Characterisation of airborne particulates and associated trace metals deposited on tree bark by ICP-OES, ICP-MS, SEM-EDX and laser ablation ICP-MS

Keiko Suzuki

Department of Geography, Queen Mary, University of London, Mile End, London, E1 4NS, UK

Received 9 August 2005; received in revised form 28 November 2005; accepted 7 December 2005

Abstract

Particulate matter accumulated on tree bark specimens was examined in order to investigate its potential use as a natural monitor to study the impact on local atmospheric conditions. Tree bark from sargent cherry (Prunus sargentii) and sugar maple (Acer saccharum Marsh) trees was collected from four locations: Drax (North Yorkshire), Darley Dale (Derbyshire), Galway (Ireland) and Tristan da Cunha. Particulates accumulated on tree bark were prepared for analysis using a microwave-assisted HNO3 digestion. The bulk elemental content was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) and trace metals were analysed by inductively coupled plasma mass spectrometry (ICP-MS). Analysis of bulk tree bark samples revealed that the highest mean Pb concentration was obtained in Darley Dale samples, 1069 ng g⁻¹, with 147 and 3.2 ng g⁻¹ Pb in Drax and Galway samples, respectively. In Tristan da Cunha samples 0.12 ng g⁻¹ of Pb was detected. Pb, As, Cr, Sb, Sn and Zn were enriched by factors of 10–8650 relative to the background elemental abundance in tree bark obtained from Tristan da Cunha. Particulates accumulated on the tree bark were characterised by SEM-EDX and LA-ICP-MS to provide information on the particle composition and morphology. This study supports the suggestion that the major particulate sources are high-temperature combustion processes. Direct analysis by LA-ICP-MS revealed the potential of this alternative method to investigate the distribution of suspended particulates and their elemental association on the bark specimen.

Keywords: Suspended particulate matter; Tree bark; Trace metals; ICP-OES; ICP-MS; SEM-EDX; LA-ICP-MS

1. Introduction

Heavy metals are present in the atmosphere in ever increasing levels as a result of anthropogenic and natural emissions. Recent researches focus on the analysis of airborne particulate deposits in the environment as a strong association between size fraction of inhalable particulate matter and acute health effects recently identified (Haapala, 1998; Monn et al., 1995; Wilson and Suh, 1997; Harrison and Yin, 2000).

Current air monitoring programmes involve high costs and considerable technical support and both of these factors limit sampling and monitoring to a small number such as in cities, heavily industrialised and high-traffic areas. The emission of heavy metals are highly associated with anthropogenic activities and these facts are well recognised; however,
measurements of heavy metals are not currently carried out under the air-monitoring programme used across the UK (Harrison and Yin, 2000).

Sampling the naturally accumulated airborne particulate matter on biological media is an effective, low cost and reliable method of assessing airborne heavy-metal contamination (Satake and Tanaka, 1996; Bacic et al., 1999; Schulz et al., 1999; Fernandez Espinosa et al., 2000). Trees are one of the typical biological sinks for airborne particulates, through both wet and dry deposition processes. Due to its constant exposure to the environment, tree bark, the outermost layers of tree trunk have been used to assess local and regional airborne heavy-metal contamination in selected regions throughout the world (Satake and Tanaka, 1996; Bellis et al., 2001; Suzuki, 2002).

Automotive emission research with the aid of tree bark by Gómez et al. (2002) revealed high levels of platinum group element containment in airborne particles as a consequence of catalysts used in automotive traction. Kruuczynsk et al. (1997) examined the chemical composition of needles and stems of Scots Pines (Pinus sylvestris L) to assess atmospheric pollution. Significant accumulation of Ni and Cu in the wax of pine needles was correlated with local air pollution.

The tree bark samples from the world’s most remote island, Tristan da Cunha, were obtained and analysis revealed its suitability for use as the current natural background level for ambient atmosphere across the world (Suzuki, 2002).

