Approaches to Understand Historical Changes of Mercury in Tree Rings of Japanese Cypress in Industrial Areas

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Abstract: Historical changes of mercury (Hg) concentrations in tree rings of Japanese cypress (Chamaecyparis obtusa) and the role of dendrochemistry over the last 50 years in Yeosu and Gwangyang National Industrial Complexes of South Korea were evaluated. Mercury uptake in trees were found to be bidirectional and variable depending on atmospheric Hg conditions. With low atmospheric Hg concentrations, Hg concentrations in tree rings were significantly influenced by soil Hg concentrations via roots. With high atmospheric Hg concentrations, Hg concentrations in tree rings were dominated by atmospheric Hg uptake via foliage. Patterns of Hg concentration in sampling sites were divided into: (1) a linear increase in low concentration of Hg originated from soils via roots during 1967–1977 and (2) an elevated and constant concentration with spatial variation of Hg concentration due to foliar uptake from atmosphere during 1978–2014. Between 1967 and 1977, when shrubs and vegetation senesced each year, there was an annual source of Hg in soils due to continued deposition of Hg to soil via litterfall and debris. Thus, Hg concentration was increased over time. During these periods, Hg concentrations in tree rings reflected uptakes of Hg through roots under young forest and low atmosphere Hg conditions. Whether tree rings can serve as reliable proxies for atmospheric Hg concentrations remain unclear due to Hg uptakes from soils and limits from atmosphere under low atmospheric Hg conditions. Intensified chemical plants and steel mills have continued throughout Yeosu and Gwangyang industrial areas since late 1970s, resulting in high Hg emissions. Hg concentrations in tree rings during 1978–2014 showed elevated and constant levels. In addition, tree ring Hg concentrations at study sites were increased gradually with decreasing distance from industrial areas, with a high concentration of 11.15 ng/g at the Yeosu site located the nearest to industrial areas and a low concentration of 4.34 ng/g at the Suncheon site which was the farthest away from industrial areas.

Keywords: mercury; industrial activity; litterfall; dendrochemistry; tree ring; Japanese cypress

1. Introduction

The behavior and fate of mercury (Hg) in the environment are currently receiving increasing attention because of growing evidence that Hg is a potential threat to ecosystems and human health [1,2]. Mercury is input into the atmosphere by anthropogenic and natural processes. Natural sources of Hg to the atmosphere include soils, water bodies, vegetation, and wildfires [3,4]. Mercury is also emitted by anthropogenic sources including combustion of fossil fuel, petrochemical processes, fertilizer production, iron and steel mills, waste incineration, and metal ore treatment [5–14]. In particular, the iron and steel industry is one predominant anthropogenic sources of atmospheric Hg emissions.
worldwide [11]. In complex manufacturing processes of iron and steel, Hg is released by a variety of raw materials at different stages. It is emitted by dozens of stacks. Mercury emissions from sintering machines and coal gas-burning are significant [11]. Mercury is also emitted into the atmosphere from coal combustion by thermoelectric power plants [8]. Mercury is also present in coal [6,8]. Manufacture of phosphate fertilizers is also a source of environmental Hg contamination [5,9,12]. Mercury released from phosphate ores is attributed to the high heating temperature.

Abiotic and biotic passive samplers have been used to measure air concentrations of Hg and understand its spatial and temporal trends through observations [15]. Mercury in tree rings is closely associated with atmospheric Hg since atmospheric Hg is the predominant form of Hg absorbed by foliage [10,12,16]. However, limited work on reliable proxies for atmospheric Hg concentrations has been published regarding records of Hg in tree rings [17]. Plants can uptake Hg from soils via roots and from the atmosphere via leaves [4,18–21]. With low atmospheric Hg concentrations, Hg concentrations in tree rings are significantly influenced by soil Hg concentrations via roots. With high atmospheric Hg concentrations, Hg concentrations in tree rings are dominated by atmospheric Hg uptake via foliage [4,18,19]. Many studies have found that significant Hg contributions are from forest soils via throughfall and litterfall [4,20] and plant uptakes of Hg via roots [19,21].

