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The Effect of Different Cleaning Methods on Needles for Assessing the Atmospheric Heavy Metal Retention Capacity of Three Coniferous Trees

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Abstract: Urban air pollution has received increasing attention in recent years. To investigate the interaction between several heavy metal elements and the degree of atmospheric pollution, the leaves of three evergreen tree species—Chinese juniper (*Juniperus chinensis* L.), dragon juniper (*Juniperus chinensis* L. 'Kaizuca'), and cedar (*Cedrus deodara* (Roxb. ex D.Don) G.Don)—were collected from main road intersections in the urban area of Tianjin, China. Two different treatments—water washing (WW) and ethanol washing (EW)—were used, and the contents of Cu, Mn, Cd, and Zn were measured in both washed and unwashed (UW) leaves. It was found that the heavy metal contents within Chinese juniper and dragon juniper were ranked as Mn > Zn > Cu > Cd, and the metal accumulation index (*MAI*) value was higher for dragon juniper. For the three plants, water washed off 5.36% to 58.58% of the total heavy metals in the needles, while ethanol washed off 16.08% to 71.60% of the total. Both washes were more effective for Cu, Zn, and Cd, and especially for the element Cd. Ethanol could clean off 38.64% to 71.60% of the total Cd from the leaves. Ethanol had a better elution effect compared to water, and the trend of the Cd content in the leaves of the three plants showed a change after the use of different washing methods, which suggests that the water washing may have masked the real difference.

Keywords: evergreen tree species; needle leaves; heavy metals; urban environment; ethanol

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Citation: Liu, T.; Zhang, M.; Wang, Y.; Tang, L.; Wang, K.; Shi, F. The Effect of Different Cleaning Methods on Needles for Assessing the Atmospheric Heavy Metal Retention Capacity of Three Coniferous Trees. *Appl. Sci.* **2021**, *11*, 1668. https://doi.org/10.3390/app11041668

Academic Editor: Wojciech Zgłobicki

Received: 29 December 2020

Accepted: 8 February 2021

Published: 12 February 2021

1. Introduction

Heavy metal pollution has received increasing attention in recent years because it can threaten human health to different degrees [1,2]. Heavy metals can penetrate the tissues of plants and animals as well as humans, and their ability to penetrate is determined by the size and shape of the particles [3]. In recent years, many studies have been conducted on the sources and contents of heavy metals in soil, the atmosphere, and water [4–6]. The main sources of heavy metals in the atmosphere are automobile exhaust emissions, fossil fuel combustion, and heavy industrial emissions [7,8]. A method for directly detecting the degree of atmospheric heavy metal pollution is to detect heavy metals in different particle matters (PM). However, the use of this method to indicate environmental pollution has not been comprehensively analyzed. This is because the level of heavy metals in the environment may be high, but only a small proportion belongs to the bioavailable fraction. Therefore, many studies have used plants as monitors to reveal the relationship between atmospheric heavy metal pollution and living organisms [9]. Plants can be used not only to monitor the level of heavy metal pollution in the atmosphere, but also to reduce the heavy metal content in the environment via root uptake and leaf retention, thus reducing heavy metal pollution.

Woody plants have huge root, stem, and leaf areas that are able to act on the environment [10]. Their leaves are less hydrophobic than herbs [11], and rainfall washing has less of an effect on their surface heavy metal content. Therefore, the leaves of woody plants are a good choice for the study of the retention of heavy metals in the atmosphere. The leaves of evergreen plants rarely fall off, and therefore evergreen plants can be used as indicator plants to monitor heavy metals in the air [12]. Coniferous trees are more capable of absorbing heavy metals than deciduous trees. Among common landscaping species, Chinese juniper (*Juniperus chinensis* L.), dragon juniper (*Juniperus chinensis* L. 'Kaizuca'), and cedar (*Cedrus deodara* (Roxb. ex D.Don) G.Don) show a strong heavy metal uptake capacity [13].