Heavy metal monitoring using biological media typically uses destructive methods to determine the total metal contamination in the specimen. However, recent studies of particulate sizes and their association with respiratory illness and death showed that PM$_{10}$ and PM$_{2.5}$ classified particles are potentially dangerous. Clearly, destructive analysis of samples negates the ability to identify this problem directly. Scanning electron microscopy-energy dispersive X-ray spectrometer (SEM-EDX) is a non-destructive solid analysis method often used to characterise the mineralogical phase of individual particles. SEM-EDX can be used to identify airborne particulate deposits and their distribution on biological materials from multiple pollution sources (Haapala, 1998). In many cases, however, this method is restricted to size of aerosol particle diameter analysed. Alternatively, the semi-destructive method of laser ablation coupled with ICP-MS (LA-ICP-MS) was successfully applied to determine the distribution of platinum group elements on tree bark (Ma and Staton, 2001). In this study, both SEM-EDX and LA-ICP-MS techniques will be tested to characterise physico-chemical composition of the airborne particulate deposits on tree bark samples.

The aim of this paper is to assess the use of tree bark as a biomonitor and present a new insight into the physico-chemical assessment of airborne particulate matter. Bulk elemental analysis will be coupled with two additional analytical techniques, SEM-EDX and LA-ICP-MS. This will reveal in depth information on chemical speciation of airborne particulates accumulated on tree bark, and identify metallic tracers of local anthropogenic emission. Individual suspended particulates are characterised in order to evaluate emission sources, thus allowing the qualitative analysis of the sites studied.

2. Materials and methods

2.1. Sampling locations and description

Tree bark samples were collected between August 2001 and September 2001 from four locations: Drax (North Yorkshire; 53°43’50"N and 0°59’41"W), Darley Dale (Derbyshire; 53°09’26"N and 1°36’42"W), Galway (Ireland; 53°16’00"N and 9°03’55"W) and Tristan da Cunha (Overseas Territory of the United Kingdom; 37°15’00"S and 12°30’00"W). Tree bark samples in Drax ($n = 23$), Darley Dale ($n = 28$) and Galway ($n = 15$) were collected, subject to tree availability and road access. Drax has one of the largest coal-fired power stations in Europe and sampling was carried out within a 5 miles radius from the power station in all directions. Sampling locations in Darley Dale were collected from 10 miles radius of the Pb smelting plant. Tree bark samples from Galway were collected near the coastline to represent the natural background level in Britain and Ireland samples.

2.2. Sampling and chemical analysis

Tree bark sampling was based on tree species availability. Sargent cherry (Prunus sargentii) and sugar maple (Acer saccharum Marsh) were the dominant tree species for this investigation. At least three specimens of the same species with similar age (20–30 years) were randomly selected at each sampling point to obtain representative samples.
Ten grams of outer bark was removed from the trunk at a height of 1.5 m above the ground, and stored at \(-18^\circ C\) until required for analysis.

For the analysis of total elemental composition of particulate matter, 0.2 g of sample was digested in 5 ml concentrated nitric acid (ARISTAR, BDH, UK) in a PTFE digestion vessel, mixed and left standing for 2 h. The sample was digested using a Mars X (CEM Corporation, Matthew, North Carolina, US) extraction system. Microwave digestion was carried out for 0.5 h heating at 1200 W with pressure incrementing from 80 to 150 psi. Sample digests were filtered (Whatman No. 42) to remove any solid residues and diluted to 50 ml volume. The digests and the blanks were analysed by ICP-OES (Spectro Analytical CIROS, Kleeve, Germany) and ICP-MS (Agilent 4500, Agilent Ltd, Cheshire UK). The accuracy of the analysis was checked by concurrent analysis of standard reference materials; Poplar Leaves (GBW07604) from the National Institute of Standards and Technology (Gaithersburg, USA).