Since the 1970s, the country’s leading industrial complex that consists of chemical industry, steel mills, and thermoelectric power plants has existed primarily in the Yeosu and Gwangyang areas located in southern Korea (Figure 1). It represents Korean industrial area [22]. In the early 1970s, the demand for electricity began to increase to promote urban and industrial development in the Yeosu industrial areas. Two coal-fired power plants were installed in Yeosu industrial areas during 1973–1975 [23,24]. Furthermore, a food project was promoted due to rapidly growing population in the mid-1970s. A fertilizer plant was also installed in Yeosu industrial areas to increase rice production [14]. This plant is the largest agricultural fertilizer plant in Korea. In addition, a steel mill was operated in 1987 to support the development of automobile and shipbuilding industries in Gwangyang industrial areas [25]. The mill is the largest steel mill in the world. Its average production capacity is approximately 18 million tons per year [25]. Industrial activities in Korea occur primarily in the Yeosu and Gwangyang areas. These areas are used as a proxy for regional production. Industrial activities were increased steadily from the 1980s. They have since remained elevated. Industrial areas are exposed to severe environmental contamination known to be human health hazard due to the release of a number of air pollutants into the atmosphere caused by intense industrial activities in the area [2,12,26,27]. To date, few studies have evaluated historical Hg exposure in these regions, despite potentially high atmospheric deposition from coal-fired power plants, petrochemical and agricultural plants, and a steel mill that has been active since the 1970s [12].

Studies analyzing past Hg pollution recorded in tree rings are rare in Korea [12]. A previous study has focused on the record of historical Hg emissions in Yeosu industrial areas of Korea, a region known for phosphate fertilizer production since the late 1970s [12]. However, in that study by Jung and Ahn (2017) [12], the distinction between phosphate fertilizer production and the impact of coal-fired power plants and steel mills on Hg emissions was limited. In particular, Hg concentrations in tree rings showed a gradually increasing pattern of low Hg levels during 1960s–1970s when there was no industrial activity. Jung and Ahn (2017) [12] did not address whether these low concentrations of Hg in tree rings were uptakes from the soil in the 1960s–1970s. In the present study, we measured Hg concentrations in tree rings of Japanese cypress (Chamaecyparis obtusa), and examined historical changes of Hg concentrations in Yeosu and Gwangyang industrial areas of Korea. In addition, this study examined changes from soil versus atmospheric uptake as the primary source of Hg in tree rings of Japanese cypress.
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Figure 1. Map of tree ring sampling sites at Yeosu, Namhae, and Suncheon stations and locations of main industrial activities at Yeosu and Gwangyang National Industrial Complexes in southern Korea. Wind-rose patterns represent Hg levels in Yeosu City from 1978 to 2014 and Gwangyang City from 1987 to 2014.

2. Materials and Methods

2.1. Study Area Description

Yeosu and Gwangyang industrial areas are characterized by flat reliefs with a ridge of low dunes and reclaimed lands along the ocean coastline surrounded by Gwangyang, Yeosu, and Namhae areas (Figure 1). Soils of the peninsula are composed of fine-grained sand. Average temperatures in the past approximately 50 years at Yeosu, Namhae, and Suncheon areas were 14.2 °C, 14.1 °C, and 12.6 °C, respectively (Figure 2a) [28]. In the period of 1965–2015, average precipitation amounts at Yeosu, Namhae, and Suncheon areas were 1471 mm, 1825 mm, and 1541 mm, respectively (Figure 2b). Precipitation in the Namhae area was 284 mm or 354 mm higher than that in Yeosu or Suncheon site, respectively. The wind in Yeosu City varied (Figure 1) [28]. It was predominated by northwestern, southwestern, and northeastern directions. The wind in Gwangyang City flowed mainly in northwestern, western, and northeastern directions.