The difference in elemental content between washed and unwashed leaves was studied by De Nicola et al. [14]. They used the fraction washed off with water to represent the heavy metals deposited by the atmosphere on the surface of the leaves, and many subsequent studies have used this method. However, it has been suggested that care should be taken when using the rinsing method to explore atmospheric contamination and that washing leaves with water is not sufficient [15]. Studies have found that the effect of water washing depends on the chemical nature and material characteristics of heavy metals [16]. In urban fine particulate matter, Mn, Cu, and Cd are more often present in their organic bound states [17], and water washing does not perform well for removal of this fraction of metal content. Several studies have investigated the effect of different detergents, such as HCl and Na_2EDTA, on the elution of heavy metals [15]. However, these detergents may make the experimental operation more complicated. Ethanol, a common organic solvent, is widely used in various fields, given its low price, low toxicity, and low pollution. In this study, we selected Chinese juniper, dragon juniper, and cedar on the main roads in a central city. We used ethanol detergent to elute heavy metals from needles and compared the elution effects of it and water, from which we tried to explain the following: (a) the interaction between several heavy metal elements, (b) the degree of atmospheric pollution, (c) the effect of alternative washing methods on the needles.

2. Materials and Methods

2.1. Overview of the Sampling Site

Tianjin is located in the northeastern part of the North China Plain (116°42′ E–118°03′ E, 38°33′ N–40°15′ N), on the east coast of Eurasia at mid-latitude. It is mainly dominated by the monsoon circulation and has a warm–temperate, semi-humid monsoonal climate; it is near Bohai Bay, and the influence of the marine climate on Tianjin is relatively obvious. The population density in the central urban area of Tianjin is about 29,372 people per square kilometer, and the average traffic flow on the main roads is 4071–4083 vehicles per hour [18]. The average content of heavy metals in $PM_{2.5}$ in Tianjin is 0.1 $\mu g \cdot m^{-3}$ for copper, 0.68 $\mu g \cdot m^{-3}$ for zinc, 0.01 $\mu g \cdot m^{-3}$ for cadmium, and 0.06 $\mu g \cdot m^{-3}$ for manganese. [19] Three main road intersections were selected in the central city of Tianjin, and a circle was drawn with the intersection as the center and a radius of 1 km to find three sampling points: 1, 2, and 3 (Figure 1).

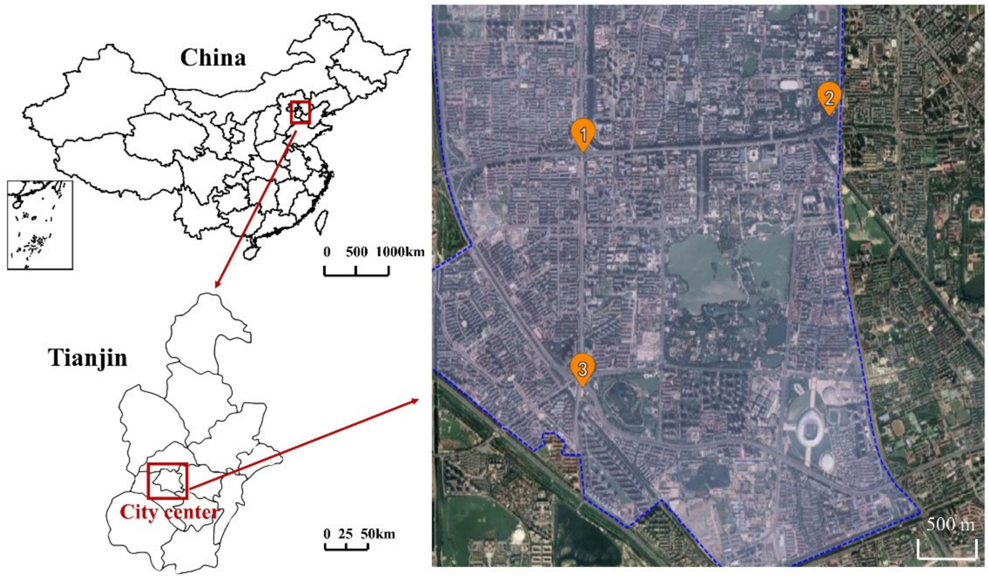

Figure 1. Sampling location in Tianjin, China. The satellite image is derived from Google Satellite.

