

A NOVEL SAMPLING METHOD FOR PRESENT AND HISTORICAL MONITORING OF AIR POLLUTION BY USING TREE BARK¹⁾

WANG Qiu-quan²⁾ ZHU Chen WANG Yu HUANG Zhi-yong LI Zhen-ji HUANG Bei-li

(Department of Chemistry & the MOE Key Laboratory of Analytical Sciences, Xiamen University, Xiamen, 361005)

TSUNODA Ken-ichi

(Department of Chemistry, Gunma University, Kiryu 376-8515, Japan)

SATAKE Kenichi

(National Institute for Environmental Studies, Onogawa 16-2, Tsukuba 305-8506, Japan)

Abstract The concentrations of lead and cadmium in the tree bark from Sanming and Xiamen, Fujian province, China were determined by atomic fluorescence spectrometry and inductively coupled plasma mass spectrometry. The results obtained in the outer tree bark and tree bark pocket could reflect the degree of present and historical air pollution at different sampling locations. Tree bark and tree bark pocket should be expected to be as a useful biomonitor of present and historical condition of air pollution.

Keywords: air pollution monitoring, tree bark, tree bark pocket, lead, cadmium.

1 Introduction

Besides the usual sampling methods, the concentrations of pollutants in tree bark and tree bark pocket have been proposed for evaluating the degree of air pollution of present and in the past^[1-4].

In this study the concentrations of lead and cadmium in the outer tree barks of redbud, which were collected in Sanming, Fujian province, China, were determined by atomic fluorescence spectrometer (AFS) and inductively coupled plasma mass spectrometry (ICP-MS), and the results were used to evaluate the degree of air pollution around the sampling sites. Moreover, the concentrations of lead and cadmium and the isotope ratios of ²⁰⁶Pb/²⁰⁸Pb and ²⁰⁶Pb/²⁰⁷Pb in the mango tree bark pocket were respectively determined for historical monitoring of air pollution and recognizing the lead emission sources in Xiamen, Fujian province, China.

2 Experimental

2.1 Chemicals and instruments

Standard solution of lead and cadmium were prepared by dissolving an appropriate amount of specpure lead and cadmium in 7 mol L⁻¹ HNO₃, and diluted by Milli-Qwater (Millipore, Bedford).

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2) Corresponding author. Tel: 0592-2181796; E-mail: qqwang@jingxian.xmu.edu.cn.

MA, USA) to 100 ml in a polyethylene bottle to give $1000 \mu\text{g} \cdot \text{ml}^{-1}$ Pb and Cd solutions in 2% HNO_3 , respectively. Pb isotope standard reference material SRM 981 (NIST) was used for calibration during determination of Pb isotope ratios. Thallium standard stock solution of $1000 \mu\text{g} \cdot \text{ml}^{-1}$ (GSB G62070-90 (8101), National Analytical Center for Steel Materials, China) was used as internal standards during ICP-MS determination. A certified reference material GBW07603 of tree leaves was used to ensure AFS and ICP-MS in good conditions.

A Hewlett-Packard (Yokogawa Analytical Systems, Tokyo, Japan) 4500 ICP-MS system fitted with a concentric nebulizer kit was used for the determination of lead and its isotope ratios. Cadmium was determined by ASF 2002 (Beijing Vital Instrumental Co. Ltd., China) with a FIA sample introduction system of hydride generation, and a cadmium high strength HCL lamp (No. 12 Institute of Electronics, Beijing, China) was used as an excitation source, $\lambda_{\text{ex}} = 228.8 \text{ nm}$.

2.2 Sample collection and pre-treatment

Tree bark and tree bark pocket samples were collected at the industrial area of Sanming and urban area of Xiamen, Fujian province, China. After sampling the tree barks were divided into four parts of outer bark, inner bark, cambium and wood, and then the outer tree barks were put into a 60 °C stove for drying until constant weight were attained. An appropriate amount between 100—200 mg of the dried sample was put into a double layer Teflon digestion bomb, which contained 0.5—2.0 ml high purity concentrated HNO_3 in the outer layer. After 4h digestion at 140 °C, the left one drop of residue in the inner Teflon vessel was diluted with Milli-Q water, filtered through a 0.45 μm membrane, and finally diluted to 10 ml for further determination.

3 Results and discussion

3.1 Lead and cadmium in the outer tree barks in Sanming

Pollutants in airborne could deposit into the outer bark of a tree through two ways: dry deposition (gases and particles) and wet deposition (rain, snow, fog, and mist). The concentrations of pollutants in it might reflect the degree of air pollution at present time. Sanming city was built in a valley located in the southeastern part of China, a heavy industrial base in the central part of Fujian province. Shaxi river crosses the city from southwest to northeast, and wind blows from northeast to southwest all the time in a year. The northeastern side of Shaxi river is the industrial area having many big smelters, steel plants, chemical factories, and the other side is the living area for citizen. Redbud tree barks was collected from the lower to the upper along Shaxi river. Tree bark samples of pine were also collected at different height above sea level on Hutou mountain near Shaxi river.

The concentrations of lead and cadmium in the outer tree barks collected in Sanming were shown in Fig. 1 indicating that lead and cadmium concentrations determined in the outer bark varied according to the sampling locations. Both of the concentrations of lead and cadmium in the outer tree barks collected along Shaxi river increase in general along the wind direction (Fig. 1(a)), this phenomenon is in agreement with the fact that pollutants may concentrate at the site at the down direction of wind. However, those on Hutou mountain have two peaks at 380m and 1020m above sea level.

vel (Fig. 1 (b)). It might be because of air convection, but the reason has not been clear so far.

