg, mean = 117,797 mg/kg) around residence and port areas are significantly higher than those of topsoil in the control area (488 mg/kg). Manganese has a very important position in the steel industry. The majority of Mn used in the steel industry is for strengthening and desulfurization of steel, while the remaining 5% is used in chemical and battery industries. This is because Mn improves toughness, hardness, and strength and is used in steel alloy applications [77]. It is also widely used in batteries, metallurgy, glass materials, ceramic objects, pigments, dyes, glass, fireworks, food, and medicine [78,79]. Many Mn-related factories are located in the study area, and higher Mn concentration in the urban dust may result from industrial processes from steel, battery, and chemical plants. It is indicated that particles derived from Mn-related industries may be deposited in the urban dust. However, Mn concentrations were 15- to 60-fold higher than in domestic industries with the most Mn-related factories [4,12] as well as industries of the world (Table 1). These results suggest that there is another major Mn source apart

from the known sources previously described; the particles scattered by the wind from the uncovered Mn ore stockpile in the factory and port area might be deposited in the surrounding urban and road dust.

The concentrations of Cd in urban dust (max = 192 mg/kg, mean = 44.5 mg/kg) and topsoil (max = 119 mg/kg, mean = 18.5 mg/kg) around residence and port areas are significantly higher than those of topsoil in the control area (0.8 mg/kg). It is indicated that the Cd from various industries might be deposited in the surrounding environment. Cd and Cd compounds are used in a variety of industries, including in the manufacture of Ni-Cd batteries and pigment manufacturing [80]. In addition, car tires, body corrosion, and the lubrication and wear of galvanized parts of vehicles have been reported as a major source of Cd contamination [81]. Cd is 3-fold higher than in the Shihwa industrial complex in Korea [4,12] and 4- to 10-fold higher than in most of the literature data in the world (Table 1). Therefore, industrial activities, transportation by means of automobile, and the manufacturing and processing of raw materials could have a greater impact on Cd concentration in urban dust. In addition, because the Zn ore stockpile itself contains a very high Cd concentration, it is very likely that the particles from the Zn ore stockpile have affected the Cd concentration in urban dust.

The concentrations of Pb in urban dust (max = 3389 mg/kg, mean = 501 mg/kg) and topsoil (max = 751 mg/kg, mean = 337 mg/kg) around residence and port areas are significantly higher than those of topsoil in control area (19.8 mg/kg). Lead is mainly derived from coal power plants, burning fossil fuels, metal coatings, paint factories, lead batteries, leather whipping, and waste pyromania, and it is also used as a component in plastics and rubber [82–84]. In Korea, high Pb concentrations (82 mg/kg) occur in urban dust from the Ulsan industrial complex, where large factories are located [64]. Argyraki (2014) reported Pb concentrations of 1660 mg/kg [66], Li et al. (2018) reported 1165 mg/kg in China [3], and Kelepertizis et al. (2020) reported 85.3 mg/kg in Greece [11] (Table 1). However, unlike Mn, Zn, and Cd, Pb-ion concentrations are higher than those in domestic industrial complexes, but lower than those in other urban area in the world. This is because lead smelting facilities and PCB manufactures are few in Donghae port.

The study area is a port where raw materials are loaded and moved more frequently than in urban are, and the number of industrial facilities (metal manufacturing, ore processing) and power plant operated per unit area is the highest in Korea. The main sources of urban dust may be pollutants emitted from industrial complexes (steel, cement, coal, alloy factories), construction and repair activities largely operating in the city and asphalt pavement weathering, pollutants generated during cargo entry and unloading operations, pollutants generated from vehicles passing through the port and surrounding roads for transportation, and spills from adjacent industrial areas. However, this study area has unique characteristics compared to other area. Due to a lack of storage warehouses, raw materials (Mn and Zn ore, coal, coke, cement) are stockpiled in the surrounding area of the port and steel related plants, all within 3 km of the residence, and they are often left for decades. Therefore, particles scattered by wind from stockpiles (Mn and Zn ore, coal, coke, cement), which are stacked near ports or factories, is considered to be the main pollutant source. Among the stockpiles of raw material in the port area, the Mn ore stockpile has a very high Mn concentration, and the Zn ore stockpile has a high Zn, Cd, and Pb concentration in comparison with other ions, which supports the preceding hypothesis.