2.2. Sample Collection and Processing

At each sampling point, three Chinese juniper, dragon juniper, and cedar trees with similar heights, diameters at chest height, as well as health statuses were selected at 10–15 m intervals. The leaves were collected at a height of 2 m from the ground in four directions: east, west, south, and north. After collection, the leaves were brought back to the laboratory and treated in three ways: without washing (UW); with water washing (WW), including a long rinse with tap water, rinsing three times with distilled water, and rinsing once with deionized water; and with ethanol washing (EW), including a long rinse with tap water, rinsing three times with distilled water, rinsing once with deionized water, draining, soaking in 75% ethanol for 30 s, and finally rinsing once with deionized water. The treated leaves were placed in an oven, denatured at 105 °C for 20 min, and dried at 65 °C until the weight was stable. We then weighed the leaves from the four different directions, equally and evenly mixed them to give a combined sample, ground them into powder, passed them through a 65-mesh sieve, and set them aside.

2.3. Heavy Metal Content Determination

Samples of 0.5 g of needle leaf powder were placed into a Teflon soluble sample cup, to which was added 3 mL of hydrochloric acid (high purity) and 9 mL of nitric acid (high purity). Next, gradient temperature digestion was carried out. After digestion, the sample was fixed with deionized water to give 25 mL. The solution to be measured was filtered through a 0.45-μm microporous membrane, and the heavy metals (Cu, Mn, Zn, Cd) in the sample were determined sequentially using an atomic absorption spectrophotometer (SP-3520AA, Shanghai Spectrum, Shanghai, China).

The *MAI* (metal accumulation index) can be used to assess the combined accumulation capacity of plants for heavy metals [20].

$$MAI = \left(\frac{1}{N}\right)\sum_{j=1}^{N} I_j, \tag{1}$$

where N is the number of species of heavy metal elements and I_j is the ratio of the mean value to the standard deviation of the content of a particular heavy metal in the leaves. In this article, $N = 4$.

The heavy metal content of unwashed leaves minus the heavy metal content of water-washed leaves was defined as the water-eluted fraction (C_w), and the heavy metal content of unwashed leaves minus the heavy metal content of ethanol-washed leaves was defined as the ethanol-eluted fraction (C_e):

$$C_w = C_{unwashed} - C_{water-washed}, \quad (2)$$

$$C_e = C_{unwashed} - C_{ethanol-washed} \quad (3)$$

The percentage of elution of the two (P_w, P_e) was expressed as follows:

$$P_w = \frac{C_w}{C_{unwashed}} \times 100\%, \quad (4)$$

$$P_e = \frac{C_e}{C_{unwashed}} \times 100\%. \quad (5)$$

2.4. Data Analysis

All the data contained three sets of replicates. The data were initially processed and analyzed using MSTM Excel (Microsoft, USA) and IBM SPSS 22.0 (IBM, USA). A one-way ANOVA was used to analyze the differences in heavy metal contents of the leaves of the three plants treated with the same washing method. The Duncan test was used to compare the significance level with the mean of 5%. The mean of each treatment is designed by letters (a, b, c...), which represent the significance of the difference between the averages ($p < 0.05$) A correlation coefficient analysis was conducted using the heavy metal contents of unwashed leaves, C_w, and C_e. A principal component analysis was performed, and the results were plotted using Sartorius (R) SIMCA 14.1 (MKS Umetrics, USA).

3. Results

3.1. Heavy Metal Content of the Unwashed Leaves of Three Plants

The heavy metal content of the unwashed leaves of Chinese juniper, dragon juniper, and cedar varied with the plant species (Table 1). The contents of Mn and Zn in Chinese juniper were significantly higher ($p < 0.05$) than those in the other two plants, with the content of Mn being 1.57 times higher than that in dragon juniper and 1.90 times higher than that in cedar, and the content of Zn being 1.13 times higher than that in dragon juniper and 1.29 times higher than that in cedar. The differences in the contents of Cu and Cd within the three plants were not significant, ranging from 18.53 to 20.98 $\mu g \cdot g^{-1}$ and 5.59 to 6.52 $\mu g \cdot g^{-1}$. The ranking of heavy metal contents in both Chinese juniper and dragon juniper was Mn > Zn > Cu > Cd, which was similar to the trend of heavy metal contents in PM_{10} and $PM_{2.5}$ reported by Chen et al. for Tianjin [21]. The *MAI* values of the three plants were dragon juniper > Chinese juniper > cedar.

