minerals

MDPI

Article

Determination of Metal Concentration in Road-Side Trees from an Industrial Area Using Laser Ablation Inductively Coupled Plasma Mass Spectrometry

Jee Young Kim [1,2], Jaeseon Park [1,2], Jongwoo Choi [2] and Jinwook Kim [1,*]

1 Department of Earth System Sciences, Yonsei University, Seoul 03722, Korea; jykim1984@yonsei.ac.kr (J.Y.K.); jspark0515@korea.kr (J.P.)
2 Environmental measurement and analysis center, National Institute of Environmental Research, Incheon 22689, Korea; cjw111@korea.kr
* Correspondence: jinwook@yonsei.ac.kr; Tel.: +82-2-2123-5668

Received: 20 December 2019; Accepted: 12 February 2020; Published: 14 February 2020

check for updates

Abstract: Historical pollution can be elucidated with variations of elements' concentration in tree rings by using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). However, the capacity of chemical elements' absorption significantly depends on the tree species and element types. Metal concentrations in the rings for five species (*Platanus occidentalis, Salix koreensis, Chamaecyparis obtusa, Pinus densiflora, Ginkgo biloba*) were investigated in light of metal pollution history in ambient air of D industrial site located in Daejeon, Korea. The calibration for LA-ICP-MS was performed using cellulose-matrix matched standards with ^{13}C normalization. Tree ring series except for *Ginkgo* sp. showed that the accumulation rates of Pb and Cd were higher between 1992 and 1999. Other elements, such as Fe, Cr, Mn, Cd, Zn, and Sr, showed a variation in the rings, likely due to the different physiological processes of element uptake and radial mobility. Concentrations of Pb and Cd in the annual rings of *Pinus* sp. corresponded to the metal monitoring data for the ambient air with the correlation coefficients of 0.879 and 0.579, respectively. Moreover, Cd in *Platanus* sp. and Pb in *Salix* sp. showed a positive correlation to ambient metal concentration compared to *Chamaecyparis* sp. and *Ginkgo* sp. Therefore, caution should be taken to select candidate elements as well as tree species to reconstruct the ambient air metal pollution history by measuring the concentration of metal in the tree ring.

Keywords: Environmental pollution history; Dendrochemistry; Tree ring, LA-ICP-MS

1. Introduction

The use of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to detect the presence of metals within solid samples is advantageous because it is relatively easy to prepare the sample and the analysis time is short. LA-ICP-MS was first attempted in the mid-eighties by Gray et al. [1], but the laser energy and beam size were difficult to control, resulting in low precision and accuracy. However, more recently developed pulsed Nd:YAG and excimer lasers have made it possible to analyze solid samples using laser beams with diameters of 1 to 200 µm. LA-ICP-MS has been applied to analyze a variety of materials, including biological samples (e.g., protein and lichen) [2,3] and in-situ grain-scale minerals [4]. Prior environmental science research revealed that characteristics of past environments can be inferred from the distribution of metals in tree growth rings [5–7], and this is called dendrochemistry. Moreover, studies have been conducted on the movement characteristics of metals in plants [8] and the environmental events such as volcanic eruption or acidic rain [9] through analyzing metal concentrations in tree growth rings. The United States Geological Survey has proposed an alternative method for tree ring analysis using LA-ICP-MS to determine the annual metal component deposition in Ponderosa Pine tree cores [10,11]. Annual growth rings also have the potential to record atmospheric pollution [8,12], which is related to the route of metal uptake in trees. Airborne particulates are deposited on leaves, tree surfaces, and soil. The metals in the deposited particulate matter were leached by mild acidic rain and the bioavailable metals moved to the tree roots and stems. Metal uptake in wood primarily occurs through soil minerals or pore water and the metals are subsequently transported into the wood through the roots and stem vessels. The other routes are through the respiration process in foliar stomata or direct deposition onto tree stems [13]. The variations in the accumulation of metals in plants is likely associated with tree species which have different absorption pathways through root for metals from groundwater and soil layers [14] or through leaf for metals from air [15]. The xylem structures of trees have an important role in water absorption and transfer. Generally, the seed plants are phylogenetically divided in gymnosperm (e.g., coniferous wood) and Angiosperm (e.g., porous wood) and they have different xylem anatomy with tracheid cells which make a difference in metal mobilities and binding efficiencies [16]. Moreover, each cation has different movement characteristics in the xylem [10,17]. The inner wall of wood stem has several negatively charged carboxyl, and exchangeable transporting cations. The exchange capacity of cations is related to their abundance and chemical form [13]. Therefore, we have to consider these physiological processes for dendrochemistry. We investigated metal distributions in tree rings of roadside trees planted in industrial areas as well as metal atmospheric pollution records to determine which species of roadside tree can be used as an indicator of historical pollution.

2. Materials and Methods

2.1. Site Description and Sampling

Construction activities on the D industrial complex began in 1969, and it had a total built up area of 1256 m^2 by 1979. It currently houses 353 businesses, including machinery, petrochemicals, and electronics firms [18]. Two points of a soil measurement network and one point of an atmospheric metal measurement network are located in the vicinity and interior of the complex. They have been operational since 1991 and 1994 respectively, and continue to collect environmental pollution data. Management reports about the creation of tree-lined roads in South Korea (2013) informs that tree-lined roads in the Daejeon region are planted largely with *Prunus* sp., *Gingko* sp., *Betula* sp., *Platanus* sp., and *Chionanthus* sp. [19]. The region for analysis, the D industrial complex, was mainly seeded with *Gingko* sp., *Platanus* sp., and *Salix* sp. Five main tree species, *Platanus* sp., *Salix* sp., *Ginkgo* sp., *Chamaecyparis* sp., and *Pinus* sp., were selected and samples were obtained (Figure 1). A Haglof increment borer (30 cm) was used to obtain core samples at a height of less than 30 cm from the ground. The collected samples were placed in polyethylene bags, stored on ice until they were transported to the lab, and subsequently stored at 20 (±2) °C in low humidity in a 1000 class clean room until their sectioning. At each sampling point, the topsoil (0–5 cm) was collected using a plastic trowel and samples were transferred to the lab in amber glass bottles sealed with Teflon-coated caps. The details of sampling sites and tree core samples are given in Table 1.

