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Influence of Different Types of Land Use on the Contents of Potentially Toxic Elements and De-icing Salts in Roadside Soils and Trees in Urban Areas

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Abstract: In order to manage the urban environment and reduce pollution, it is essential to determine potentially toxic elements and de-icing salts in roadside soils and plants, which are major components of green infrastructure. A field study was conducted to elucidate the influence of land use on potentially toxic elements and de-icing salts in roadside soil and trees in urban areas. The effect of land use was determined in commercial, residential, industrial, and green areas of Cheongju city. The roadside soil and plant samples were collected from four different sites along a major roadway in the city. The chemical parameters determined were pH, electronic conductivity, potentially toxic elements (Cd, Cu, Zn, Cr, As, Pb, Ni), and de-icing salts (Na, Ca, Mg). The pH, electronic conductivity, potentially toxic elements (except copper), and de-icing salt values were significantly ($p < 0.05$) affected by the land use. On the other hand, the potentially toxic element (except zinc and nickel) levels in roadside tree leaves (*Ginkgo biloba*) were not affected by the different land use, whereas the de-icing salt levels were significantly different ($p < 0.05$). The enrichment factor (EF) of potentially toxic elements was found to be lower than that of de-icing salts with the highest values of sodium in green areas and of magnesium in commercial areas. These results provide information on the implications of land use, including the surrounding area of influenced roadside soil and plant chemistry for the urban ecosystem.

Keywords: best management practices; green infrastructure; soil–plant–atmosphere continuum; soil pollution; urban ecosystem

1. Introduction

Potentially toxic elements (PTEs) [1,2] and de-icing salts are substances naturally present everywhere in the environment, however, human activities have led to an increase in their concentration within certain areas. Roadside soils and road dust often contain potentially toxic elements from brake and tire wear, remnant leaded gasoline, and other car additives and components [3]. De-icing salts such as NaCl, $CaCl_2$, and $MgCl_2$ have also been determined in high concentrations in traffic areas [4]. These pollutants are transported into the roadside environment through aerial spread or the infiltration of spray water and road runoff [5]. There is increasing concern that soluble salts may displace metal from soil and then increase the dissolution rate of these metals [6]. The dissolved potentially toxic elements and de-icing salts contents may reach potentially toxic levels with high road use [7]. In particular, de-icing salts that are distributed in the winter could be highly elevated in roadside soils and plants in the following growing season [8]. An adequate supply of nutrients and the appropriate chemical composition of roadside soils are important factors affecting the health and life span of roadside trees

in urban environments [9]. Roadside soil and plant chemistry can change from year to year depending on a number of environmental factors. In addition, rapidly increasing population and unplanned urbanization processes have been challenging the ecological balance [10]. Anthropogenic soil pollution is usually not limited to a single pollutant. There is more concern that increased concentrations of soluble salts may displace metal from soil and then increase the dissolution rate of these metals. For example, during applications of NaCl in road maintenance, increases in Cd, Cu, Ni, and Zn concentrations were detected in the effluent constructed wetlands [6]. Norrström et al. [11] reported that a large part of Pb, Cd, and Zn in highway roadside soils is vulnerable to leaching when exposed to high NaCl concentrations. The dissolved concentrations of the potentially toxic element and de-icing salts contents reach potentially toxic levels with high road use [7]. If salt and potentially toxic elements are likely to be elevated, this results in toxicity within the environment. However, these studies were mainly related to aquatic systems [6,10–12]. Only a few studies have been conducted to examine the effects of the land use of surrounding areas on potentially toxic elements and de-icing salts in urban roadside soils and trees. Therefore, in this study we examined the concentrations of potentially toxic elements and de-icing salts, as well as the mobility of these elements in the soil to trees by the land use in commercial, residential, industrial, and green areas.

2. Materials and Methods

2.1. Site Description and Sampling

This study was carried out in the city of Cheongju (127°29′ E, 36°38′ N), which is located in the central part of South Korea and contains the largest amount of road by area in this country [13]. Human-modified areas have commercial, residential, industrial, and agricultural land uses beyond the roadside [14]. Therefore, in this study the sampling locations for roadside soils and trees were classified into 4 categories (commercial, residential, industrial, and green areas) based on the Enforcement Decree of the National Land Planning and Utilization Act, characterized by coarse loamy fluvaquentic endoaquepts soils [13,15]. The investigation was performed in May (spring) in 2018, and the roadside soil and plant samples were collected from 4 different areas along a major roadway in the city (Figure 1).