#### 3.2. Spatial Distribution of Metals in Urban Dust

The concentration of heavy metals in the urban dust samples was examined as a spatial distribution (Figure 2). The Zn concentration was the highest, with an average of 13,860 mg/kg for urban dust in port area, followed by Mn > Cu > Pb > Sr > Ba > Cd > As >Cr > Ni > Co. In particular, the maximum concentration (57,584 mg/kg) occurs at the I-3 site closest to the port, where the Zn ore stockpile is located, with the concentration being 4-fold higher than the average value and 494-fold higher than the control area, indicating severe Zn contamination. The Mn concentration was the highest, with an average of 68,793 mg/kg for urban dust in residence area, followed by Zn > Pb > Cu > Sr > Cr > Ba > Ni > Cd > As > Co. The maximum concentration (157,119 mg/kg) occurred at the O-4 site adjacent to the ferroalloy and Mn-related plant where the Mn ore stockpile is located, with severe Mn contamination being twice the average value and 321-fold higher than that in the control area (Figure 2). The Cd and Pb concentrations are, respectively, dozens of orders of magnitude higher at I-3 and O-1 than those in the control area. The I-3 site, closest to the port where the Zn ore stockpile is located, is thought to have an effect on the Cd concentration. Mn, Zn, Cd, and Pb in urban dust showed a smooth decrease with distance from the pollution source (Mn:  $R^2 = 0.67$ , Zn:  $R^2 = 0.67$ , Cd:  $R^2 = 0.69$ , Pb:  $R^2 = 0.69$ ) (Figure 2), which indicates that atmospheric deposition from pollutants (Mn and Zn ore stockpiles) is the main source of heavy metals in urban dust.



**Figure 2.** Spatial distribution of (**A**) Mn, (**B**) Zn, (**C**) Cd, and (**D**) Pb in topsoil and urban dust in Donghae port.

As the distance increases, it is less susceptible to being transported or scattered by the wind. Nevertheless, the Mn concentration was 39-fold higher than in the control area, while the Zn concentration was 3-fold higher than in the control area at site O-1, which is farthest from the ferroalloy plant. In this study, the general spatial distribution indicates that the Mn ore stockpile in the ferroalloy production plant and the Zn ore stockpile on empty space in the port area are the main sources of Mn and Zn in urban dust. However, several factors may affect the concentration of Mn and Zn ion observed within a specific spatial region. There are relevant contributions from vehicular and pedestrian traffic, agricultural activities, street sweeping, specific industrial processes, and incineration and construction operations [85–87]. Street dust and the fine soil resuspension fractions are enriched in anthropogenic trace elements, which, if resuspended, can make a notable contribution to the inhalable trace element load of an urban aerosol [4]. Furthermore, the emissions profile of refuse incineration depends on a number of process factors; Pacyna (1983) and Kowalczyk et al. (1982) reported that incineration is a major source of Zn, Cd, and Sb [88,89]. Wadge et al. (1986) found high levels of Pb and Cd in the finest fraction of refuse incineration fly ash [90]. However, the concentrations of Mn, Zn, Cd, and Pb in our studies are dozens to hundreds of times higher than those reported in the literature; the previously described processes cannot be regarded as the origin of urban dust. Therefore, it indicates that the origin of the main pollutants in urban dust in this study area is the Mn and Zn ore stockpiles.

## 3.3. Metal Enrichment in Urban Dust: Heavy Metal Pollution Assessment

To assess the anthropogenic contamination level, we calculated the EF against the local baseline (Table 3). Co, Ba, and Sr showed a range from  $2 \le EF \le 5$  in all samples, indicating that they are mainly of crustal origin. Cr, Ni, Cu, and As were characterized by moderate enrichment on average ( $2 \le EF \le 5$ ), but some samples showed  $5 \le EF \le 10$ , suggesting that they were affected by anthropogenic pollutants. These results may reflect the impact of intensive industrial activities, especially metal processing industries, in this region. Cd and Pb were characterized by moderate enrichment or higher, and Mn and Zn especially had extremely high enrichment values of EF exceeding 200, often reaching 400; as the distance decreases from the ore stockpile, the EF tends to increase. These results also exhibit a similar trend as in recent studies [4,12]. In the case of Mn, EF is the highest in the topsoil in residential areas, and this is the closest place to the Mn ore stockpile in the factory.