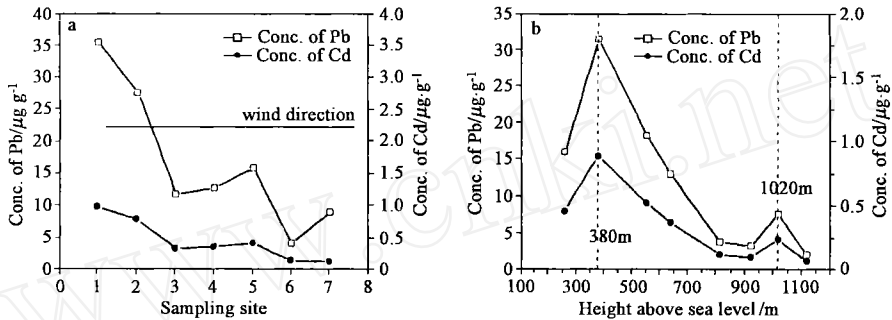


Fig. 1 Concentrations of Pb and Cd in the outer tree barks of redbud along Shaxi river (a) and in the outer tree barks of pine on Hutou mountain (b)

3.2 Lead and cadmium in mango tree bark pocket in Xiamen

As mentioned above the concentrations of pollutants in the outer tree bark might reflect the degree of air pollution at present; furthermore those in the outer tree bark of the tree bark pocket enclosed in a tree trunk could offer the information of the degree of air pollution in the past. The time of the tree bark pocket may be dated by the annual ring of a tree. A mango tree bark pocket sample was collected in the urban area of Xiamen. The concentrations of lead and cadmium in the tree bark pocket from 1993 to 2001 were shown in Fig. 2. The results in Fig. 2 indicated that both concentrations of lead and cadmium in the bark pocket are relative high in the years of 1995 and 2000, reflecting that air pollutions of the two years are relative more serious in Xiamen.

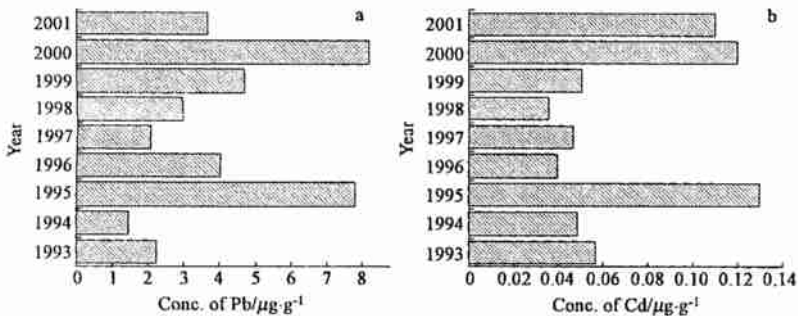


Fig. 2 Concentrations of lead and cadmium in mango tree bark pocket in Xiamen

3.3 Isotope analysis of lead in the mango tree bark pocket

There are almost no heavy industries in Xiamen. The possible sources of pollutants are the exhaust gases from thermal stations, automobiles and waste incineration as well as transportation from other areas. To distinguish the possible sources of lead pollution in Xiamen, isotope analysis of lead by ICP-MS was performed. The results of $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ in the mango tree bark pocket from 1993 to 2001 were illustrated in Fig. 3. Clearly, both of $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ in the

mango tree bark pocket from 1999 to 2001 are lower than those from 1993 to 1998. The ratios of $^{206}\text{Pb}/^{207}\text{Pb}$ in the petrol with the Pb additives that imported from Europe countries and USA are from 1.10 to 1.21^[5-7], and that in the earth crust of China is about 1.19^[8], however there is no the values for waste incineration recorded in China now. From 1999 Xiamen municipal government decided to stop using the leaded petrol (gasoline), this might be one of the reasons why the ratios began to decrease from the year. However, the concentrations of lead did not decrease from 1999 (Fig. 2(a)), and that in 2000 is very high. Such a phenomenon implies that there must be other sources of lead in Xiamen besides the automobiles and thermal stations, the contribution from waste incineration^[4], which is recently used for waste disposal in Xiamen, should be also taken into account for the total amount of lead and the reduction in the ratios of $^{206}\text{Pb}/^{207}\text{Pb}$.

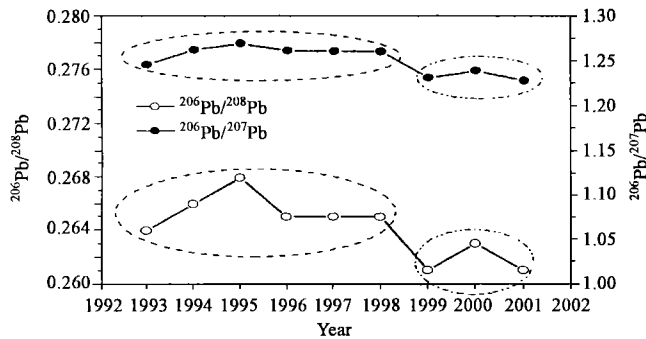


Fig. 3 Isotope ratios of $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ in the mango tree bark pocket

4 Conclusions

Tree bark and tree bark pocket are effective biomonitor for evaluating air pollution. The concentrations of pollutants in the tree bark and tree bark pocket may provide valuable information on present and historical condition of air pollution. Moreover, with such a sampling method isotope analysis technique could be applied to identifying the sources of pollutants.

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利用‘树皮’进行大气污染历史监测的新采样方法

王秋泉, 朱晨, 王宇, 黄志勇, 李振基*, 黄本立

厦门大学化学系, 教育部现代分析科学重点实验室, 厦门, 361005 (*厦门大学生物系)

角田欣一

Department of Chemistry, Gunma University, Kiryu 376—8515, Japan

佐竹研一

National Institute for Environmental Studies, Onogawa 16-2, Tsukuba 305—8506, Japan