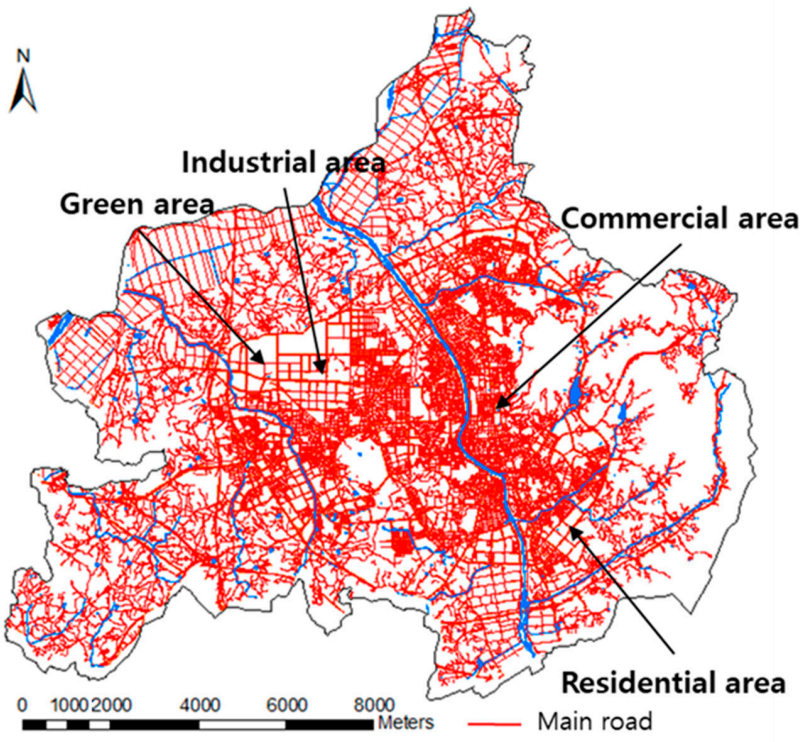


Figure 1. Location of the sampling areas of roadside soils and trees in Cheongju city.

The chemical parameters determined were pH, electronic conductivity, potentially toxic elements (Cd, Cu, Zn, Cr, As, Pb, Ni), and de-icing salts (Na, Ca, Mg) because of their environmental relevance. Due to the concentrations of these potentially toxic elements and de-icing salts being higher in samples collected close to the road edge [7], we targeted roadside soils and trees. A total of 48 soil samples (4 categories × 12 replication) were collected following standard methods for the examination of soil pollution. At least 500 g of fresh topsoil (0–15 cm) was collected from each roadside tree pit after removing foreign matter such as weeds and other organic matter. After mixing them evenly, the fresh soils were transported to the laboratory immediately. Soil samples were air-dried for approximately 10 days and passed through a 0.15 mm plastic sieve prior to chemical analysis. The sampling of all plants was performed in roadside trees (*Ginkgo biloba*), which are the most common roadside tree species in South Korea, with a consistent size in breast diameter (25–30 cm) and tree height (7–8 m). We collected the current year's fresh and healthy leaves at the lowest branches and surrounding soils from the four land use categories. All the samples were then packed into polyethylene bags and taken to the laboratory. Plant samples were cleaned five times with distilled water and dried at 70 °C for 48 h and then ground to powder with a metal-free plastic grinder.

2.2. Preparation and Chemical Analyses

Soil pH and electronic conductivity (EC) analyses were carried out as follows: 10 g of soil was placed in a 250 mL beaker, and 25 mL of deionized water was added. After fully mixing the sample in a horizontal shaking incubator for 1 h at 25 °C, the beaker was left to equilibrate for 30 min. The upper layer of clear water was taken and a calibrated pH meter electrode (ST-3100pH, Ohaus Corp., Parsippany, NJ, USA) was placed in it to measure the pH. The electrical conductivity (EC) was measured with an electrode (ST-3100C, Ohaus Corp., Parsippany, NJ, USA) after the soil slurries were filtered through qualitative filter papers (No. 2, Whatman, Loughborough, UK). Salinity measurements were taken using a hand-held meter (GMH 3431, Greisinger, Regenstauf, Germany).