Table 1. Heavy metal content ($\mu g \cdot g^{-1}$) and metal accumulation index (*MAI*) values of unwashed leaves.

	Cu	Mn	Cd	Zn	*MAI*
Chinese juniper	20.35 ± 0.85 a	57.89 ± 1.56 a	5.81 ± 0.23 a	39.58 ± 2.15 a	8.72
Dragon juniper	18.53 ± 1.64 a	36.91 ± 1.23 b	6.52 ± 0.27 a	35.01 ± 0.79 ab	9.13
Cedar	20.98 ± 1.06 a	30.42 ± 0.90 c	5.59 ± 0.30 a	30.64 ± 1.15 b	8.22

Data are expressed as mean ± standard error. Different letters in the same column represent significant differences ($p < 0.05$).

3.2. Comparison of Different Cleaning Methods

3.2.1. Changes in the Trends of Heavy Metal Content

After washing, the trends of Cd and Zn content within the leaves of the three plants changed (Figure 2). There was no significant difference in the Cd content in the unwashed leaves of the three trees. The Cd contents of cedar and dragon juniper were higher than that of Chinese juniper after water washing, and the difference between the three after ethanol washing was significant ($p < 0.05$), with the order being cedar > dragon juniper > Chinese juniper.

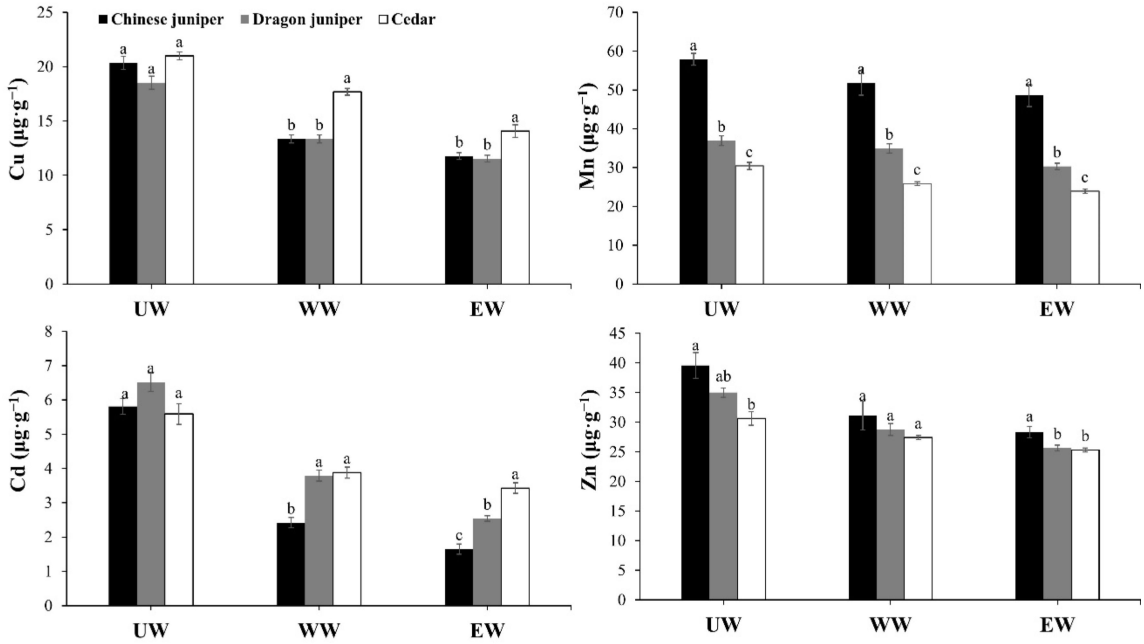

Figure 2. Heavy metal contents in needles of the three plants under different treatments. Different letters represent significant differences among the three types of needles under the same treatment for the same heavy metal content ($p < 0.05$). UW: without washing; WW: water washing; EW: ethanol washing.