It is essential to obtain the natural background concentration for the ambient atmospheric condition (i.e. Tristan da Cunha) as the global atmosphere is exposed to constant mixing and are becoming more difficult to identify the origin of atmospheric contamination. Identifying a true background level of current ambient atmospheric condition such as in Tristan da Cunha is a significantly important data which will enable further discrimination of natural or anthropogenic heavy metal inputs in present date. Since individual blanks of bark samples were not available, tree bark samples from Tristan da Cunha were digested and used to provide natural background levels of heavy metals (Suzuki, 2002). To appreciate the level of current atmospheric condition in the United Kingdom and Ireland, elemental concentration determined in tree bark was compared with values from Tristan da Cunha.

2.3. Physico-chemical analysis of airborne particulates

Morphological and mineralogical studies of the aerosol particles were carried out using a Philips XL20 (Philips, UK) with Pentafet EDX detector (Oxford Instruments Ltd., UK). The deposited airborne particles were detected using back-scattered secondary electrons (BSE) with a 25 keV electron beam, a spot diameter of 5 μm, take off angle of 15°, and with an acquisition time of 60 s. A piece of bark sample was coated with 100–150 Å carbon, and particulate size was calibrated using an abrasive “diamond sheet” (10 μm particles). For each bark sample, a minimum of 300 particles was analysed.

Microanalysis of aerosol particles using LA-ICP-MS did not require preparation. The bark samples were directly mounted onto the stage in the ablation chamber for investigation. A CETAC LSX Laser Ablation System (CETAC technologies Inc. Omaha, USA) was equipped with Agilent 4500 ICP-MS; the Nd:YAG laser was operated at the wavelengths of 266 nm with a pulse frequency of 1–20 Hz and maximum energy of 4 MJ per pulse in the Q-switched mode. Single point ablation and line rastering were implemented via the \(x-y-z\) translation stage. The sample cell was connected to the ICP-MS via a Teflon tube with 1 ml min\(^{-1}\) argon carrier gas flow rate. Tuning of the ICP-MS instrument and the laser parameters was optimised using a glass standard reference material (SRM 612; NIST), monitoring \(m/z\) 59, 139 and 232, and to maximise sensitivity and limit signal fluctuation to 5% RSD.

3. Results and discussion

3.1. Bulk multi-elemental analysis of tree bark

The total elemental concentrations in tree bark samples for the four locations are summarized in Table 1. The concentration of Al, Fe, Ni, Pb, Sb, V and Zn were examined due to their toxicity and direct association with industrial and motor vehicle emissions.

Elemental concentration in tree bark digests from Darley Dale and Drax were significantly higher than those from Tristan da Cunha. In particular, Pb, V, and Sb were highly enriched in the UK and the Galway samples, indicating that dominant sources of these elements are likely to be a range of anthropogenic emissions (Ebert et al., 2000). The degree of elemental accumulation in Galway is significantly less than those UK test sites. Elements closely associated with lithogenic minerals, such as Ca, Al, Mg and Fe, were examined due to their toxicity and direct association with industrial and motor vehicle emissions.

Elemental concentration in tree bark digests from Darley Dale and Drax were significantly higher than those from Tristan da Cunha. In particular, Pb, V, and Sb were highly enriched in the UK and the Galway samples, indicating that dominant sources of these elements are likely to be a range of anthropogenic emissions (Ebert et al., 2000). The degree of elemental accumulation in Galway is significantly less than those UK test sites. Elements closely associated with lithogenic minerals, such as Ca, Al, Mg and Fe, revealed a greater difference in concentrations between study sites due to variable dust and soil particle loading on the outer bark. Al (50–926 μg g\(^{-1}\)), Fe (49–1440 μg g\(^{-1}\)) and Si (9–428 μg g\(^{-1}\)) were abundant in all bark samples. The highest concentration was detected in the Drax...
samples with Al (926 μg g⁻¹), Fe (1400 μg g⁻¹) and Si (109 μg g⁻¹). These elements have been associated with fly ash pollution, as fly ash contains primarily SiO₂, Al₂O₃, Fe₂O₃, and is enriched in many toxic elements (Be, Zn, As, Cd, Pb, U) (Bohm et al., 1998; Jalkanen et al., 2000). Large volumes of combustion residues, including fly ash, bottom ash, flue gas and desulphurisation sludge produced from the Drax power station may be contributing to this significant local elemental load.