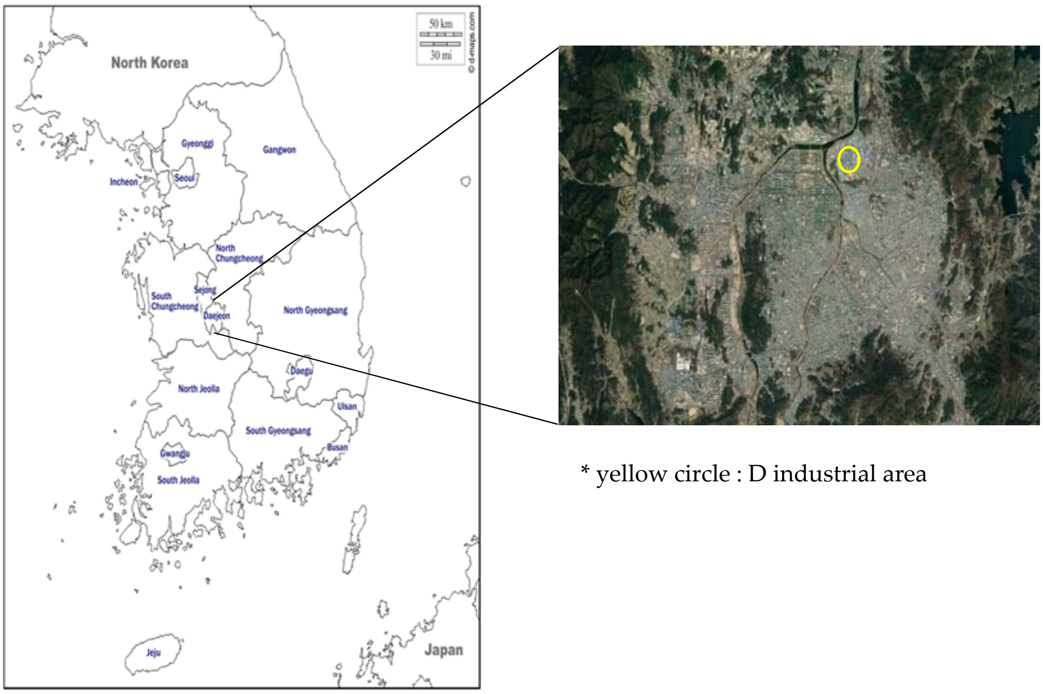


Figure 1. Sampling site location in D industrial area, Daejeon, Republic of Korea.

Table 1. Details of wood core samples collected and sites of collection

Site No.	Tree Species (Scientific Name)	Ring Structure Type	Number of Tree Rings	Site GPS
D1	American sycamore (*Platanus occidentalis*)	Diffuse to semi-porous	32	36°22′12.66″ N 127°24′46.45″ E
D2	Willow (*Salix koreensis*)	Diffuse to semi-porous	28	36°22′20.96″ N 127°24′43.25″ E
D3	Japanese cypress (*Chamaecyparis obtusa*)	Coniferous	40	36°22′16.84″ N 127°24′43.77″ E
D4	Korea red pine (*Pinus densiflora*)	Coniferous	42	36°22′3.43″ N 127°23′58.73″ E
D5	Ginkgo (*Ginkgo biloba*)	Coniferous-like structure	37	36°22′29.00″ N 127°24′56.00″ E

2.2. Wood Sample Preparation for LA-ICP-MS Analysis

The sample surfaces were washed sequentially with methanol, distilled water, and 1% (*v*/*v*) HNO_3 and dried at room temperature for 24 h. The dried samples were longitudinally sectioned and ground using 400 grit silicon carbide. Then, they were washed twice in the same manner and cut into two pieces with a Teflon-coated blade. Prior to analysis, each ring was marked with a sharp blade for counting the number of rings and measuring ring width. The segments of the cores were fixed in a stainless-steel holder and put into the chamber of a laser ablation system (ESI NWR193, Bozeman, MT, USA). The element concentrations were collected by using ICP-MS (Perkin Elmer Elan DRC-e, Vaudreuil-Dorion, QC, Canada) interfaced with a 193 nm ArF excimer laser ablation system. The spot's size was 100 μm and ablation speed was 50 μm/s. The surfaces of wood cores were analyzed in line scan mode and the average concentration in each annual ring was calculated. After quantifying the metals in the tree samples, it was observed that hardness and properties varied according to tree type and wood age. Thus, ^{13}C was used as an internal standard to correct for baseline shift of ICP-MS and differences in matrix ablation efficiencies, and changes in wood density in the ablation process [6,20–22].

2.3. Preparation of Matrix Matched Standard for Quantitative LA-ICP-MS Analysis

For metals' (Pb, Cd, Cr, Mn, Sr, Zn, Fe) quantification within the tree rings, the cellulose powder, a major wood component, was mixed with a standard solution of metals at concentration levels to create matrix-matched calibration standards [11]. Cellulose (2 g) from Sigma Aldrich was mixed with 15 mL of 20% (*v*/*v*) HNO_3 for 4 hours for washing residual metals in the powder. The mixture was filtered using a 0.45 µm PVDF teflon filter, compacted into a cake, dried in a 1000 class clean booth, and finely ground with agate for 3 min. Metal multi-standard solutions (AccuStandard, ICP-MS-CAL-R-1-SET, USA) at concentrations of 10, 50, 100, 200, and 500 mg/L (13 mL each) were mixed with 2 g of dried cellulose powder and shaken for 4 h at 150 rpm. Then, the mixtures were filtered, dried, and finely pulverized in the same conditions as cited above. The fine powder was pressurized for 10 min at 120 bars using a compression molding machine (Perkin Elmer, Shelton, UK) to create a solid material in the form of 13 mm diameter pellets. The concentration of metals in standard pellets was confirmed by acid digestion. Standard powder samples (0.1 g) were placed in 50 mL Teflon tubes and digested with high-purity HNO_3 and H_2O_2 for 24 h at 70 °C, and subsequently with high-purity HNO_3 under reflux condition at 70 °C for 3 h. The solutions from standard pellets were analyzed for metals by using ICP-MS. The resulting pellets were used as matrix-matched standards for LA-ICP-MS calibration for metals' quantification in wood core samples.