The population in Yeosu and Gwangyang areas in 2015 was 414,974 persons, an increase of 59,363 persons compared to the 1960s (Figure 2c) [29]. On the other hand, the population in Namhae areas has continued to decrease since the 1960s. It was 42,696 persons recently. The population in Suncheon areas was 208,033 persons in the 1960s and 268,033 persons in 2015 [29].
Forests 2020, 11, 1200

2.2. Sampling and Sample Preparation

In July 2013 and February 2014, tree rings were sampled at three study sites (Figure 1). Yeosu sampling site was located near Yeosu industrial areas, approximately 12 km from the steel mill in Gwangyang industrial areas. Namhae and Suncheon sampling sites were used as references. They were located in forests far from industrial and resident areas (Table 1). Namhae and Suncheon sites were located approximately 26–33 km and 38–40 km from Yeosu/Gwangyang industrial area, respectively.

Table 1. Distances from industrial areas to study sites and average Hg concentrations in tree rings at Yeosu, Namhae, and Suncheon sites between 1967 and 2014.

| Site         | Distance from the Industry Area (km) | Hg Concentration (ng/g) | 1967–1977 | 1978–2014 |
|--------------|--------------------------------------|-------------------------|-----------|-----------|
|              | Yeosu Gwangyang Average ± SD (Median) |                         |           |           |
| Yeosu        | 4 12                                 | Average ± SD (Median)   |           |           |
| Namhae       | 26 33                                | 2.51 ± 0.59 (2.47)      | 6.54 ± 1.32 (6.57) b |
| Suncheon     | 40 38                                | 2.15 ± 0.84 (2.27)      | 4.34 ± 0.66 (4.23) c |

Note: Different letters indicate significant differences among three sites at \( p < 0.017 \) after Bonferroni correction.

The Japanese cypress as a sample tree thrives in southern parts of Korea. Namhae and Suncheon sites were afforested in the 1960s. The forest from the Yeosu site was afforested in the 1990s. Thus, the tree age at the Yeosu site was less (24 years) than those at other sites. One disk in each sampling site was collected from the stump at a height of 1 m. These disks were collected using a stainless steel saw. To reduce chemical contamination of samples, latex gloves were worn at all time. The stainless steel saw was wiped down with a new Kimwipe wetted with methanol before cutting into the tree as well as after every cutting. These disks were air-dried for 7 days and polished with progressively finer sandpaper up to 600 grit to expose ring boundaries for identification. Each sample disk was scanned. Growth rings were marked with a CooRecorder program (version 7.8; Cybis Elektronik &
Data AB, Saltsjöbaden, SE). Individual disks were cut into 1-year segments using a stainless steel knife and air-dried. These segments were shattered using an MM 400 ball-mill grinder (Retsch GmbH, Haan, DE) [12].

2.3. Mercury Analysis

Tree ring Hg concentrations were determined at Korea Basic Science Institute using the Direct Mercury Analyzer (DMA)-80 (Milestone Srl, Rome, Italy). The analyzer uses thermal decomposition, gold amalgamation, and atomic absorption spectrometry. The Hg detection limit was 0.005 ng. Operation conditions for the DMA-80 were based on Environmental Protection Agency Method 7473 protocol [30]. A calibration curve was generated using a reference material obtained from the National Research Council of Canada Institute for National Measurement Standards MESS-3 (marine sediment, certified value = 90 ± 9 ng/g HgT (dry weight)) with $R^2 > 0.999$. Measurement standard MESS-3 was used to calculate the accuracy and precision. Recovery ranged from 97% to 102%. Machine blanks and reference samples were included every 5–20 samples.

2.4. Statistical Analysis

The $t$-test was used to determine differences of Hg concentration in tree rings between Namhae and Suncheon sites during 1967–1977 (Table 1). Samples at the Yeosu site before 1991 did not exist because trees were younger than established industrial factories. Differences in tree ring Hg concentration at sampling sites during 1978–2014 were determined using the Kruskal–Wallis test followed by the Mann–Whitney $U$-test for pairwise comparisons with $p$ adjusted < 0.017 after Bonferroni correction. All statistical tests were performed using SPSS statistics program (version 21; IBM SPSS Statistics, Chicago, IL, USA) at a significance level of $p < 0.05$.