Drax (147 ± 379 μg g⁻¹) and Darley Dale (1070 ± 1760 μg g⁻¹) exhibited high levels of Pb accumulation in the bark samples. In Darley Dale, Pb concentrations were nearly 3 orders of magnitude higher than in the Galway samples (3.2 ± 0.9 μg g⁻¹). This excessive atmospheric Pb loading directly reflects the presence of the Pb refinery in Darley Dale and the coal-fired power station at Drax, along with road transport and other transport and machinery. The effect of atmospheric Pb loading from road transport is thought to be less significant due to dramatic reduction of vehicle emission of Pb as a consequence of ban on use of leaded fuel in European countries since 2000. In recent study, the association of Pb with Ba and Zn has been proposed as a reliable indicator of unleaded fuel and diesel oil powered motor vehicles (Monaci et al., 2000). No statistical correlation between these elements was found for either the Darley Dale or Drax samples in this work.

The concentrations of Mn, Zn, Cu and Fe were also elevated by at least an order of magnitude in the Drax and Darley Dale samples in comparison to the levels in the Galway samples. These elements are often considered to be indicators of anthropogenic emissions such as fossil fuel combustion and incineration along with emission from natural sources (Gao et al., 2002). The mean Mn concentration in the Drax bark (31 μg g⁻¹) was the same as the reported average concentration of Mn in air filters from 20 urban sites in UK (Pacyna, 1986), but both Darley Dale and Galway exceeded this level. An elevated concentration of Mn measured in bark samples could be associated with atmospheric deposition, rather than a result of nutrient uptake (Schiele, 1991). The influence of local industrial activities on their atmospheric condition was therefore highly considered in the case of Drax and Darley Dale study sites.

3.2. Concentration Index factors

The relative contribution of anthropogenic emissions to atmospheric load was calculated using the Concentration Index (CI). The CI is the quantification of the elemental concentration in bark specimens from a study area and was compared with the concentrations in Tristan da Cunha sample:

\[ CI = \frac{C_{\text{Tree bark}}}{C_{\text{Tristan Da Cunha Tree bark}}} \text{Element} \]
where $C_{\text{Tree bark}}$ is the elemental concentration in tree bark at individual sampling locations and $C_{\text{Tristan Da Cunha Tree bark}}$ the elemental concentration in tree bark from Tristan da Cunha. A CI close to unity therefore indicates elements are predominantly from natural sources. The results obtained are shown in Fig. 1.

Enrichment of As, Sb, Cd, Cr, Pb and Zn in the Drax and Darley Dale samples was illustrated in Fig. 1. The degree of elemental accumulation in Galway is significantly less than in the other two study sites. The mean concentration indices of Pb in the Darley Dale (8650) and Drax (1186) are not illustrated in Fig. 1.

3.3. Physico-chemical analysis of airborne particulates

3.3.1. SEM-EDX analysis

Analysis of particle morphologies is based on SEM-EDX observation. The average of 92% of the particles examined on the Darley Dale sample were less than 10 $\mu$m (PM$_{10}$) grain size (equivalent projected area diameter), and of which 69% were constituted of PM$_{5}$ ($<5 \mu$m). Fewer fractions of particle deposits found on Drax samples (68%) were PM$_{10}$ and of those 61% were in the PM$_{5}$ fraction. The Galway samples had a similar particle distribution to those from Darley Dale (PM$_{10}$, 82.5% and PM$_{5}$, 57.7%). Broad ranges of particle sizes found on tree bark are reflection of dispersion efficiency, climate, topography and activities of the area are influencing the elevated PM$_{10}$ particulate deposition in Darley Dale and Galway. Alves et al. (1998) found anthropogenic activities such as combustion processes are responsible for the emission of essentially fine mode particles, as were evidently found in this study.