2.4. Experimental Conditions of LA-ICP/MS

For laser ablation, the preprocessed samples were inserted and fixed by using a stainless-steel holder in the ablation chamber. The ablation chamber was safely sealed and flushed with N_2 for 30 min. With the ICP-MS instrument connected, plasma was turned on and the carrier gas (Ar) flow rate was set to 1 L/min, while the He flow rate was gradually increased to 700 mL/min into the carrier gas (total flow; Ar-He 1.7L/mL). For laser tuning, NIST612 (metal in a glass) standard was used to perform three or more rounds of analysis (energy 40%, repetition. rate 30 Hz, spot size 100 µm, 10–20 lines, 32 s ablation). The actual wood sample was considered for data collection when the target value (^{208}Pb: 50,000 cps) was reached. Laser ablation was performed in line scan mode [23]. The ICP-MS set-up and other parameters are provided in Table 2.

Table 2. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and ICP-optical emission spectrometry (OES) instrumental parameters and operating conditions.

Laser System	ESI NWR193UC Laser Ablation System
Laser type	ArF 193 nm Coherent Excimer laser
Ablation mode	Line scan
Energy	50%
Repetition rate	30 Hz
Purging gas	N_2, 2 mL/s
Spot size	100 µm
Scan speed	50 µm/s
Depth/pass	5 µm
Beam focusing	Z auto movement
Sample carrier gas	He 0.7 mL/min
ICP-MS	**Perkin Elmer Elan DRC-e**
RF power	1300 W
Coolant gas flow rate	19 L/min
Auxiliary gas flow rate	1.3 L/min
Nebulizer gas flow rate	1 L/min
Elements (m/z)	Pb (208), Cd (111), Cr (52), Mn (55), Sr (88), Zn (66),Fe (56), Ni (60)

Table 2. *Cont.*

ICP-OES	Perkin Elmer Optima 5300 DV
RF power	1300 W
Plasma gas	15 L/min
Carrier gas	0.5 L/min
Makeup gas	0.65 L/min
Nebulizer gas	0.8 L/min
Sample flow rate	1.5 mL/min
Replicate	3
Wavelength (nm)	Fe (259.940), Mn (257.610), Cu (324.754), and Pb (220.353)

2.5. Soil Sample Preparation and Metal Analysis

The soil samples were air-dried at 20 (±2) °C for 7 days, sieved to <2 mm, grounded to a fine powder (<180 µm), and then refrigerated (below 4 °C) until analysis. The ground soil samples (10 g, minimum) were digested in a Teflon tube with 50 mL of high-purity HCl and HNO_3 (3:1) for 2 h, then concentrated in 0.5 M HNO_3 using a reflux condenser, filtered through Whatman No. 40 filter paper, and diluted with 0.5 M HNO_3 to 50–100 mL for subsequent analysis. The solution samples were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 5300 DV, Perkin Elmer, Wellesley, MA, USA) for Fe, Mn, Cu, and Pb, and by ICP-MS for Cd, Cr, Sr, Zn, and Ni.

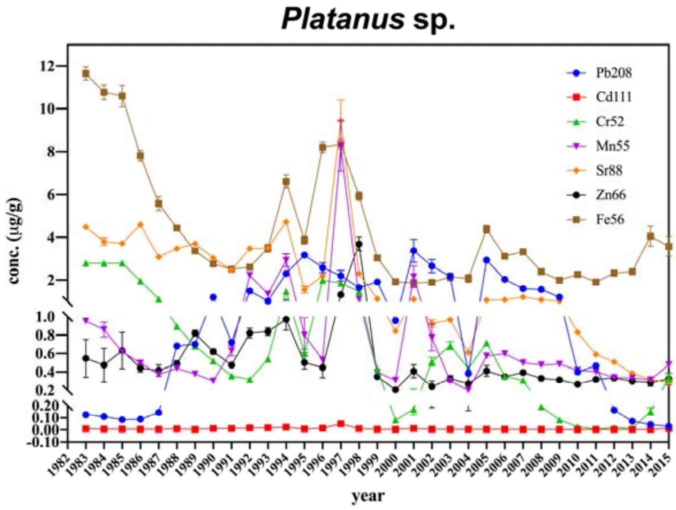
2.6. Atmospheric Monitoring Data and Statistics

The annual atmospheric metal monitoring data, available from a national atmospheric heavy metal measurement network site for points within 5 km, were reviewed. The monitoring has been focused on 7 elements (Cd, Pb, Ni, Cu, Mn, Fe, Cr) in the atmosphere since 1991, following the October 1990 establishment of the Clean Air Conservation Act of Republic of Korea. The metal concentration monitoring and climate (temperature, precipitation) data were obtained from the National Air Pollution Monitoring Information System (NAMIS; http://namis.or.kr). To verify the relationship between historical atmospheric metal pollution and metal concentrations in annual rings of wood, Pearson's correlation analysis was performed (SPSS version 21.0) for the metal concentrations in tree rings at a significance level of $p < 0.05$.