3.2.2. Comparison of the Differences between the Two Cleaning Methods

By comparison, ethanol had a better elution effect, showing $C_e > C_w$, $P_e > P_w$ in all three plants, with a range of 5.36–58.38% for P_w and 16.08–71.60% for P_e (Table 2). For manganese in dragon juniper, the C_e was 3.34 times higher than the C_w; for copper in cedar, the C_e was 2.10 times higher than the C_w. The heavy metals that could be eluted by different washing methods varied with the plant species and heavy metal type. The two elution methods were more effective for Cd elements. Ethanol washing removed 38.64–71.60% of the total cadmium on the leaves.

Table 2. Differences in content (μg·g^{-1}) and percentages (%) between the two cleaning methods for different plants. C_w: water-eluted fraction; P_w: percentage of elution for water-washing treatment; C_e: ethanol-eluted fraction; P_e: percentage of elution for ethanol-washing treatment.

	Chinese Juniper				**Dragon Juniper**				**Cedar**			
	C_w (μg·g^{-1})	P_w (%)	C_e (μg·g^{-1})	P_e (%)	C_w (μg·g^{-1})	P_w (%)	C_e (μg·g^{-1})	P_e (%)	C_w (μg·g^{-1})	P_w (%)	C_e (μg·g^{-1})	P_e (%)
Cu	7.01	34.45	8.58	42.16	5.18	27.95	6.99	37.72	3.29	15.68	6.90	32.89
Mn	6.10	10.54	9.31	16.08	1.98	5.36	6.60	17.88	4.55	14.96	6.50	21.37
Cd	3.39	58.35	4.16	71.60	2.73	41.87	3.98	61.04	1.71	30.59	2.16	38.64
Zn	8.49	21.45	11.24	28.40	6.24	17.82	9.38	26.79	3.23	10.54	5.33	17.40

3.2.3. Principal Component Analysis of Four Heavy Metals in Three Plant Species

According to the results of the principal component analysis (Table 3), the cumulative variance contribution of the first two principal components reached 91.17%, so the first two principal components were deemed sufficient to explain the original data. The loadings of Cu, Cd, and Zn in principal component 1 (PC1) were greater than 0.86, and the loading of Mn in principal component 2 (PC2) was larger than 0.876 (Table 4).

Table 3. Total variance explained.

Component	Initial Eigenvalues		
	Total	**% of Variance**	**Cumulative %**
1	2.43	60.85	60.85
2	1.21	30.31	91.17
3	0.24	6.06	97.23
4	0.11	2.77	100.00

Table 4. Component matrix.

	Component	
	1	**2**
Cu	0.864	0.381
Mn	0.414	0.876
Cd	0.880	0.401
Zn	0.861	0.371

For PC1 (Figure 3), the two washing methods and unwashed treatment were distinct from each other, showing a trend of UW > WW > EW. There was no significant difference between the three methods for PC2 (Figure 3). It was presumed that PC1 represents the heavy metals that were effectively cleaned off and PC2 represents the heavy metals for which cleaning was averagely effective. PC1 was mainly copper, cadmium, and zinc, and PC2 was mainly manganese. This means that the cleaning was more effective for Cu, Cd, and Zn, while the effect was not as obvious for Mn as it was for the other three elements. For PC2, the trend in the manganese content of the three plants was Chinese juniper > dragon juniper > cedar.