Location	Type	Metal Ion (mg/kg)											
Location	Type	Cr	Mn	Со	Ni	Cu	Zn	As	Cd	Pb	Sr	Ba	
Donghae, Korea	Urban dust (Port area)	0.7	28.1	1.6	1.7	6.2	119.0	6.4	60.2	10.6	2.3	0.3	_
	Urban dust (Residence area)	4.6	140.9	3.0	7.4	7.0	104.0	7.4	51.9	40.1	2.2	0.3	This study.
	topsoil (Residence area)	6.5	241.2	3.6	6.5	4.5	43.6	3.9	18.7	17.1	3.9	1.8	_
Shihwa, Korea	dust (industry)	6.3	1.0	1.2	4.7	43.5	22.7	5.3	24.2	95.2	-	-	[4]
Busan, Korea	dust (urban)	4.2				12.6	19.1	4.5	21.9	11.8			[15]
Shijiazhuang, China	dust (industry)	2.4	1.1	1.4	1.6	5.7	7.6		38.7	9.5	-	-	[91]
Kathmandu, Nepal	dust (urban)	2.8				7	4.6		2.8	2.5	-	-	[81]
Palermo, Italy	dust (urban)	4	8.2	2.1	1.9	14	16.4		4	72	-	-	[92]
Bolgatanga, Ghana	dust (urban)	0.01	0.02	0.01	0.01	0.03	0.003		0	0.01	-	-	[93]
Taraba, Nigeria	dust (urban)					48.3	61.7		17.4	1.3	-	-	[94]
Baghdad, Iraq	dust (urban)	3.8	4.9		16.5	6.6	12.4		42.5	107.6	-	-	[73]
Kayseri, Turkey	Urban dust	0.95	1	2.8	2	5.2	20.2		190	111	-	-	[95]
Paris, France	dust (rural highway)			12			62.5		11.5	126	-	-	[96]
Sonora, Mexico	dust (urban)	17.1		1.7	0.9	8.1	79.4		601	39.1	-	-	[69]
Vellore, India	dust (urban)	1.3		0.6	0.4	3.6	22.7		0.9	16.3	0.5		[97]
Enugu, Nigeria	dust (urban)	2.3	0.5	83.5	171.9	129.3	13.7		596	180			[34]
Huainan, China	dust (industry)	2.3	1.3	0.4	1.5	4.2	13		2.9	4.5			[53]
: EF > 40; Extremely high enrichment; : 20 < EF < 40; Very					nment;	: 5 < EF	< 20; Significa	nt enrichme	ent;	: 2 < EF < 5; M	oderate enr	ichment;	:

Table 3. Comparison of EF value in pollution source, control soil and urban dust sample of this study and other literature values. (EF < 2, minimal enrichment; 5 < EF > 2, moderate enrichment; 20 < EF > 5, significant enrichment; 40 < EF > 20, very high enrichment; and EF > 40, extremely high enrichment).

: EF > 40; Extremely high enrichment; EF < 2; Deficiency to minimal enrichment.

On the other hand, in the case of Zn, EF is the highest in the urban dust in the port area near to the Zn ore stockpile on empty land. This relationship indicates that the Mn and Zn ore-processing facility and ore stockpile in Donghae port presents a distinct point source. The EF results for urban dust in this study were significantly higher than those reported in other studies (Table 3). The average EF of Mn was 28.1 in the urban dust (port) sample and 140.9 in the urban dust (residence area) sample, which is substantially higher than that reported by Jeong (2020, EF = 1) [4], Wan (2016, EF = 1.1) [91], Varrica (2013, EF = 8.2) [92], and Hameed (2013, EF = 4.9) [73] in urban areas. The average EF of Zn is 119 in the urban dust (port) sample and 104 in the urban dust (residence area) sample. Our results for the EF values are significantly higher than those in industrial areas of China (Wan et al., 2016) [91], near highways in France [96], and urban areas in Mexico [69] and India [97]. Therefore, our results show that heavy metals, especially Mn and Zn ions, in urban dust and topsoil might severely impact biota and human health. Long-term exposure to Zn can lead to respiratory compression, high fever, chills, and gastroenteritis [98]. Mn toxicity occurs when excessive manganese is inhaled (or when drinking water contains abundant Mn) and results in neurotoxic symptoms such as muscle pain, tremors, and memory loss, which can lead to neuromotor disorders [99]. Cadmium is used for plastic plating and is classified as a Class 1 human carcinogenic substance by the International Cancer Institute (IARC). Long-term exposure to Cd dust can increase the risk of developing kidney stones composed of Ca and P [100]. Pb is one of the most important environmental pollutants, which is highly toxic even at low concentrations and can threaten human life due to rapid bioaccumulation and a long biological half-life when exposed [101,102]. Therefore, the high concentrations of some ions in dust and topsoil in this study area may adversely affect the health of residents. These observations confirm that the contamination of urban dust and topsoil in Donghae port should be a concern for local authorities, as these elements threaten both ecological and human health.