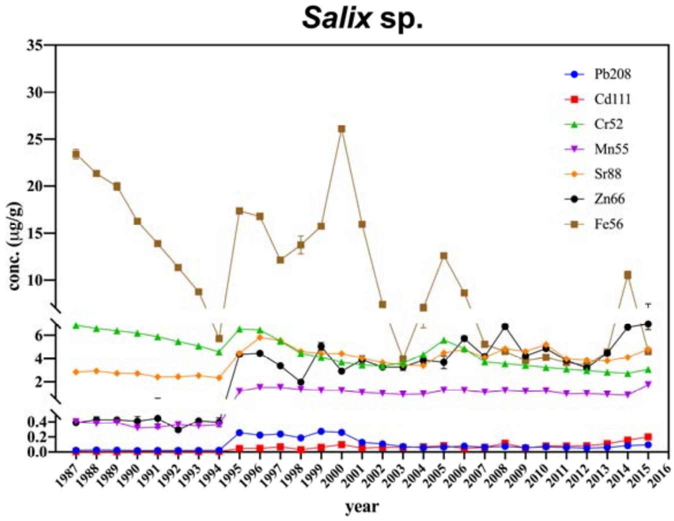
3. Results

3.1. Metal Distribution in the Annual ring of Roadside Trees

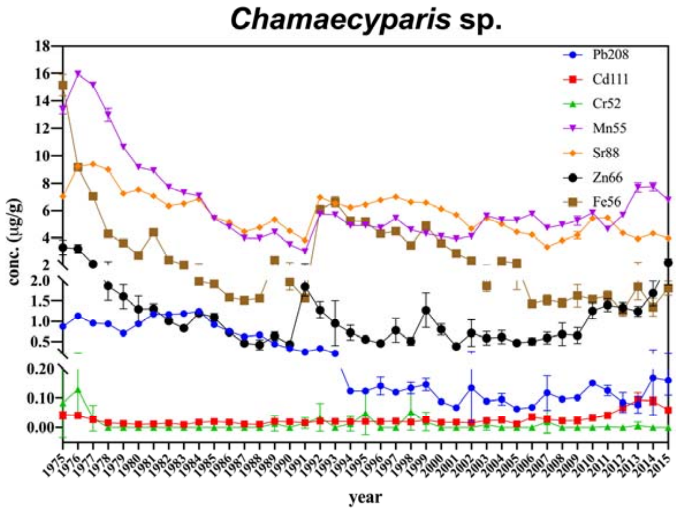
Seven metals (Pb, Cd, Cr, Mn, Sr, Zn, Fe) were determined in core samples obtained from roadside trees (five species) planted in the D industrial complex area. The tree species analyzed were between 28 and 42 years old (±5), and the concentration of elements was distributed in a variety of ways over time. The highest metal concentration by tree species was 1.87–11.65 ug/g Fe in *Platanus* sp., 3.44–26.10 µg/g Fe in *Salix* sp., 1.25–15.14 µg/g Fe in *Chamaecyparis* sp., 231.0–11.5 µg/g Mn in *Pinus* sp., and 2.3–80.1 µg/g Fe in *Ginkgo* sp. The lowest metal concentrations were 0.002–0.049 µg/g Cd in *Platanus* sp., 0.02–0.27 µg/g Pb in *Salix* sp., 0–0.129 µg/g Cr in *Chamaecyparis* sp., 0–0.0004 µg/g Cr in *Pinus* sp., and 0–5.80 µg/g Fe in *Ginkgo* sp. Considering the changes in metal concentrations over time for each tree species, Pb and Fe concentrations were high in the 1990s (1992–1999) for all species except *Ginkgo* sp. The other five elements (Cr, Mn, Cd, Zn, and Sr) exhibited different distribution patterns for each tree species (Figure 2a–e). The metal concentration between early wood and late wood in each annual ring showed a seasonal variation. The range of metal concentrations in trees were widely distributed, so that some small error bars cannot be visualized in the graph.



(**a**) *Platanus* sp.

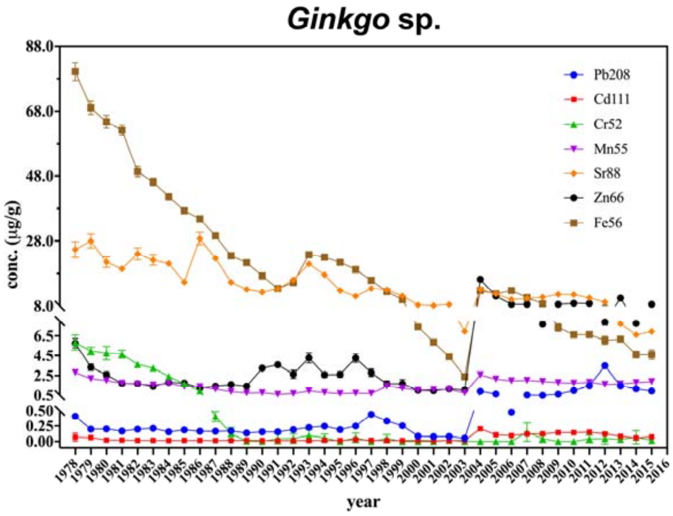


(**b**) *Salix* sp.

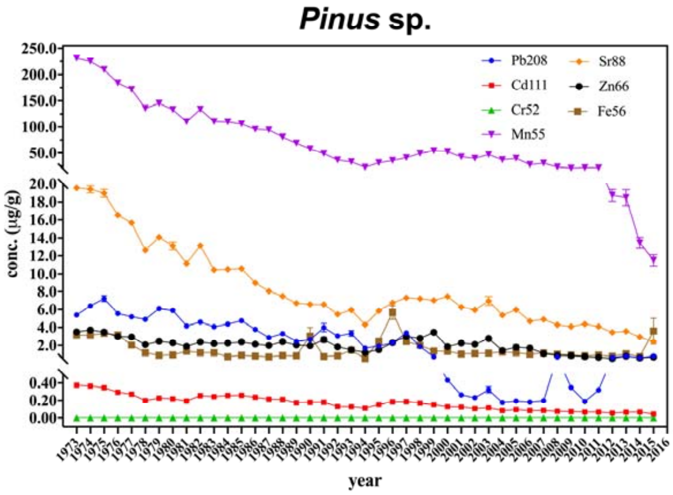


(**c**) *Chamaecyparis* sp.