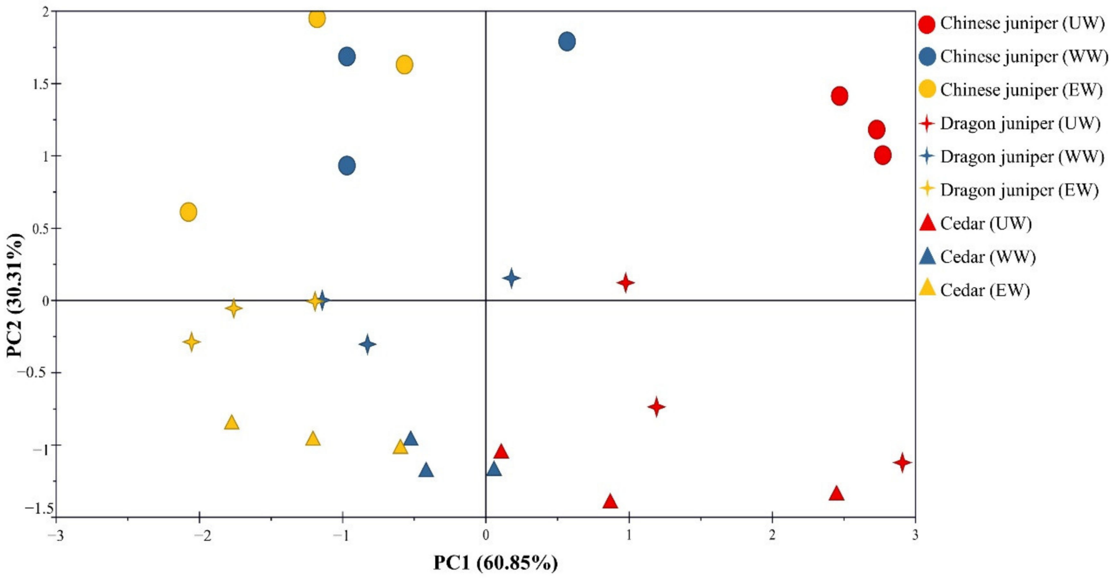

Figure 3. Principal component analysis scores for the three plant species.

The composite score model was calculated according to Tables 3 and 4 [22]

$$Y = 0.254\ Cu + 0.442\ Mn + 0.255\ Cd + 0.481\ Zn. \quad (6)$$

The coefficients corresponding to each indicator in the model are the weights of each indicator. It can be seen that the contents of the four heavy metals in the three plants were in the order of Zn > Mn > Cd > Cu.

3.3. Correlation Analysis of Heavy Metal Elements

The results of the correlation analysis (Figure 4) showed that the Cu, Cd, and Zn contents on the leaf surface had a strong correlation with the relative total heavy metal contents after the three treatments. This may have been due to the fact that these elements mainly existed on the surface of the leaves, while Mn mainly existed inside the leaves. The correlation coefficients between Cd and Cu on the leaf surface were from 0.422 to 0.625, indicating that Cd and Cu are partially homologous, similarly to Zn and Mn.

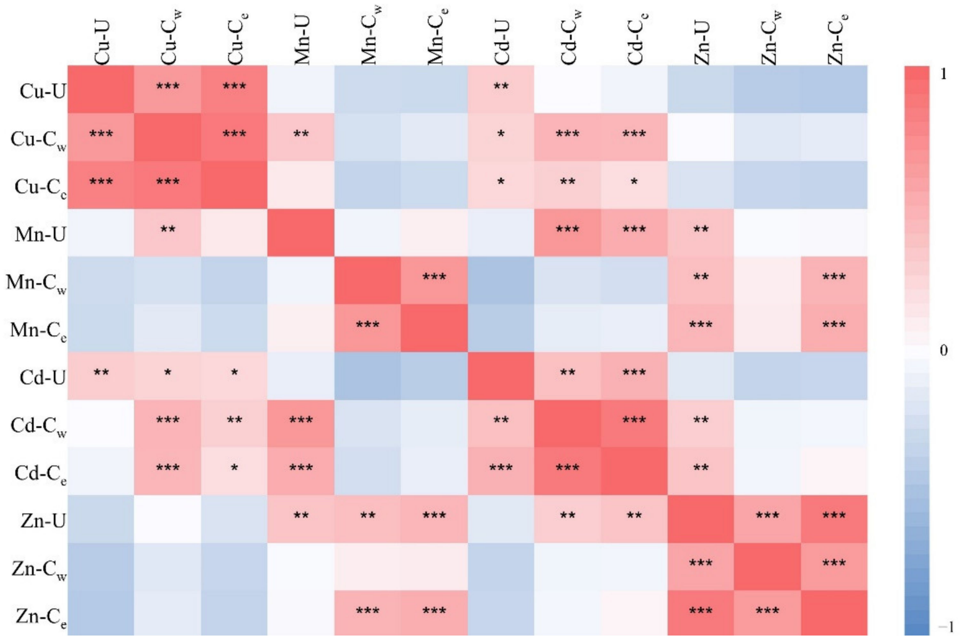

Figure 4. A heavy metal correlation analysis heat map of the unwashed leaves for C_w and C_e. "U" presents the content of the unwashed needles. ***, **, and * represent significant differences at 0.001, 0.01, and 0.05, respectively.