# 3.4. Contribution of Heavy Meatal Pollution to Urban Dust from the Pollution Source

The stable C isotope ratios ( $\delta^{13}$ C) in the urban dust (port) samples range from -23.8to -25.8%, except at the I-5 site (-20.8%); urban dust (residence area) ranges from -23.5to -25.1%, and the topsoil samples from -24.3 to -25.8% (Figure 3). Urban dust (port) shows a heavy value of -20.8% at I-5, but the rest of the study area exhibits a similar range between urban dust (port) and topsoil, from -24.0 to -25.0%. Among the pollutant sources, the stable C isotope ratios of Mn ore, cement, coke, Zn ore, coal, and control topsoil were -24.8, -19.9, -26.9, -24.2, -23.6, and -25.1‰, respectively, with a clear difference. The stable C isotope values of soils reflect the isotopic composition of the local vegetation, which in turn, depends on their photosynthetic pathways and land use [103]. However, the within-site  $\delta^{13}$ C values in topsoil samples in the study area were smaller, such that there is no effect from local vegetation on the relative proportions of C<sub>3</sub> and C<sub>4</sub> plants. The  $\delta^{13}$ C values in urban dust ranged from -23.5 to -25.1‰, except at I-5 (-20.8‰). Morera-Gomez et al. (2018) characterized the  $\delta^{13}$ C of aerosols emitted by several sources of contamination in Cienfuegos: soot particles from the combustion of diesel ( $\delta^{13}$ C: -26.3‰), shipping ( $\delta^{13}$ C: -25.7%), and power plants ( $\delta^{13}$ C: -27.1%) [42]. The  $\delta^{13}$ C value of urban dust in this study were enriched relative to these sources. In Mexico city, the  $\delta^{13}$ C values in urban dust (-17.0%) and PM<sub>2.5</sub> (-22%) are more enriched [104], and are also more enriched, ranging from -16.4 to -18.4%, in street dust in Japan [105], and more depleted, ranging from -26.4 to -26.6% of aerosol in France [106] (Figure 3). However, our results are similar to those from Kumasi street dust in Africa, which range from -23.9 to -26.6% [46]. We cannot easily explain the differences between the values for urban dust from our study and that from previous studies. This trend may be due to the concentration of black carbon, organic carbon, and inorganic carbon contained in the urban dust. The  $\delta^{13}$ C value of black carbon is more depleted than that of TC because of the higher contribution of fossil fuels [106].



**Figure 3.** Comparison of  $\delta^{13}$ C values between this study and literature reports, including coalcombustion [106], biomass burning from C<sub>3</sub> and C<sub>4</sub> plants [107,108] and various urban region: Kumasi, Ghana [46]; Mexico city, Mexico [104]; Akita, Japan [105]; several major cities in China [109]; Rio de Janeiro, Brazil [110]; Tuscany, Italy [111]; and Paris, France [112]).

The combustion of biomass and automobile fuels (gasoline, LPG, and diesel) can also contribute to the carbon content of urban dust. Previous studies have reported the typical  $\delta^{13}$ C values associated with various fossil fuels, biomass, and their combustion products [45,82,84]. The  $\delta^{13}$ C values in urban dust from the study area were out of range of the C<sub>3</sub> and C<sub>4</sub> plants [104,106]; also burning has not occurred in or near the study area for decades. Therefore, urban dust at each location in the study area are notably impacted by mixtures of the main sources (Mn ore, Zn ore, cement, cokes, coal, and topsoil) with different  $\delta^{13}$ C values. The most negative  $\delta^{13}$ C values were found at a coke stockpile, while the most enriched  $\delta^{13}$ C values were found at a cement stockpile. The  $\delta^{13}$ C values at site I-5 (port area) were <sup>13</sup>C-enriched relative to the other sites, which likely reflects different carbon sources. The location of site I-5 is close to the cement stockpile, where the  $\delta^{13}C$ values are similar to those of cement source, such that there is a possible influence from cement. However, the  $\delta^{13}$ C values at site I-4 (port area) had more negative values than the other sites, i.e., similar to the coke source, which had the most negative  $\delta^{13}$ C value. The variations in the  $\delta^{13}$ C of urban dust from the different locations may therefore reflect differences in the sources and/or intensity of pollution.