Figure 2. *Cont*.



(**d**) *Ginkgo* sp.



(**e**) *Pinus* sp.

Figure 2. Time-resolved metal concentrations in the tree rings (±standard error). (**a**) *Platanus* sp., (**b**) *Salix* sp., (**c**) *Chamaecyparis* sp., (**d**) *Ginkgo* sp., (**e**) *Pinus* sp.

3.2. Monitoring Data of Atmospheric Metals

Records of seven metals (Cd, Pb, Ni, Cu, Mn, Fe, Cr) for the period ranging from 1991 to 2014 were obtained from a national atmospheric heavy metal measurement network site in the D industrial complex area. As shown in Figure 3, the results suggest that the levels of Pb, Cd, Ni, Cu, and Mn for 1992–1998 were significantly higher than after 1998. The highest concentration values were: 1.0416 μg/m^3 of Pb in 1995, 0.0027 μg/m^3 of Cd in 1995, 0.1056 μg/m^3 of Ni in 1992, 0.2540 μg/m^3 of Cu in 1996, and 0.1228 μg/m^3 of Mn in 1995. Notably, the highest level of Pb was in 1995 (1.04 μg/m^3), a much higher value than the Korean regulated level of 0.5 μg/m^3 for Pb, but it gradually declined to 0.04 μg/m^3 in 2014. This decrease was likely due to the strengthened permissible emission levels regulations for air pollutant emission facilities that took effect in 1995 and have continually phased down the permissible levels.

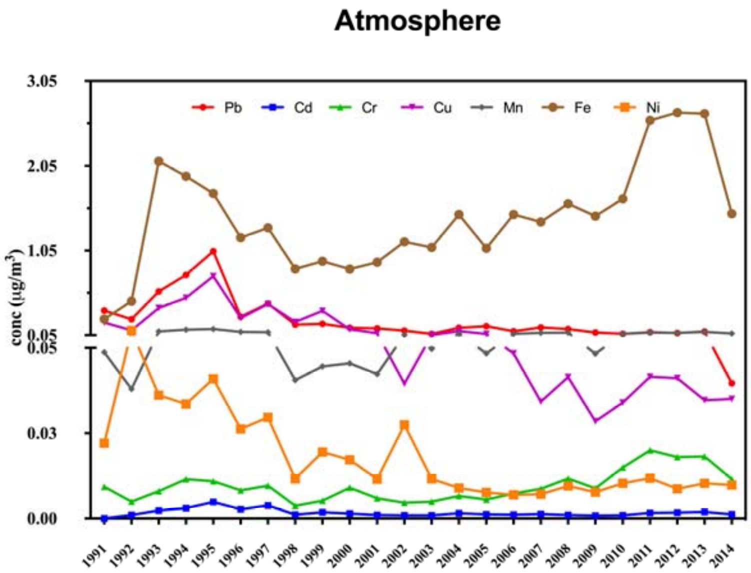


Figure 3. Metal concentrations in ambient air in D industrial site (1991–2014; data from Korean ambient air monitoring network). Metal concentrations suggest the annual average value of each metal.

3.3. Metal Concentration in Surface Soil

Nine metal elements (Pb, Cd, Cr, Mn, Sr, Zn, Fe, Cu, Ni) were determined to identify the pollution index [24,25]. The pollution index (PI) of soil is calculated by the average ratio of metal concentrations in topsoil to the reference values [26], which represent tolerable metal levels in soil. Details of the soil samples and PI values are given in Table 3. The results show that Fe was the most abundant element in all soil samples, but upper crust soil typically contains 1%~5% of Fe, so this seems to be a natural range. However, Pb was remarkably high in all soil samples, with the highest value of 730.4 mg/kg in the D1 site. Further, the surface soil of D2 and D3 sites contained 623.6 mg/kg of Pb, and 646.8 mg/kg of Pb respectively, likely because D1, D2, and D3 are located near a battery manufacturing plant that is a major Pb emission facility. These values exceed the concern level for soil contamination in Korea (200 mg/kg Pb). However, Pb concentrations in surface soils of D4 (34.3 mg/kg) and D5 (126.5 mg/kg) did not exceed the concern level, but were higher than the average upper crustal Pb concentration (17 mg/kg) [27]. The D1, D2, and D3 sites were also considered metal-contaminated because the pollution indexes (PI) were above 1.0.

Table 3. Metal concentrations in surface soil samples and pollution index (PI) values. (Unit: mg/kg).

Site No.	Tree Species	Pb	Cd	Cr	Mn	Fe	Sr	Zn	Cu	Ni	PI *
D1	*Platanus sp.*	730.4	0.324	57.6	353.3	16,285.6	157.3	161.5	74.6	17.6	1.604
D2	*Salix sp.*	623.6	0.400	90.9	379.1	21,758.6	147.1	315.0	87.0	27.5	1.625
D3	*Chamaecyparis sp.*	646.8	0.195	38.6	479.8	13,714.0	203.4	88.1	53.3	13.5	1.337
D4	*Pinus sp.*	34.3	0.032	9.4	137.6	13,450.1	92.2	0.1	38.3	5.4	0.156
D5	*Ginkgo sp.*	126.5	0.181	47.8	385.6	17,361.2	143.6	110.5	68.0	18.4	0.537

* Pollution index > 1 identifies soil contaminated with metals.

3.4. Tree Growth and Climate Condition

The average ring width of trees were 6.7 mm (minimum (min.) 2.0 mm to maximum (max.) 15 mm) in *Platanus* sp., 7.0 mm (min. 3.0 mm to max. 11.5 mm) in *Salix* sp., 6.1 mm (min. 3.5 mm to max. 11 mm) in *Ginkgo* sp., 4.4 mm (min. 2.0 mm to max. 10.5 mm) in *Chamaecyparis* sp., and 3.7 mm (min. 1.0 mm to max. 9.5 mm) in *Pinus* sp. The ring width of trees varies for the same year. The annual temperature and precipitation data (1970~2015) were obtained from the weather station in the atmospheric metal monitoring site. The maximum rainfall was 2070 mm in 1998, and the lowest was 828.7 mm in 2001. The annual average temperature ranged from 10.9 °C in 1974 to 13.9 °C in 2004. After the maximum precipitation in 1998, the ring width of *Platanus* sp. was 14.5 to 15.0 mm (maximum) from 1999 to 2000, but other trees did not show any remarkable correlation with the ring growth. The precipitation and temperature are important factors for tree growth; nevertheless, the samples of our studies did not reveal a distinct correlation with weather condition.