3. Results

Age of sampled Japanese cypress trees varied by study site (Figure 3b). Trees at Suncheon and Namhae sites dated back to 1967 and 1968, respectively. Trees at the Yeosu site were the youngest, with the earliest rings occurring between 1991 and 2014. Industrial development has progressed, and surrounding forests have been depleted in the Yeosu and Gwangyang areas since 1970s–1980s.

Tree cores during 1967–1977 showed linear increases for low Hg concentrations at Namhae and Suncheon sites (Figure 3b). However, Hg concentrations in tree rings during 1978–2014 at study sites were elevated with a constant distribution. Mercury concentrations in tree rings were compared over the two periods (1967–1977 and 1978–2014) of the last 50 years and between sampling sites located away from Yeosu and Gwangyang industrial areas (Table 1). Hg concentrations in tree rings between 1967 and 1977 were relatively low. They were 2.51 ng/g and 2.15 ng/g at Namhae and Suncheon sites, respectively, showing no significant difference ($p > 0.05$).

Since the late 1970s, industrial activities including coal-fired power plants, chemical plants, and steel mill continued near Yeosu and Gwangyang industrial areas (Figure 3). Average Hg concentrations in tree rings at Yeosu, Namhae, and Suncheon sites during 1978–2014 were 11.15 ng/g, 6.54 ng/g, and 4.34 ng/g, respectively (Table 1). Average Hg concentrations in tree rings between 1978 and 2014 appeared to be relatively higher than those prior to that period (1967–1977). There were significant differences among these three sampling sites ($p < 0.017$). The Yeosu site located nearest to the Yeosu and Gwangyang industrial areas showed the highest Hg concentrations in tree rings after 1977. In contrast, the Suncheon site, which was the farthest away from Yeosu and Gwangyang industrial areas, had the lowest concentrations of Hg in tree rings. In addition, Hg concentrations in tree rings at the Suncheon site after 1987, when the largest steelworks in Gwangyang industrial area was started, did not show increase. Instead, they had a constant distribution. However, Hg concentrations in tree rings at Namhae site were abruptly elevated, coinciding with the operation of steelworks in 1987.
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4. Discussion

4.1. Historical Hg Recorded in Tree Rings

In the Namhae and Suncheon areas between 1967 and 1972, low Hg concentrations in tree rings showed linear increases, although there was limited Hg inflow from industrial activities (Figure 3b). Many factories needed electricity to operate. Therefore, coal-fired power plants were installed in Yeosu areas in 1973 which was the beginning of industrial development in Yeosu areas [23]. Previous studies [16] have reported that high temperature promotes the growth of trees, resulting in increases of Hg uptake from atmosphere. Although the average temperature at Namhae area was approximately 1.5 °C higher than that at Suncheon area, tree ring Hg concentration at Namhae site was similar to that at Suncheon site (Figures 2a and 3b). In this study, it was thought that tree ring Hg concentration was not influenced by temperature variation. In addition, residential heating could cause Hg emissions into the atmosphere [13,14]. Population at Namhae areas had a significant decrease after the 1960s, whereas the population in the Suncheon areas was gradually increased over time (Figure 2c). However, tree ring Hg concentrations at Namhae and Suncheon sites showed similar trends during 1967–1972.
No evidence showed a relation between factors affecting Hg uptake associated with temperature and population and corresponding Hg concentration in tree rings during 1967–1972. Data reported by Becnel et al. (2004) [31] showed a correlation between Hg concentrations in lichens and tree cores in a large area of Louisiana. They suggested similar patterns of uptake for both trees and lichens known to absorb atmospheric pollutants. However, lichens were not distributed on the bark of trees collected in this study (Figure 3b). Therefore, it was thought that tree ring Hg concentration did not reflect Hg uptake from the atmosphere at the Namhae and Suncheon sites prior to 1972.