The Pb isotope signatures of urban dust (port) range from 0.864 to 0.889 for <sup>207/206</sup>Pb and 2.102 to 2.136 for <sup>208/206</sup>Pb. The <sup>207/206</sup>Pb and <sup>208/206</sup>Pb ratios of urban dust (resident) range between 0.863 and 0.882, and 2.093 and 2.127, respectively. The <sup>207/206</sup>Pb and <sup>208/206</sup>Pb ratios of topsoil range between 0.869 and 0.891, and 2.107 and 2.139, respectively (Figure 4). Among the pollutant sources, the Pb stable isotope ratio of Mn ore, cement, coke, Zn ore, coal, and control topsoil is 0.911, 0.859, 0.874, 0.917, 0.836, and 0.774, respectively. In general, the results show that these source groups are notably different in terms of their Pb isotope compositions. The <sup>207/206</sup>Pb and <sup>208/206</sup>Pb ratios plotted in Figure 4 show a linear trend for all samples with an excellent regression coefficient ( $R^2 = 0.89$ ), although a slightly better regression coefficient is obtained when only dust is considered ( $R^2 = 0.92$ , not shown in figure). The linear array is interpreted to illustrate mixing. The control topsoil has more radiogenic Pb isotope values, forming a restricted field that defines the lithologic Pb isotope signature for this region. The Pb isotope value of the pollution source sample does not overlap the soil sample, suggesting it may be an important component of the geogenic end-member. In contrast, urban dust, such as the topsoil sample, has a less radiogenic Pb value, which represents the isotopic imprint of a yet unknown anthropogenic

end-member. In general, the characteristics of Pb isotopes, after the smelting of nonferrous metals, reflect the Pb isotope values in the ore before processing because the fractionation of Pb isotopes rarely occurs during the smelting process, or its effect is minimal. In general, the Zn concentrations in Zn ore are 4–10%, but when Zn ore is used as a raw material in Korea, the concentration is increased to 55-60% through flotation [67]. All of these materials are imported from Australia, Peru, and Mexico (http://www.kita.net accessed on 10 June 2021). In general, Zn ore from Central and South America is known to have <sup>207/206</sup>Pb values of 0.829 to 0.851, while Zn ore from Australia ranges from 0.909 to 0.970. For Australian Zn ore used in domestic Zn smelting facilities, <sup>207/206</sup>Pb was found to have a value of 0.929 to 0.956. The Pb isotope ratio of Zn ore in the study area falls within the range of the Pb isotope ratios of Australian Zn ore rather than those from Central and South America; furthermore, these ratios follow the characteristic Pb isotope line of large sulfide mines such as the Broken Hill mine in Australia. However, in the study area, the Pb isotope ratio in the urban dust sample was 0.864–0.891, which is different from the Pb isotope ratio of the Zn and Mn ore. These results indicate that Pb-induced pollutants in the urban dust are not only from Zn or Mn ore, but also from a wide variety of pollutants, such as cement, coke, Zn, and soil. The contribution rate was calculated using the C and Pb stable isotope ratio of the sample.



Figure 4. Relationship between <sup>208</sup>Pb/<sup>206</sup>Pb and <sup>207</sup>Pb/<sup>206</sup>Pb of soil and urban dust in Donghae port.

As a result of the evaluated contribution of pollutant sources on deposited dust through the Iso-source and SIAR models using the stable isotope ratios ( $^{13}C$ ,  $^{207/206}Pb$ ), we found that the largest contribution was derived from Mn (20.4%) and Zn (20.3%) from industrial factories (Figure 5). These results are consistent with the results of high concentrations of Mn and Zn in the urban dust mentioned above. In previous studies, Pb or C isotope ratios alone were used to trace pollution sources, but this is the first study to identify pollutants using both isotopes ratios.