4. Discussion

4.1. Air Pollution Correlation with Metal Concentrations in Annual Rings of Trees

This study analyzed the correlation between atmospheric metal concentrations measured at the atmospheric metal measurement network located in the D industrial region (data for 1991–2014) and the metal concentrations determined in the present study for five roadside tree species (Table 4).

Table 4. Correlation coefficients of metal concentration in five tree species and ambient air (1996–2012).

Species	Ambient Air Metal Concentrations				
	Pb	Cd	Cr	Mn	Fe
Platanus sp.	0.353	0.825**	−0.391	0.234	−0.243
Salix sp.	0.671**	−0.029	−0.408	0.166	−0.655
Chamaecyparis sp.	0.249	0.052	−0.366	0.363	−0.573
Pinus sp.	0.879**	0.579*	−0.289	-0.506	−0.234
Ginkgo sp.	−0.266	−0.233	0.188	0.105	−0.189

* Significant correlation at $p < 0.05$ level; ** Significant correlation at $p < 0.01$ level.

The results confirmed that *Pinus* sp. exhibited a correlation between Pb (0.879) and Cd (0.579). *Platanus* sp. showed a correlation with Cd (0.825), and *Salix* sp. showed a correlation with Pb (0.671). The other two tree species, *Chamaecyparis* sp. and *Ginkgo* sp., had low correlations with atmospheric metal concentrations.

4.1.1. Metal Concentration in the Tree Species

This study showed that *Pinus* sp. (coniferous tree) reflected Pb and Cd concentrations in the atmosphere more effectively than the other elements measured, as confirmed by other studies [5,28–30].

Nonetheless, the radial movement of elements in xylem has to be considered. The radial distribution of trace elements in xylem are influenced by the stability of the minerals in annual rings [31,32] and the radial movement in xylem is attributed to the tree ring structure. Navais et al. [31] reported that water passes through the annual ring via radial parenchyma cells in coniferous wood, such as *Fagus*, *Acer*, and *Populus* sp., while water movement is mainly confined to the outer stem in porous wood, such as those in the sycamore tree, making these porous species (e.g., *Platanus* sp.) more favorable for dendrochemistry. However, depending on the elements, the radial and vertical movements vary [21]. For example, elements with low levels of movement through the xylem in Norway spruce (coniferous) include Pb, Cd, Al, and Ba, elements with moderate movement include Sr, Ca, Zn, Cu, and Cr, and elements with high movement include As, Na, and Mg [33]. *Genus Salix* is able to accumulate significant quantities of metals in both leaves and roots, but the elements were detected with different patterns in the leaves, stems, and roots [34]. In some plants, a counteracting behavior of elements in the root is likely to occur for exclusion of toxic metals [35]. Therefore, potential errors associated with dendrochemistry are related to the behavior of chemical element species in the wood, and it is necessary to examine the application cases, respectively.

Generally, trace metals may differ in their wood entry routes. Pb is primarily transported into xylem via foliar deposition in the aerosol form rather than through the roots [5,11,36,37]. Complexed Pb has low transferability in the wood annual rings, while Ca and Mg as free ions absorbed from soil can be readily carried into the xylem inner walls and transported from sapwood to hardwood. This may indicate that Pb is a better indicator of historical air pollution than Ca or Mg. Nevertheless, Fe is an essential nutrient required in large amounts for chlorophyll synthesis and electron transfer in the trees. The high level of Fe in the initial age of annual rings compared to the other elements does not necessarily imply anthropogenic air pollution [37].

4.1.2. Source of Atmospheric Metals and Their Concentration in Tree Rings

The wood sampling sites in our study were located 1 km away from a battery plant, which had been in operation since 1979. The plant has the second largest battery manufacturing facility in Korea and was considered as a major air pollutant emitter by the Korean government. Emissions from the battery industry contain toxic metals such as Cd, Pb, Li, Mn, and Zn [38,39], which is consistent with the high levels of ambient Pb observed in the study area. Further, the historical ambient Pb concentrations were correlated with Pb concentration in the annual rings of *Salix* sp. and *Pinus* sp. The ambient Cd concentration recorded was correlated with the annual rings of *Platanus* sp. and *Pinus* sp. Therefore, it may be inferred that tree rings were affected by activities from the industrial plant.

Ginkgo sp. is referred as a living fossil and has a similar xylem structure to conifer trees (e.g., *Pinus* sp.), which has tracheid cells for water transfer. *Chamaecyparis* sp. also belongs to the Order Pinales, the same as *Pinus* sp., so they basically have a similar transfer system (tracheid) in the xylem. However, Pb, Cd, Cr, Mn, and Fe concentration in tree rings and in ambient air did not correlate, while *Pinus* sp. did. This lack of correlation is probably linked to the physiological activity in each tree species.

4.2. Distribution of Metals in Topsoil and in Tree Rings

The high levels of Pb, Cd, Cr, Mn, Sr, Zn, Fe, Cu, and Ni in the topsoil denote contamination from particulate matter emitted by the industrial plant and deposited onto nearby soils. However, no similarities in element distribution were identified for these elements' concentration in the most recent five annual tree rings (sapwood part). Sapwood has some living cells and is conductive, which have a function of water transfer, while heartwood is nonconductive. So, non-fixed cations can move easily in the sapwood in the annual rings. This is likely the reason for the lack of correlation among metal concentrations in the soil (Table 3) and the tree rings.