Limited work has been published regarding levels of Hg in tree rings due to uncertainty about whether tree rings could serve as reliable proxies for atmospheric Hg concentrations given that its atmosphere concentrations were low. In addition, there was uncertainty regarding the mechanism of Hg uptake into vegetation [4,18,19]. Plants can take up Hg from soils via roots and from the atmosphere via leaves [4,18,19]. According to many studies [4,18,19], under a low air Hg concentration condition, soil Hg concentration has a significant effect on foliar Hg concentration, whereas under a high air Hg concentration condition, foliar Hg concentrations are dominated by atmospheric uptake. Foliar uptakes are bidirectional and variable depending on air Hg conditions. The pattern of Hg concentration across dated tree rings could help distinguish the importance of atmospheric versus soil source of Hg to wood. If soil is the source of Hg to wood tissues, tree ring Hg concentrations should be relatively increasing over time due to continued Hg accretion in soils from throughfall and litterfall [32–34]. The residence time of Hg in soil is quite long. Thus, we anticipate limited loss of Hg from soil pools [35]. Although there are no data on past mercury emissions from the Yeosu and Gwangyang industrial areas, high Hg concentrations are expected to be emitted consistently as coal-fired plants, chemical plants, and steelworks continue industrial activities since the late 1970s. If atmospheric deposition to foliage is the source of Hg in tree tissues, radial Hg in the bole would show elevated and constant concentrations since late 1970s in formed tree rings.

Tree ring Hg concentrations in this study can be divided into two patterns: (1) linear increase of low Hg levels during 1967–1977 and (2) elevated and constant Hg concentrations during 1978–2014 (Figure 3b). Before 1977, Hg concentrations in tree rings were influenced by root uptakes under young forest and low atmosphere Hg conditions. No evident relationship was found between annual growth and corresponding Hg concentrations in trees [16]. Under young forest condition before 1977, Japanese cypress seedlings were covered lushly by shrubs and vegetation known to accumulate Hg (Figure 3b). Since shrubs and vegetation senesce each year, they could become an annual source of Hg to soils. In addition, atmospheric Hg may be deposited into soil by wet processes [3]. Although the average precipitation in the Namhae area was approximately 350 mm higher than that in the Suncheon area (Figure 2b), tree ring Hg concentrations were similar between Namhae and Suncheon sites (Figure 3b). There was no relation between precipitation and tree rings Hg concentration in this study. Previous studies have found significant Hg contributions to forest soils via throughfall and litterfall, with the contribution of litterfall being the greatest [3,20]. A soil source would be expected to result in increased Hg concentration over time due to continued deposition of Hg to soil via litterfall [32–34]. Godbold and Hutterman (1988) [36] have found that regardless of external Hg concentration, Hg concentration in roots exceeded that in foliage. It remains unclear whether tree rings can serve as reliable proxies for atmosphere Hg concentrations due to Hg uptakes from soils and limits from atmosphere under low atmospheric Hg conditions.

Chemical plants and steel mill in Yeosu and Gwangyang areas have shown intensified activities. They represent a proxy for regional production since late 1970s (Figure 3a). This might have led to a large amount of Hg emissions to the atmosphere [5–12]. Frescholtz et al. (2003) [4] have noted that at a high atmospheric Hg concentration, foliar Hg concentrations are dominated by atmospheric uptake. An atmosphere source would be expected to result in elevated and constant Hg concentrations over time due to the continued emission of Hg to the atmosphere via industrial activities. We observed elevated and consistent concentrations since late 1970s in formed tree rings (Figure 3b). The radial pattern of elevated Hg concentrations in tree rings since late 1970s supports the possibility of an atmospheric
Results of this study indicate that tree rings in 1978–2014 could serve as an appropriate record of Hg deposition in Yeosu and Gwangyang areas affected by intensified industrial activities.