3.3.2. Chemical composition

In the PM$_{10}$ fractions, the most abundant chemical compositions of the particles are those found naturally in the Earth’s crusts: Si, Al, Fe and Ca. The SEM-EDX examination revealed 9–68% of particles were predominantly of alumino-silicate in composition and many of those particles contained a mix of Ca, Mg, K, S and Fe. The bark samples from each study site revealed its accumulation of alumino-silicate and Fe rich particles and was PM$_{10}$ particle size range with similar physical shape (irregular and crystalline shapes). Indicating their origin was lithogenic sources, whether naturally processed or resuspended (Alves et al., 1998; Ebert et al., 2000). Between 24% and 39% of the deposited particles on the bark consisted of Fe oxide and these were most common in the less than 10 $\mu$m fraction (Fig. 2a). Fe rich particles found on Drax (Fig. 2b) and Darley Dale bark were spherical in shape and some contained Pb and S indicating...
these particles were derived from high combustion sources (Ebert et al., 2004).

The most elevated toxic metal found in particulates was Pb, although it was only detected in the Darley Dale bark surfaces. Relatively high Pb-sulphide concentrations were detected (21%) in the PM$_{10}$ fraction, and 8% of those particles comprised a mixture of Pb and Sb. Detection of Pb, Sb, and Sn in the PM$_{10}$ particles suggests combustion processes caused by anthropogenic activities (e.g. automobile engines and metal smelting), as previously revealed in the bulk elemental analysis (Section 3.1).

The total multi-elemental analysis of bark digests by ICP revealed Pb was detected in every bark sample from each study site, yet SEM analysis showed Pb containing particulates were only determined in the Darley Dale samples. This contrasting result indicates that Pb determined in the digestion were possibly through root uptake or through tissue sorption. Watmough and Hutchison (2003) investigated mobility of $^{207}$Pb through the bark tissues was limited. Ohlström et al. (2000) reported that Pb emitted from power plants, smelter plants and motor vehicles are highly distributed in the finer fractions (2.5 $\mu$m). However, resolution of these fine particles is limited due to instrumental detection limit, hence, characterising particulate deposits by SEM-EDX may have been underestimated. Therefore, more sensitive method utilising semi-destructive method of laser ablation-ICP-MS is used in an attempt to solve this contrasting results.

3.3.3. Microanalysis by LA-ICP-MS

The spatial distribution of elements ($n = 24$) across the bark surface was interrogated using the time resolved profile (Fig. 3). Given that many elements exists naturally in the bark, i.e. C, Mg, K, Ca, Fe and Mn, confirmation of anthropogenic input of these elements and association with the bark tissues were further evaluated by use of statistical test, to understand the relationship between these elements. Pearson’s product moment correlation coefficient, $r$, was calculated.

NIST SRM 612 glass was used as standard to represent a homogenous sample to detect the steady signal responses when the laser parameters were kept constant. Elements homogeneously distributed in the bark samples (e.g. C) should exhibit similar steady-state signal responses to the glass standard. However, rough surface and heterogeneous characteristics of bark will exhibit large signal variances for those elements that are highly sorbed in the bark or as deposited particles. Elevated signal responses absent in the host matrix represent the signals for deposited particles.

Seventeen elements out of 24 analysed by LA-ICP-MS exhibited similar signal responses to those observed for $^{13}$C. These raw signal data showed strong linear association within the lithologically predominant elements (i.e. Si, Al and Mn), with $r > 0.9$ indicating that the elements of interest are widely distributed across the bark surface area, and thus suggesting that these elements were incorporated in bark tissues.