Therefore, the metal pollution level in the topsoil is not a reliable indicator for the past pollution events. The concentration of metal on the surface soil only represents current pollution, however the record of tree rings represents past pollution.

5. Conclusions

Dendrochemistry is a reliable indicator for environmental monitoring, but it requires an understanding of the behavior of chemical species in the wood and the physiochemical characteristics of different tree species.

The obtained results suggest that some elements (mainly Cd and Pb) in the annual rings of coniferous tree such as *Pinus* sp. can provide information about air pollution history using the LA-ICP-MS techniques, which can continuously and quantitatively detect variations of elements' concentration in tree rings. Further, it was demonstrated that concentrations of Pb and Cd in the annual rings of *Pinus* sp., *Salix* sp., and *Platanus* sp. were correlated with air pollution trends. *Pinus* sp. well-represented previous atmospheric Pb and Cd at the D industrial site.

In future studies, it will also be possible to obtain improved results by reviewing pollution data records and analyzing the correlation between metal pollution levels over time through metal concentrations at multiple points using the same tree species and collected soil cores.

Author Contributions: Experimental setting, data production, writing—original draft preparation, J.Y.K.; formal analysis, J.P.; project administration, funding acquisition, J.C.; conceptualization, writing—review, J.K. All authors have read and agreed to the published version of the manuscript.

Funding: This work was funded by the National Institute of Environmental Research R&D of the Korean government, "Establishment of pollutant screening and tracking methods in multimedia system for responding to environmental issue" (NIER-2015-01-01-051).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Gray, A.L. Solid sample introduction by laser ablation for inductively coupled plasma source mass spectrometry. *Analyst* **1985**, *110*, 551–556. [CrossRef]
2. Becker, J.S.; Sela, H.; Dobrowolska, J.; Zoriy, M.; Becker, J.S. Recent applications on isotope ratio measurements by ICP-MS and LA-ICP-MS on biological samples and single particles. *Int. J. Mass Spectrom.* **2008**, *270*, 1–7. [CrossRef]
3. Kylander, M.E.; Weiss, D.J.; Jeffries, T.E.; Kober, B.; Dolgopolova, A.; Garcia-Sanchez, R.; Coles, B.J. A rapid and reliable method for Pb isotopic analysis for peat and lichens by laser ablation-quadrupole-inductively coupled plasma-mass spectrometry for biomonitoring and sample screening. *Anal. Chim. Acta* **2007**, *582*, 116–124. [CrossRef]
4. Cooper, H.K.; John, M.; Duke, M.; Simonetti, A.; Chen, G.C. Trace element and Pb isotope provenance analyses of native copper in northwestern North America: Results of a recent pilot study using INAA, ICP-MS, and LA-MC-ICP-MS. *J. Archaeol. Sci.* **2008**, *35*, 1732–1747. [CrossRef]
5. Baes, C.F.; McLaughlin, S.B. Trace elements in tree rings: Evidence of recent and historical air pollution. *Science* **1984**, *224*, 494–497. [CrossRef]
6. Watmough, S.A.; Hutchinson, T.C.; Evans, R.D. Development of solid calibration standards for trace elemental analyses of tree rings by laser ablation inductively coupled plasma-mass spectrometry. *Environ. Sci. Technol.* **1998**, *32*, 2185–2190. [CrossRef]
7. Märten, A.; Berger, D.; Köhler, M.; Merten, D. The dendroanalysis of oak trees as a method of biomonitoring past and recent contamination in an area influenced by uranium mining. *Environ. Sci. Pollut. Res.* **2015**, *22*, 19417–19425. [CrossRef]
8. Brabander, D.J.; Keon, N.; Stanley, R.H.; Hemond, H.F. Intra-ring variability of Cr, As, Cd, and Pb in red oak revealed by secondary ion mass spectrometry: Implications for environmental biomonitoring. *Proc. Natl. Acad. Sci. USA* **1999**, *96*, 14635–14640. [CrossRef]
9. Padilla, K.L.; Anderson, K.A. Trace element concentration in tree-rings biomonitoring centuries of environmental change. *Chemosphere* **2002**, *49*, 575–585. [CrossRef]
10. Gough, L.; Ridley, W.I. *Laser Ablation ICP-Mass Spectrometry—A New Tool for Analyzing Metals in Tree Rings*; Fact Sheet 2004–3031; USGS: Denver, CO, USA, 2004.
11. Witte, K.M.; Wanty, R.B.; Ridley, W.I. Engelmann Spruce (*Picea engelmanni*) as a biological monitor of changes in soil metal loading related to past mining activity. *Appl. Geochem.* **2004**, *19*, 1367–1376. [CrossRef]
12. MacDonald, H.C.; Laroque, C.P.; Fleming, E.B.; Gherase, M.R. Dendroanalysis of metal pollution from the Sydney Steel Plant in Sydney, Nova Scotia. *Dendrochronologia* **2011**, *29*, 9–15. [CrossRef]
13. Navais, C.; Freitas, H. Chapter 15. Tree rings and dendroanalysis. In *Metals in the Environment: Analysis by Biodiversity*, 1st ed.; Prasad, M.N.V., Ed.; CRC Press: New York, NY, USA, 2001; p. 338.
14. Monticelli, D.; Iorio, A.D.; Ciceri, E.; Castelletti, A.; Dossi, C. Tree ring microanalysis by LA-ICP-MS for environmental monitoring: Validation or refutation? Two case histories. *Microchim. Acta* **2009**, *164*, 139–148. [CrossRef]
15. Novak, M.; Mikova, J.; Krachler, M.; Kosler, J.; Erbanova, L.; Prechova, E.; Jackova, I.; Fottova, D. Radial distribution of lead and lead isotopes in stem wood of Norway spruce: A reliable archive of pollution trends in Central Europe. *Chemochim. Cosmochim. Acta* **2010**, *74*, 4207–4218. [CrossRef]
16. Gartner, B.L. Chapter 6. patterns of xylem variation within a tree and their hydraulic and mechanical consequences. In *Plant Stems: Physiology and Functional Morphology*, 1st ed.; Academic Press: London, UK, 1995; pp. 125–149.
17. Bukatka, A.R.; Kyser, T.K. Tree-ring elemental concentrations in oak do not necessarily passively record changes in bioavailability. *Sci. Total Environ.* **2008**, *390*, 275–286. [CrossRef]
18. Korea Industrial Complex Corporation. Available online: http://www.e-cluster.net (accessed on 15 December 2015).

