

**Multielement Analysis of Tree Bark
with Special Reference to
Measurement and Mapping of Air
Pollution**

Elvio Luiz Schelle

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To Catarina, Gustav, Radmila and Rafaela Schelle

also

*Em eterna honra e gratidão à todos os Peleadores Farrapos, Índios
Guaranys e Lanceiros Negros que tomaram empurrando fronteiras e
defendendo a guapa Pátria Gaúcha (República Riograndense).
-Xiru Elvio-*

Sometimes you can't see the wood for the trees

Abstract

This thesis has the objective to investigate the use of tree bark for monitoring heavy metals in the environment in urban centers and industrial regions in the UK and in the vicinity of gold mining regions in Brazil. In addition to producing multielement concentration data sets a key aspect of the research is to produce new elemental distribution maps for urban regions. EDXRF is the main analytical technique used for analysis but, in the case of Hg, ICP-MS with laser ablation was utilised. Following an introduction about the sources and fates of heavy metals and environmental pollution, subsequent chapters deal with method development (EDXRF and LA-ICP-MS) studies on heavy metals (particularly Hg), survey analysis (Sheffield) and map production.

Chapter 1 is an overview of environmental contamination by heavy metals from human activities (industrial, agricultural, mining, power generation) and natural sources (volcanoes and fumaroles) and their impact on human health. Analytical techniques and the production of geochemical maps are discussed followed by the aims of research.

Chapter 2 refers to the development of techniques for sampling, sample preparation and analysis by Energy Dispersive X-Ray Fluorescence (EDXRF). Samples from many locations throughout the world including diverse points across the UK were analysed. EDXRF was shown to be a useful new approach for multielement analysis of tree bark. The use of pressed pellets provided a rapid and simple method for elemental measurements in solid samples and avoids loss of volatile elements during acid digestion.

The results of survey analysis show the clear potential for apportioning elements between sources.

Chapter 3 investigates a new method for Hg measurement using pressed pellets made from tree bark. Survey samples from diverse environments across Brazil and around a chlor-alkali plant in the UK were investigated for total and particulate Hg. LA-ICP-MS provides a reliable alternative method by which to determine Hg in tree bark (pressed pellets) and also for identifying particulate Hg in raw bark. High levels of Hg (6.5 µg/g) were found near gold smelters in Brazil. In the UK, levels up to 2.04 µg/g were found in the vicinity of a chlor-alkali plant. The methodology developed to analyse pressed pellets and raw bark by LA-ICP-MS provided an alternative and reliable strategy for Hg determination and speciation.

Chapter 4 presents a multielement survey of Sheffield using tree bark samples and EDXRF analysis. A total of 642 samples were collected from woods, parks, near steelworks and areas of intense traffic over an area of 88 km². Three species of trees (Sycamore, Oak and Cherry) were preferentially selected and analysed for 19 elements. Data from West Ireland served as background concentration levels. Interesting hot spots of pollution were found and significant correlations between heavy metals were identified. Distribution maps for Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Ag, Cd, Sn, Sb, Ba, Hg and Pb analogous to those produced by the British Geological Survey from soils and stream sediments were produced for Sheffield using the survey data. The maps clearly show points of heavy metal pollution in the industrialised regions of Sheffield. A map showing Hg pollution in the Staveley area in the vicinity of a chlor-alkali plant was also produced.

Chapter 5 gives the concluding remarks and general information gained from the research. Suggestions are made about the possible future uses and applicability of the developed technique and how it can be of use to city councils for air quality monitoring as a complementary method to conventional ones. The maps produced can be compared with BGS soil maps and could be more meaningful in urban areas. The data and maps could also be beneficial for town planning and public health issues.

Declaration

I declare that this thesis, submitted in fulfillment of the degree of Doctor of Philosophy at the University of Sheffield, is my own work. It has not been previously submitted for a degree at this or any other university.

Elvio Luiz Schelle
The University of Sheffield
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