Zn, Cu and Pb in Drax and Darley Dale bark samples were highly correlated with $r = 0.92$–0.95. Interrogation of Drax sample resolved broader peaks for Fe, Pb and Sb, indicating these elements were highly enriched within bark surface (Fig. 3a and b). Darley Dale sample, however, revealed distinctive time-resolved signals for Sb peaks that
coincided with Pb peaks recorded at the start of the analysis. However, extremely high detection of Pb across the bark resulted, diminishing the initial Pb peaks in the graph illustrated in Fig. 3c and d. Numerous sharp peaks of Sb along the bark sample suggests that numerous fine particles containing Sb and Pb were present on the Darley Dale bark sample. Broader Pb peaks detected during the line raster of the Darley Dale bark sample indicates the significant Pb enrichment. On the basis of this data, it is considered that Pb is possibly dispersed across the bark surface and fine particles containing Pb and Sb are deposited above this highly Pb enriched surface. In addition, presence of individual Sb particles is clearly distinguished on the Darley Dale bark sample. This particular association was only found in Darley Dale bark sample with the correlation coefficient value of \( r > 0.9 \). This study confirms SEM-EDX analysis for Drax sample where Pb determined in the bark from the bulk analysis was through surface sorbed Pb or Pb accumulated through root sorption (Watmough and Hutchinson, 2003), while fine particles containing Pb and Sb were detected in LA-ICP-MS and SEM-EDX analysis.

Investigation of Drax and Darley Dale bark samples for the association of Pb to carbonate, hydrous iron, Mn oxides and silicate phases revealed a high degree of association for Fe/Mn phases (\( r = 0.92 \)) and Ca/Mg/Sr phases (\( r = 0.96-0.98 \)), reflecting the effect of local industries on their immediate atmosphere.

LA-ICP-MS analysis of bark demonstrated a rapid scanning capability to evaluate heterogeneity of bark surface and indicate the possible presence of particle deposits. In addition to visual interpretation of time-resolved graphs, determination of correlation coefficient of the elements aided to identify the relationship between the key elements on the bark samples. SEM-EDX and LA-ICP-MS both revealed that tree bark samples from Drax and Darley Dale were strongly interrelated with those heavy metals associated highly with the local industries (e.g. coal-fired power station and Pb smelter).
4. Conclusions

The bulk analysis of tree bark from Darley Dale and Drax revealed that local industrial activities influence significantly the levels of airborne Pb in these locations, with the maximum concentration reaching to 5177 and 1548 µg g⁻¹, respectively. These high levels of Pb were at least 3 orders of magnitude greater than those of a Tristan da Cunha reference sample.

The physico-chemical analysis by SEM-EDX and LA-ICP-MS revealed that many trace elements detected in the bulk analysis were found in the bark tissues. Particulates detected on the bark were predominantly lithogenic in origin; few particles containing Pb were detected on Darley Dale samples.

Current work has demonstrated that bulk elemental analysis of tree bark does not necessarily assess the direct impact of local atmospheric loading. The application of the additional analysis by LA-ICP-MS and SEM-EDX does, however, distinguish between sources of heavy metal accumulation from atmospheric input or from other sources. Further, this study has demonstrated the potential of using LA-ICP-MS to qualitatively analyse elemental composition in the particulate matter. Elemental composition established by the line raster technique correlated highly with the results obtained from SEM-EDX. Using ICP-MS as detector, multi-elemental analysis in trace level concentration was possible.

In addition to visual understanding of elemental association through the time-resolved graph of the line raster, determining the correlation coefficient of these elements has enhanced assurance of their relationships within the bark samples.

Acknowledgements

The author would like to acknowledge John Proctor and Graham Revell (Health and Safety Laboratory Sheffield, UK) for assisting with the SEM-EDX, Professor Cameron McLeod, Dr. Renli Ma and staff at the University of Sheffield for technical advice and sample collection, and NERC for funding throughout this project.

References


Moon, C.H., Braendli, O., Schaeppi, G., Schindler, C.H., Ackermann-Liebrich, U., Leueberger, P.H., Sapuldaia team,
1995. Particulate matter <10 μm (PM10) and total suspended particulate (TSP) in urban, rural and alpine air in Switzerland. Atmospheric Environment 29, 2565–2573.


