ELSEVIER

Chemosphere 60 (2005) 1293–1307

CHEMOSPHERE

www.elsevier.com/locate/chemosphere

Trace element accumulation in the moss *Hypnum cupressiforme* Hedw. and the trees *Quercus ilex* L. and *Pinus halepensis* Mill. in Catalonia

Jordi Sardans *, Josep Peñuelas

Unitat d'Ecofisiologia CSIC-CEAB-CREAF (Center for Ecological Research and Forestry Applications), Edifici C, Campus Universitat Autònoma de Barcelona, Bellaterra 08193 (Barcelona) Spain

Received 15 July 2004; received in revised form 27 November 2004; accepted 18 January 2005
Available online 21 March 2005

Abstract

We studied trace element accumulation in the moss *Hypnum cupressiforme* and the widely distributed Mediterranean trees *Quercus ilex* and *Pinus halepensis* located at increasing distances from the Barcelona Metropolitan Area. *Hypnum cupressiforme*, *Quercus ilex* and, to a somewhat lesser extent, *Pinus halepensis*, have proved to be adequate as possible accumulative monitoring species in relation to trace elements pollution. No significant effects of crown orientation were found. One-year old leaves generally accumulated more trace elements than current-year leaves. All the studied trace elements showed greatest concentrations in the Barcelona Metropolitan Area, with lead, cadmium and arsenic concentrations being especially high. In general, trace element concentrations in biomass were similar or higher than the values reported from other Mediterranean urban areas of Europe. The top soil-layer concentrations were also higher in the Barcelona Metropolitan Area indicating the existence of mechanisms of atmospheric deposition and/or concentration in the soil. The lower values of Pb of airborne origin relative to other elements such as Cd, Cu, Zn and Sb suggest that traffic exhausts are not the only important focus of pollutants in this area. The results of biomass concentrations and of enrichment factor of biomasses respect to bedrock and soils show that atmospheric inputs account for the higher trace element concentrations in the Barcelona Metropolitan Area.

Keywords: Arsenic; Atmospheric deposition; Bedrock; Cadmium; *Hypnum cupressiforme*; Lead; *Pinus halepensis*; *Quercus ilex*; Soil; Trace elements

1. Introduction

The presence of trace elements in ecosystems is due to both natural and anthropogenic causes. While natural forms are usually found in relatively low concentrations, in recent decades the number and intensity of anthropogenic sources such as rubbish tips, smelter stacks, waste incineration, fertilizers, vehicle emissions, agricultural waste and sewage sludge have increased overall environmental trace element concentrations (Bargagli, 1998; Koch and Rotard, 2001).

Accumulation of trace elements in the stand biomass over large areas and during long periods of time causes

* Corresponding author. Tel.: +34 93 581 18 77; fax: +34 93 581 41 51.
E-mail address: j.sardans@creaf.uab.es (J. Sardans).

0045-6535/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2005.01.059

chronic damage to living organisms. Accumulative biomonitors are indispensable for evaluating long range tropospheric transport and deposition of trace elements on regional and global scales. Over the last 20 years mosses, lichens and higher plants have been used as biomonitors and bioindicators (Loppi and Bonini, 2000; Fernández and Carballeira, 2002) for drawing reliable pollution maps of the areas to which these persistent pollutants have been transported, but where instrument recordings would be impossible or at best very difficult (Thomas and Schunke, 1984; Steinnes et al., 1992).

Among plants, bryophytes are the most extensively used biomonitors and bioindicadors of trace element pollution (Herpin et al., 1997; Weiss et al., 1999; Fernández et al., 2000; Carballeira et al., 2002). Due to their lack of root systems, mosses are dependent on aerial uptake. This trait, together with their lack of cuticle and epidermis, facilitate chemical penetration and the absorption of transitory fluctuations in levels of chemicals in the environment, thereby converting bryophytes into useful trace elements biomonitors, and bioindicators. In fact, many surveys performed over the last 30 years have shown that a number of species of cryptogams can be used to detect quite quickly and at a reasonable cost trace element deposition in terrestrial ecosystems due its characteristics that permits accumulate the trace elements in its tissues.

