

DISTRIBUTION OF THALLIUM IN SCOTS PINE FROM A PYRITE MINING AND SMELTING AREA, SOUTH CHINA

Juan Liu¹, J. Wang¹, M. Yin¹, Y. Chen^{1*}, J. Qi², L. He¹, X. Luo¹, Y. Lin¹, C. Wang³

¹*Innovation Center and Key Laboratory of Waters Safety & Protection in the Pearl River Delta, Ministry of Education, Guangzhou University, Guangzhou, China.*

²*South China Institute of Environmental Science, Ministry of Environmental Protection, Guangzhou, China.*

³*Guangdong Provincial Academy of Environmental Science, Guangzhou, China.*

liujuan858585@163.com

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Introduction

Thallium (Tl) is one of the most toxic metals with no known beneficial biological role, and it can cause chronic as well as acute poisoning (Li et al., 2012; Xiao et al., 2012). In China, the behavior and fate of Tl in the environment have received soaring attention in recent years, due to successive occurrence of Tl pollution incidence. In the Western Guangdong Province, China, ultra-large pyrite ore deposits with preservation of Tl over 7000 t, have been exploited since the 1970s. Huge amounts of pyrite ore rejects and acid waters have been produced and introduced into the environment. According to our previous investigation, Tl content in the soils from the mining site, tailing site and smelting site ranged from 2.0–20, 1.60 – 15.36, and 1.8 – 15.4 mg kg⁻¹, respectively; Tl content in the aerosols around the pyrite smelting site amounted to 18.6 – 33.1 mg kg⁻¹; Tl concentration in the spring water, mineral water, washing wastewater and surface runoff were 0.35 to 3.82, 4.82, 15.4 – 400, and 0.19 – 65.25 µg L⁻¹. To date, very limited studies have investigated distribution of Tl in trees at sites contaminated by anthropogenic sources.

In this study, concentrations of metals (Tl, Pb, Zn, Cd, Co, Ni, Cr, and Mn) were determined in pine needles and tree rings of Scots pine (*Pinus sylvestris* L.) grown in the pyrite mining and smelting area of the Western Guangdong Province, South China. Metal concentrations in the respective soils were also investigated. The aims of this study were to: (i) explore the distribution of Tl and associated metals in the pine needles and tree rings for better understanding their biogeochemical behavior in contaminated tree-soil systems; (ii) test the applicability of Tl as an environmental indicator for metal pollution and (iii) evaluate the feasibility of pine as an environmental archive for reconstructing Tl pollution.

Methods

In April, 2012, trees and soils were sampled at five woodland sites located downwind from the pyrite mining and smelting area in Yunfu city, Guangdong Province, China. Pine needles were taken from a representative pine tree at each site. Three dendrological cores were selected from the pine trees, by using a 5-mm stainless steel incremental borer (Haglöf, Sweden). The cores were subsequently placed into the polyethylene tubes prior to chemical analysis. Each tree core was divided into 1-year segments using a stainless steel knife. The segments were dried at 60 °C for 48 h and digested with concentrated HNO₃ at 200 °C overnight. Concentrations of Tl, Pb, Zn, Cd, Co, Ni, Cr, and Mn were determined by using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Elan 6100 DRCII, PerkinElmer, USA).

Results

The concentrations of Tl in the soils ranged from 3.96 to 26.16 mg/kg, which were obviously higher than those reported in background soils. Concentrations of Cd, Cr, Pb and Ni were in the range of 1.52 – 5.00 mg/kg, 507.81 – 8924.37 mg/kg, 98.11 – 565.97 mg/kg and 299.46 – 6243.11 mg/kg, respectively. Pine needles from the industrial site also showed relative accumulations of Tl, Cd, Pb, Cr, Ni, Zn and Mn, with concentrations of 0.94 – 4.15 mg/kg, 0.90 – 2.31 mg/kg, 5.74 – 14.06 mg/kg, 9.41 – 41.49 mg/kg, 3.73 – 13.50 mg/kg, 70.75 – 132.9 mg/kg, and 195.9 – 1805 mg/kg. The highest concentration of Tl (4.15 mg/kg) in the needles was observed in the pine closest to the industrial site. Tl concentrations in the needles generally showed a decreasing trend as the distance from the industrial site increased. However, such trend was not found in the concentrations of other metals. The characteristic absorption of Tl in the needles may result from Tl deposition from local mining and smelting of Tl-containing pyrite minerals.

The tree rings also exhibited an apparent accumulation of Tl from the pines in the industrial site. Tl concentrations in these tree rings fell in the range of 0.41 – 2.03 mg/kg, with a mean of 1.12 mg/kg. Vaněk et al. (2011) also observed an accumulation of Tl in the tree rings of pines affected by Pb-Zn smelting activities. Correlation analysis further unveiled that Tl in the tree rings were significantly positive correlated with Cd, Co, Mn, Pb, and Zn ($p=0.54 - 0.86$). The distribution pattern of annual production of pyrite minerals was generally similar to the Tl distribution in the tree rings.

Conclusion

Elevated levels of Tl in the studied pine needles and tree rings indicate that conifers tend to accumulate this metal to some extent. The Tl levels in the needles were overall correlated with the distance, suggesting applicability of using Tl as an environmental indicator of metal pollution from the utilization of specific minerals. Tree-ring patterns of Tl significantly correlated with the mining production implied possible use of dendrochemistry for tracing the history of Tl inputs.

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