4.2. Spatial Distribution of Hg Concentrations in Tree Rings

Between 1967 and 1977, Hg concentrations in tree rings did not vary among study sites \( (p > 0.05) \) due to Hg uptake from soils (Table 1). Industrial activities in Yeosu and Gwangyang industrial areas were intensified and continued since late 1970s (Figure 3a). In general, atmospheric Hg levels are influenced by wind flow [37]. Mercury is highly volatile. It might be transported through a long distance [10,12]. Hg concentrations of tree rings during 1978–2014 at study sites were elevated and constant. Spatial distributions of Hg concentrations were associated with decreased distance from industrial areas \( (p < 0.017) \) (Table 1). During 1978–2014, the highest concentration of Hg in tree rings was found at the Yeosu site near Yeosu and Gwangyang industrial areas. However, the lowest concentration of Hg in tree rings during 1978–2014 was found at the Suncheon site, which was far away from Yeosu and Gwangyang industrial areas. Especially, Hg concentrations in tree rings at Suncheon site after 1987 did not increase. They showed a constant concentration distribution despite the operation of the largest steelworks in Gwangyang industrial area in 1987. Wind in Gwangyang industrial area was predominantly in northwestern, western, and northeastern directions during 1987–2014 (Figure 1). The site of Suncheon located to the west of Gwangyang industrial areas was relatively less affected by wind transmission of Hg from the steel mill in Gwangyang industrial area. Tree ring Hg concentration at the Suncheon site was mainly influenced by the Yeosu industrial area. However, the abruptly elevated Hg concentration in tree rings at the Namhae site coincided with the operation of steelworks in 1987. Although Namhae sites are located far in the east of Yeosu and Gwangyang industrial areas, Hg might have input from two sources in Yeosu and Gwangyang industrial areas due to wind directions.

Temperature and residential heating of population seem to affect Hg concentrations in tree rings [13,14,16]. Higher temperature seems to stimulate Hg uptake from the atmosphere [14]. Temperatures in Yeosu and Namhae areas were higher than those in Suncheon (Figure 2a). We observed that Hg concentrations in trees at Yeosu and Namhae sites were higher than those at the Suncheon site during 1978–2014 (Figure 3b). The Yeosu site, which was located near Yeosu and Gwangyang industrial areas, had the highest Hg concentration in tree rings. In addition, residential heating of the population can cause Hg emissions into the atmosphere [13,14]. The population has the largest number in Yeosu and Gwangyang industrial areas (Figure 2c). Thus, Hg concentrations in tree rings at Yeosu site were the highest during 1978–2014 compared to those at Namhae and Suncheon sampling sites (Figure 3b). The Suncheon site, which was the farthest from Yeosu and Gwangyang industrial areas with limited influence from wind direction, had a population 6.3-fold higher than the Namhae area, although Hg concentrations in tree rings during 1978–2014 were lower than those at Namhae site. In 1992, at the Suncheon site, Hg concentrations in tree rings were abruptly increased, reaching the maximum value. This was thought to be the result of Hg emission from residential heating in association with the largest population in the Suncheon area in the early 1990s (Figure 2c). The distribution of Hg concentrations in tree rings during 1978–2014 might have been influenced by temperature and population. However, spatial distribution of Hg concentrations was found to be more affected by wind direction and distance from Yeosu and Gwangyang industrial areas. These results suggest that tree ring could be used as a valuable proxy to understand changing regional air Hg conditions under intensified industrial activities.

5. Conclusions

Collectively, our dendrochronological record showed that linear increases of low Hg concentrations in tree rings before 1977 could not serve as a proxy for atmospheric Hg concentrations in areas with nonindustrial and initial industrial activities. These Hg trends reflected the pathway of tree rings before 1977 caused by Hg uptakes from soils via roots under low atmospheric Hg conditions. A soil source of Hg would be expected to result in increased Hg concentrations over time due to the continued
deposition of Hg to soil via litterfall. However, tree ring Hg concentrations during 1978–2014 were indicative of regional trends associated with industrial activities. These elevated and constant Hg trends were consistent with anthropogenic emissions following intensified industrial activities known to continue to release high Hg levels. Mercury levels decreased with increasing distance from industrial areas. Wind direction also influenced the spatial distribution of tree ring Hg concentrations.

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