2.3. Soil and Plant Potentially Toxic Elements and De-icing Salts Analyses

Homogenized soil (5.0 dried weight) and plant (2.0 dried weight) samples were prepared using the same procedures for potentially toxic elements and de-icing salts analyses. The determination of potentially toxic elements was carried out as follows: each sample was placed into a 100 mL Erlenmeyer flask with 25 mL of 0.1 N hydrochloric acid (HCl) and the soil and plant slurries, then shaken in an horizontal shaking incubator for 1 h at 30 °C, then filtered through a quantitative filter paper (Adventech, No. 5B, Tokyo, Japan). Soil and plant de-icing salt cations including Na, Ca, and Mg were determined after extraction with 1.0 M $CH_3COOHNH_4$ (pH 7) at a ratio of 5 g of soil or 2 g of plant to 100 mL of extraction solution and shaking for 1 h at 30 °C. The digested plant and soil samples were filtered before analysis, and then the concentration of potentially toxic elements and de-icing salt cations of the solution of soil and plant samples were determined by an inductively coupled plasma optical emission spectrophotometer (ICP, Optima 5300DV, Perkin Elmer, Hopkinton, MA, USA). The heavy metal concentrations were calculated as:

$$C = {}^{P \times V}/_{m} \quad (1)$$

where C represents the heavy metal concentrations of the soil or plant (mg/kg), P represents the sample concentration measured by ICP (mg/L), V represents the constant volume of the sample liquid (100 mL), and m represents the weight of the dried samples (g). Similarly, the de-icing salt concentrations were calculated as:

$$C = P \times {}^{V}/_{m} \times {}^{1}/_{Cmol} \quad (2)$$

All the indices above were same, where *Cmol* means the equilibrium concentration of Na (230 Cmol/kg), Ca (200.4 Cmol/kg), and Mg (121.5 Cmol/kg). In order to explore the mobility of potentially toxic elements and dicing salts from soil to plants, the enrichment factors (EFs) were also

tested. The EFs were determined for the metal-uptake capacities of plants. This index is calculated using the following equation [7]:

$$EF = {}^{C\ aboveground\ part}/_{C\ soil} \quad (3)$$

2.4. Statistical Analysis

All the analyses were conducted three replicates for each soil and plant samples. Statistical analyses were carried out using the SPSS v18.0 software package program (SPSS Inc., Chicago, IL, USA). The data were analyzed by one-way analyses of variance (ANOVAs) and the means were separated using Duncan's multiple range test (DMRT) and significant difference post hoc tests. All the statistical analyses above were carried out using, at the minimum, a 95% confidence level (p-value < 0.05). Statistical image analysis between the treatments was performed with the software Sigmaplot v12.0 (Systat software, San Jose, CA, USA).

3. Results and Discussion

3.1. pH, Electronic Conductivity in Roadside Soils

In the roadside soils, the pH value was not significantly different by land use, despite the lowest pH value being 6.58 pH in the green area. However, the electronic conductivity was significantly decreased in the order of commercial area (0.25) < industrial area (0.44) < residential area (0.53), green area (0.56). The salinity did not vary considerably with the land use, probably due to the competition with other potentially toxic elements and de-icing salts in the roadside soils (Table 1). There was a wide difference in the pH and EC with land use. In general, in the roadside soil the de-icing salts input near the roadway has the potential to increase the soil pH [16]. Moreover, the concentrations of EC were primarily attributed to the solubility of the de-icing salts [7]. Especially, the sodium (Na) concentration was positively correlated with the soil pH, possibly due to the displacement of H^+ by Na^+ originating from the de-icing salts [6].

Table 1. General chemical parameters in roadside soils depending on land use in the city of Cheongju (May 2018).

Land Use	pH	EC (qS/cm)	Salinity (psu)
Commercial area	8.30 a *	0.25 b	0.29 a
Residential area	7.66 a	0.53 a	0.26 a
Industrial area	7.64 a	0.44 ab	0.21 a
Green area	6.58 b	0.56 a	0.27 a

* Means with the same letter in a column are not significantly different at $p < 0.05$ by Duncan's multiple range test ($n = 12$).