The analysis of suitable accumulative biomonitors is the only possible approach to study the trace element pollution, especially in remote areas. Some species of bryophytes, lichens and vascular plants have very wide distributions and may be used for establishing background reference levels of persistent atmospheric pollutants that are already distributed at regional or wider scales (Bargagli et al., 1995; Bargagli et al., 2002; Fernández et al., 2002). Unfortunately most reported data of trace elements in plants refer to unwashed moss, lichens and vascular plants, comprising the inner plant tissues plus soil dust of surface (Bargagli, 1995). Only analytical results from samples without significant soil particles contamination in theirs surfaces are significant data in order to gain knowledge on the biological impact of pollution. The trace element concentrations in inner plant tissues can have soilborne or airborne origin. Plants are fairly sensitive to the presence of trace metals given their uptake capacity through roots from soils or by direct contact, mainly between leaves and air or water. Plants have trace element uptake capacity from soils due to mechanisms such as ion exchange (Crist et al., 1996) and chelation between macromolecules and bioavailable trace elements ions. It has been estimated that in rural sites from 10 to more than 60% of lead and cadmium of inner tissues in several plant species can be attributed to atmospheric deposition. Even in rural areas atmospheric deposition contribute to the element content of inner plant tissues (Harrison and Johnston, 1987).

In this study we have evaluated the use of a common moss and some common vascular plants as environmental accumulative bioindicators of trace element pollution in different areas of Catalonia. Catalonia is an industrial region situated in the north-west of the Mediterranean Basin, whose population is largely urban and asymmetrically distributed through the territory being concentrated in metropolitan areas, above all in the Barcelona Conurbation. In this region, industrial areas lie side-by-side zones of intensive agriculture, thereby posing a risk of trace element inputs into the environment. The large number of cars, along with widespread heavy industrial complexes (iron and steel, chemical, electronic and energy production) and intensive land-use (fertilizers, manure, the use of pig slurry), are all elements and activities which have existed for a long time in Catalonia and have all had profound and prolonged effects on the environment. Catalonia can also boast large tracts of forest with little industrial presence that facilitates the study of the extent to which pollutants emitted by urban areas have been accumulated in the landscape. On the other hand, Catalonia has not clear patterns of wind direction trait that prevents the asymmetrical distribution of pollutants since source points.

The bryophyte *Hypnum cupressiforme* was selected as a bioindicator of trace element pollution due to its wide-ranging distribution and because of the abundant data existing in the literature on this species, which is widely used in trace element biomonitoring and in bioaccumulating studies (Bargagli et al., 2002) and thus is ideal for making comparisons with other areas of Europe. The tree species *Quercus ilex* and *Pinus halepensis* were selected to evaluate the level of trace elements accumulation in plants for a number of reasons. They are both widespread in urban and rural areas of the Mediterranean basin and currently they are the most frequent tree species in the Mediterranean forests of the north-west of the Mediterranean Basin (Gracia et al., 2004). Furthermore, *Quercus ilex* has already been used for screening trace elements distribution in other Mediterranean Countries, principally in Italy, and has been shown there to be a useful biomonitor of trace element deposition in various urban environments (Valerio et al., 1989; Alfani et al., 1995; Monaci and Bargagli, 1997). Its long-lived leaves, the easy identification of the leaf and needles age cohorts, and its widespread occurrence in urban areas and natural ecosystems make these species adequate tools for trace elements bioindicator studies.

The knowledge of the spatial and temporal deposition patterns and concentration levels of trace elements in wild plants should be useful for environmental management and will at least provide information on the ecological impact of human activities that liberate trace elements into the atmosphere, and on their temporal permanence in the natural ecosystems. We aimed (i) to determine the current levels of trace elements in the