**Figure 5.** Average contribution of the different sources determined by Iso-source R to the soil and urban dust sample.

# 3.5. Application of Multi-Isotope Techniques as a Useful Indicator to Trace Pollutant Sources

This research combined the analysis of metal concentration with carbon and lead isotopes to characterize sources and source contributions for urban dust and soil in industrial complex areas near a port. Our results suggest that a stockpile of raw material and the operation of a steel factory in the Donghae port significantly influence the concentration levels of Mn, Zn, Cd, and Pb in the surrounding soil and urban dust. In this context, this study demonstrated that carbon and lead isotopes, combined with the analysis of metal concentrations, could more effectively trace the effects of anthropogenic pollutants related to urbanization on urban dust than the analysis of heavy metals alone.

Previous studies have developed numerous methods, such as metal concentration, metal ratios of some crustal elements, statistical analyses, and clustering analysis, to trace various types of environmental pollutions that are often difficult to identify. These methods are easy to use, but typically only offer general information on the source. In addition, this approach is restricted in its efficacy for determining the specific sources of pollutants and discriminating among them. In our results, when carbon or lead isotopes were used alone, it was difficult to distinguish between pollutants (Figures 3 and 4), but when carbon and lead were used together, pollutants could be distinguished (Figure 6). The source contribution analysis carry out herein shows that metal concentrations as well as C and Pb isotopes could be united to helpful quantify source contributions and supply a basis for pollution prevention. Furthermore, the application of an additional novel multi-isotope approach, such as Cd, Cu, and Zn as environmental tracers, could be important to identifying pollution sources, as well as for understanding the behavior or environmental pollution and contribution of urban dust in various environments. Finally, the establishment of a database on multi-isotopic composition would remarkably contribute to the identification and management of individual sources of heavy metal pollution.



**Figure 6.** Scatter plot  $\delta^{13}$ C vs. <sup>207</sup>Pb/<sup>206</sup>Pb of soil and urban dust in Donghae port.

#### 3.6. Implications for Environmental Management and Human Health

New ports are being built or existing ports are being expanded throughout the world to meet the increasing demands of the population and the requirements of industries [91]. This port activity has the potential to cause serious pollution problem for decades, over a large area. Port activities can have a negative effect of air quality in the surrounding areas due to various activities such as loading, transporting, and storing cargo. The particles derived from port and industrial activities are composed of a complex mixture of particles, among which the fine fraction may be resuspended by wind and thus cause a respiratory risk to human health [5,113]. This dust is highly bioaccessible through gastric and respiratory exposure pathways, leading to lethal disease. Hence, for the monitoring of pollution levels, identification of pollution sources, control of waste from point and non-point sources and estimation of pollution levels for future, regular observation and evaluation are required throughout the entire operation and construction phase of a port.

Urban and road dust runoff discharge into the ocean may also transfer a fairly large amount of nutrients. The availability of these nutrients beyond coastal ecosystem is also an important factor for algal blooms. Recently, such events have been reported in the world [114]. The local authorities in Donghae port are now investing significant efforts and resources in monitoring the local environment. Our results should help them design a more effective environmental management of air pollution in Donghae port.

#### 4. Conclusions

The heavy metal pollution of urban dust in ports and residential areas was evaluated to obtain the relative contribution to pollution source. Most of the heavy metals in the study area were found in the range of variation of those reported in industrial complex areas, but some heavy metal such as Mn, Zn, Cd, and Pb presented 85~112-fold higher levels (EF > 100) than those of the control area, indicating significant contributions of these elements from anthropogenic sources. As a result of calculating the contribution of six major pollutant sources by Iso-source model, it was seen that Mn and Zn ore stockpiles contribute to more than 40% of urban dust. This suggests that both a stockpile of raw material and the operation of a steel factory in the Donghae port significantly influence the concentration levels of Mn, Zn, Cd, and Pb in the surrounding soil and urban dust. For the first time, C and Pb stable isotope ratios in urban dust were assessed to trace pollution sources in an industrial complex port area. This study provides appropriate guidance for further assessing the contributions of pollution sources in the study area, and could help to

establish environmental strategies for the improvement of air quality and ecosystem. All of the above can be utilized by public health authorities and policymakers in Donghae port and in other areas with similar geo-environmental conditions.

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