3.2. Potentially Toxic Elements and De-icing Salt in Roadside Soils

The land use influenced the levels of potentially toxic elements and de-icing salts in the roadside soils. The mean heavy metal concentrations in the roadside soils—cadmium (Cd), zinc (Zn), chromium (Cr), arsenic (As), Lead (Pb), and nickel (Ni)—significantly differed with the land use, except for copper (Cu). The potentially toxic elements (Cd, Zn, Cr, As, Pb, and Ni) in roadside soils had the lowest contents. However, the Cd (0.753), Cr (49.391), As (16.617), and Ni (24.881 mg/kg) in the residential area and Zn (335.874) and Pb (472.221 mg/kg) in the green area had the highest concentrations in roadside soils, respectively. It is plausible that the contents of cadmium, copper, lead, and zinc were positively correlated with the conductivity in the soil [17], considering that there was a higher concentration of traffic—potentially, the toxic elements that were detected in residential and green areas had a higher electronic conductivity. Furthermore, the de-icing salts (Na, Ca, and Mg) contents in the roadside soil were also significantly different in accordance with the land use. The sodium (Na) in the commercial area was significantly higher, whereas the calcium and magnesium were lower than in

other areas. The residential area had the highest calcium (Ca) and magnesium (Mg) contents (Table 2). The commercial and residential areas had the highest concentration of de-icing salts, possibly due to the higher volumes of traffic on those streets splashing more de-icing salts [9].

Table 2. Potentially toxic elements and de-icing salts contents in roadside soils depending on land use in the city of Cheongju (May 2018).

Land Use	Potentially Toxic Elements (mg/kg)							De-icing Salts (Cmol/kg)		
	Cd	Cu	Zn	Cr	As	Pb	Ni	Na	Ca	Mg
Commercial area	0.552 b *	21.474 a	102.324 b	18.052 b	8.521 c	10.482 b	9.958 b	0.568 a	7.497 b	0.877 b
Residential area	0.753 a	35.014 a	206.774 ab	49.391 a	16.617 a	18.951 b	24.881 a	0.172 c	11.622 a	1.544 a
Industrial area	0.709 a	28.895 a	174.084 b	43.533 a	12.664 b	20.887 b	18.528 a	0.385 b	9.489 ab	1.384 a
Green area	0.720 a	31.073 a	335.874 a	37.684 a	10.937 bc	42.221 a	19.729 a	0.071 c	7.940 ab	1.263 a

* Means with the same letter in a column are not significantly different at $p < 0.05$ by Duncan's multiple range test ($n = 12$).

3.3. Potentially Toxic Elements and De-icing Salt in Roadside Tree Leaves (*Ginkgo biloba*)

With the exception of zinc (Zn) and nickel (Ni), all the heavy metal contents in roadside tree leaves (*Ginkgo biloba*) were not significantly different with land use. Zinc had the highest contents (14.663 mg/kg), whereas nickel showed the lowest value (3.035 mg/kg) in the commercial area. The sodium (Na) and calcium (Ca) contents in roadside tree leaves significantly differed with the land use. In the commercial area, the sodium content (2.426 Cmol/kg) was highest, whereas the calcium content (8.321 Cmol/kg) was lowest. The magnesium in the roadside tree had the lowest value in the green area, at 14.098 Cmol/kg, and all the others had no significant difference (Table 3). Some potentially toxic elements such as copper (Cu), zinc (Zn), and nickel (Ni) in soil are essential to plants, since they are important constituents of many enzymes and proteins [18]. Even though they are useful in small quantities, these elements become toxic to plants when they are present at high concentration in the plant. Cadmium (Cd) and lead (Pb) are not essential potentially toxic elements for plant organisms [19], and these potentially toxic elements inhibit the growth and development of plants by disturbing various biochemical and physiological processes [20]. These results are consistent with the previous study, which reported high contents of calcium and magnesium, whereas there was a low concentration of sodium in *Ginkgo biloba* leaves affected by de-icing salts [21].

Table 3. Potentially toxic elements and de-icing salts contents in roadside tree leaves (*Ginkgo biloba*) depending on land use in the city of Cheongju (May 2018).

Land Use	Potentially Toxic Elements (mg/kg)							De-icing Salts (Cmol/kg)		
	Cd	Cu	Zn	Cr	As	Pb	Ni	Na	Ca	Mg
Commercial area	0.104 a *	3.755 a	14.663 a	5.044 a	2.721 a	0.637 a	3.035 b	2.426 a	8.321 c	16.253 a
Residential area	0.159 a	3.295 a	10.711 b	5.223 a	3.455 a	0.790 a	3.023 a	0.601 b	11.162 a b	15.966 a
Industrial area	0.152 a	3.597 a	12.064 a b	6.315 a	3.732 a	0.701 a	3.552 a	0.527 b	13.713 a	16.186 a
Green area	0.185 a	4.281 a	12.371 a b	6.155 a	3.411 a	0.792 a	3.535 a	0.970 b	10.268 bc	14.098 b

* Means with the same letter in a column are not significantly different at $p < 0.05$ by Duncan's multiple range test ($n = 12$).