19. Korea Forest Service. Available online: http://forest.go.kr (accessed on 27 December 2015).
20. Hoffman, E.; Liidke, C.; Scholze, H. Is laser-ablation-ICP-MS an alternative to solution analysis of solid samples? *Fresenius J. Anal. Chem.* **1997**, *359*, 394–398. [CrossRef]
21. Prohaska, T.; Stadlbauer, C.; Winmer, R.; Stingeder, B.; Latkoczy, C.; Hoffmann, E.; Stephanowitz, H. Investigation of element variability in tree-rings of young Norway spruce by laser-ablation-ICPMS. *Sci. Total Environ.* **1998**, *219*, 29–39. [CrossRef]
22. Perone, A.; Cocozza, C.; Cherubini, P.; Bachmann, O.; Guillong, M.; Lasserr, B.; Marchetti, M.; Tognetti, R. Oak tree-rings record spatial-temporal pollution trends from different sources in Terni (Central Italy). *Environ. Pollut.* **2018**, *233*, 278–289. [CrossRef]
23. Danek, M.; Bell, T.; Laroque, C.P. Some considerations in the reconstruction of lead levels using laser ablation: Lessons from the design stage of an urban dendrochemistry study, St. John's, Canada. *Geochronometria* **2015**, *42*, 217–231. [CrossRef]
24. Lee, C.G.; Chon, H.K.; Jung, M.C. Heavy metal contamination in the vicinity of the Caduk Au–Ag–Pb–Zn mine in Korea. *Appl. Geochem.* **2001**, *16*, 1377–1386. [CrossRef]
25. Chon, H.T.; Lee, J.S.; Lee, J.U. Heavy metal contamination of soil, its risk assessment and bioremediation. *Geosystem. Eng.* **2011**, *14*, 191–206. [CrossRef]
26. Kloke, A. Content of arsenic, cadmium, chromium, fluorine, lead, mercury, and nickel in plants grown on contaminated soil. In *Effects of Air-borne Pollution on Vegetation, Proceedings of the United Nations-ECE Symp. Warsaw, Poland, 20–24 August 1979*; UNECE: Geneva, Switzerland, 1979; p. 192.
27. Wedepohl, K.H. The composition of the continental crust. *Geochim. Cosmochim. Acta* **1995**, *59*, 1217–1232. [CrossRef]
28. Lukaszewski, Z.; Siwecki, R.; Opydo, J.; Zembrzuski, W. The effect of industrial pollution on Zinc, Cadmium and Copper concentration in the xylem rings of Scot's pine (*Pinus sylvestris L.*) and in the soil. *Trees* **1988**, *2*, 1–6. [CrossRef]
29. Doucet, A.; Savard, M.M.; Bégin, C.; Marion, J.; Smirnoff, A.; Ouarda, T.B.M.J. Combining tree-ring metal concentrations and lead, carbon and oxygen isotopes to reconstruct peri-urban atmospheric pollution. *Tellus B* **2012**, *64*, 19005. [CrossRef]
30. Sensula, B.; Wilczynski, S.; Monin, L.; Allan, M.; Pazdur, A.; Fagel, N. Variations of tree ring width and chemical composition of wood of pine growing in the area nearby chemical factories. *Geochronometria* **2017**, *44*, 226–239. [CrossRef]
31. Navais, C.; Freitas, H.; Hagemeyer, J. Dendroanalysis: A tool for biomonitoring environmental pollution? *Sci. Total Environ.* **1999**, *232*, 33–37.
32. Watmough, S.A.; Hutchinson, T.C. Historical changes in lead concentrations in tree-rings of sycamore, oak and Scots pine in north-west England. *Sci. Total Environ.* **2001**, *293*, 85–96. [CrossRef]
33. Balouet, J.C.; Smith, K.T.; Vroblesky, D.; Oudijk, G. Use of dendrochronology and dendrochemistry in environmental forensics: does it meet the daubert criteria? *Environ. Forensics* **2009**, *10*, 268–279. [CrossRef]
34. Wahsha, M.; Bini, C.; Argese, E.; Minello, F.; Fontana, S.; Wahsheh, H. Heavy metals accumulation in willows growing on Spolic Technosols from the abandoned Imperina Valley mine in Italy. *J. Geochem. Explor.* **2012**, *123*, 19–24. [CrossRef]
35. Fontana, S.; Wahsha, M.; Bini, C. Preliminary observations on heavy metal contamination in soils and plants of an abandoned mine in Imperina Valley (Italy). *Agrochimica* **2010**, *54*, 218–231.
36. Bondietti, E.A.; Baes, C.F., III; McLaughlin, S.B. Radial trends in cation ratios in tree rings as indicators of the impact of atmospheric deposition on forests. *Can. J. For. Res.* **1989**, *19*, 586–594. [CrossRef]
37. Gartner, B.L. Chapter 4.4. nutrient functions and deficiency symptons. In *Introduction to Plant Physiology*, 4st ed.; Hopkins, W.G., Huner, N.P.A., Eds.; John Wiley & Sons: Danvers, MA, USA, 2009; pp. 67–76.
38. Ecklund, M. Cadmium and lead deposition around a Swedish battery plant as recorded in oak tree-rings. *J. Environ. Qual.* **1995**, *24*, 126–131. [CrossRef]
39. USEPA. *Guidance Manual for Battery Manufacturing Pretreatment Standard*; Effluent Guidelines Division and Permits Division: Washington, DC, USA, 1987.