4. Discussion

The heavy metal content in the unwashed leaves (i.e., the total amount of heavy metals in the leaves) had several sources; it derived partly from the transport of heavy metals from the soil to the leaves by the root system through transpiration [23], and partly from atmospheric particulate matter deposition. PM containing heavy metals can be captured by leaf epidermal waxes and diffused into the leaves via lipophilic or hydrophilic channels [24], or it may enter the leaves directly through the stomata and become integrated into components within the leaves. The relative contents of Cu, Mn, and Zn were higher than those of Cd in all three plant species, partly because Cu, Mn, and Zn are essential elements for plants and are transferred more effectively from roots to leaves [25–27], and partly because the atmosphere also showed this trend in content [21]. The higher *MAI* values of the dragon juniper leaves compared to the leaves of the other two plants may have been due to this plant's complex crown [28] and leaf structure [13]. These factors allow it to retain more dust particles, thus leading to a greater heavy metal accumulation effect, which has a positive effect on the selection of greening species.

Combined with the eluted heavy metal content and correlation analysis, the leaf surface had high Cu, Zn, and Cd contents. The Cu, Zn, and Cd in $PM_{2.5}$ in Tianjin are mainly derived from anthropogenic sources [29]. Most of the Cd settles on the leaf surface in a residue state [30], and less enters the leaf interior. The Cd and Cu on the blade surfaces may have come from traffic sources, such as motor vehicle exhaust and mechanical wear caused by tires and engines; the Zn and Mn may have come from steel smelting and the alloy industry [31]. Since the sampling sites were located on the main roads in the urban center, this provides some guidance for the further management of pollution caused by traffic. Studies have shown that there is a significant correlation between urban PM_{10}, $PM_{2.5}$, and mortality [32,33]. As for Tianjin, the urban population density is high and pollution is a serious issue [34]. Selecting appropriate plants, diversifying forest structure, and providing reasonable green space management can effectively improve the efficiency of atmospheric cleaning [35], which will provide assistance in reducing urban pollution.

For copper, cadmium, and zinc, cleaning, especially ethanol cleaning, showed a good removal effect. In comparison, the two washing methods were not so effective for manganese, probably because not much of it was retained on the surface of the blade itself, as the Mn mainly existed in the interior of the blade. The observed variation in the trend of the heavy metal content of the leaves suggests that water washing has a limited effect on the removal of heavy metal particles from leaf surfaces and is influenced by the plant species and the particular heavy metal element, which may mask real differences between the heavy metal contents of the leaves of different species. Water-insoluble substances in atmospheric particles include polycyclic aromatic hydrocarbons, aromatic hydrocarbons, olefins, paraffins, and phthalates [36], and some of these compounds may bind some heavy metals. Ethanol may have a better elution effect on some organically bound heavy metals, which is a possibility that needs to be further explored. The tree species and heavy metal elements studied should be varied in subsequent research to further our knowledge of the treatment effect of ethanol washing.

5. Conclusions

In an attempt to use plants for better detecting heavy metal pollution in the atmosphere, we selected needles of three common conifers (Chinese juniper, dragon juniper, and cedar) and explored the effects of water and ethanol washing. The relatively low Cd content in the needles of the three plants and the high *MAI* value in the dragon juniper provide a direction for the treatment of heavy metal pollution in the atmosphere. The experiments showed that there are limitations of water washing, a common research method, which may disguise the extent of atmospheric pollution. Ethanol washing is more effective for copper, zinc, and especially cadmium. This provides a new idea for research exploring air pollution.

Author Contributions: Conceptualization: T.L. and L.T.; methodology: F.S.; software: T.L. and M.Z.; validation: T.L., K.W., and Y.W.; formal analysis: T.L. and M.Z.; investigation: T.L., M.Z., and Y.W.; resources: F.S.; data curation: T.L., M.Z., and L.T.; writing—original draft preparation: T.L. and M.Z.; writing—review and editing: T.L.; visualization: T.L., K.W., and Y.W.; supervision: F.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available due to privacy.

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

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