3.4. Potentially Toxic Elements and De-icing Salts Mobility from Roadside Soil to Tree

The enrichment factor (EF) of the potentially toxic elements and de-icing salts in roadside trees (*Ginkgo biloba*) indicated that the Zn, Cr, and Ni for potentially toxic elements and Na and Mg for de-icing salts had significantly different EFs compared to those of the other elements. Overall, the EFs of potentially toxic elements were lower than those of de-icing salts. The highest EFs were sodium (13.76) in the green area and magnesium (18.52) in the commercial area, respectively (Figure 2). EF is a specific capacity of the plants to uptake metals from soil and transfer them to aboveground parts [22]. The difference between the EFs of sodium, calcium, and magnesium was likely due to their differences

in size and atomic mass. Magnesium is smaller and lighter than calcium, and probably replaces de-icing salts faster and more easily [23] than calcium. In addition, magnesium can compete more effectively for cation exchange sites than the monovalent Na. Elevated levels of de-icing salts such as calcium and magnesium in plants but not potentially toxic elements could be quickly taken up by roots as an essential macronutrient.

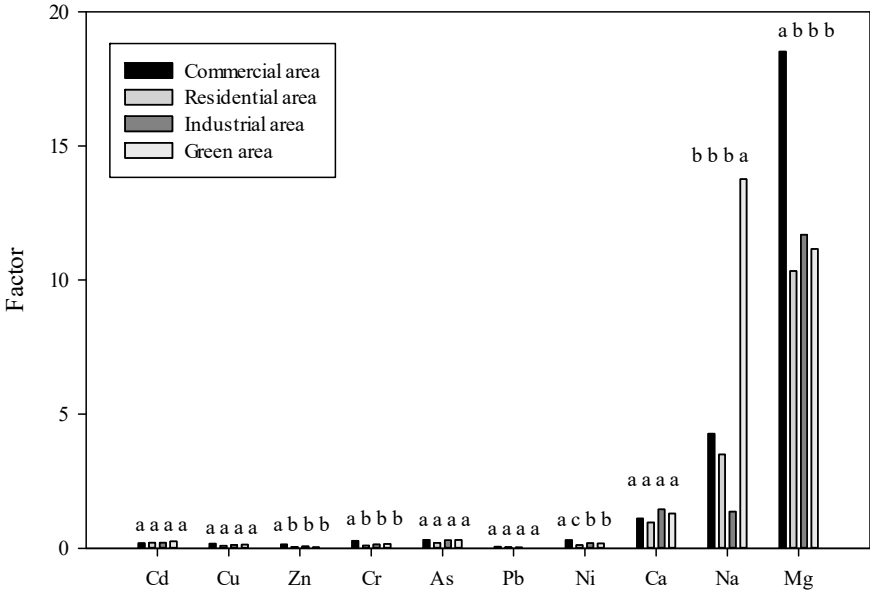


Figure 2. Enrichment factors of potentially toxic elements and de-icing salts in roadside soil to trees depending on land use in the city of Cheongju (n = 12). Different letters indicate a significant difference columns with common letters are not different at $p < 0.05$ by Duncan's multiple range test (n = 12).

4. Conclusions

The current study indicated that the potentially toxic elements and de-icing salts in roadside soils and trees can be influenced by land use beyond the roadside in urban areas. In the roadside soils, the pH, electronic conductivity, potentially toxic elements (except copper), and de-icing salts values significantly differed with the land use. On the other hand, the potentially toxic elements (except zinc and nickel) concentrations in the roadside tree leaves (*Ginkgo biloba*) were not affected by different land uses, while the de-icing salts were significantly different. The enrichment factors (EF) of potentially toxic elements were lower than those of de-icing salts. The highest EF values were sodium in the green area and magnesium in the commercial area, respectively. Even though we cannot overlook a potential limitation of the current study, which was conducted once, despite the multiple samplings in four different areas, we believe the current study provides basic information on the effect of land use on the roadside soil and plant chemistry for the urban ecosystem.

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