Metal pollution in Spanish terrestrial ecosystems during the twentieth century

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Abstract

We show here additional biological evidence of the alteration in global biogeochemistry by human activities during the twentieth century. The mineral concentration of herbarium specimens of 24 species of vascular plants and three species of bryophytes collected in North and East regions of Spain have substantially changed throughout the twentieth century. While V, a proxy tracer of oil pollution, exponentially increased in the last decades, other metals such as Cr, Ba, Sr, Al, Fe, Pb, Cd and Ti increased up to 1960–1970 and started to decrease in 1985–1995, when environmental legal regulations started to be effective. Multivariate principal component analysis showed an overall change in plant elemental concentrations throughout the different decades of the century and a clear separation of vascular plants and bryophytes. Likely important consequences for ecosystem structure and functioning and even for human health may be expected from these changes in mineral concentration. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Mankind has become the most important factor in altering global biogeochemistry of metals. Global anthropogenic heavy metal inputs to ecosystems through air, water and soils have increased substantially worldwide over the last century (Nriagu and Pacyna, 1988; Nriagu, 1996) as described in studies on lake sediments (Battarbee et al., 1985), peats (Espi et al., 1997), ice from Arctic, Antarctic and Alpine glaciers (Boutron et al., 1991; Hong et al., 1994, 1996) or annual bands of corals (Guzmán and Jarvis, 1996). Material from herbariums and museums have been also used to carry out retrospective analyses showing the evolution of environmental pollution by metals and other pollutants in the past decades or even past centuries (Rühling and Tyler, 1969; Jones, 1987; Markert and Thornton, 1990; Peñuelas and Matamala, 1990; Jones et al., 1992; Bacon et al., 1996; Herpin et al., 1997; Weiss et al., 1999; Peñuelas and Filella, 2001). Heavy metal ions such as Cu, Zn, Mn, Fe and Ni are essential micronutrients for plant metabolism but when present in excess, these, and non-essential metals such as Cd and Pb can become extremely toxic. The two latter elements are also of greatest direct concern to human health (EEA, 1998). The potential for harm of these heavy metals is increased as a result of potential bioaccumulation in edible plants.

Because of their capacity to act as efficient interceptors and accumulators of chemicals, plants are widely used as passive biomonitor in urban and rural environments (Jones et al., 1992; Market, 1993; Monaci and Bargagli, 1997). Among plants, bryophytes are being increasingly used as biomonitor of airborne chemicals such as heavy metals (Herpin et al., 1997; Weiss et al., 1999). Since they lack a root system, they are dependent
on the environmental atmosphere to which they are exposed for the uptake of chemical substances. Moreover, they lack a cuticle and epidermis and an active mechanism to mobilise chemicals. These traits facilitate chemical penetration and the integration of temporal fluctuations of chemicals in the environment. Bryophytes are moreover known to have a high metal binding capacity (Gstoettner and Fisher, 1997).

We present here evidence of significant changes in plant chemistry in response to the huge input of anthropogenic metals into the biosphere by analysing the mineral concentrations in herbarium specimens of 24 species of vascular plants and three species of bryophytes collected throughout the twentieth century in North and East regions of Spain.

2. Material and methods

2.1. Herbarium specimens

We studied the following species of vascular plants: Acer opalus, Arbutus unedo, Artemisia verlotiorum, Cistus albidus, Erica multiflora, Fraxinus excelsior, Hypericum perforatum, Juniperus oxycedrus, Lonicera implexa, Phillyrea angustifolia, Pinus halepensis, Pinus sylvestris, Plantago major, Populus alba, Prunus lusitanica, Quercus cocifera, Quercus ilex, Rhamnus alaternus, Rhododendron ferrugineum, Rosmarinus officinalis, Salix atrocinera, Thymus vulgaris and Ulmus glabra and the following species of bryophytes: Grimmia laevigata, Hypnum cupressiforme, and Pleurochaete squarrosa. Leaves had been stored in the herbaria of the “Unitat de Botànica de la Facultat de Farmàcia de la Universitat de Barcelona” and the “Unitat de Botànica de la Universitat Autònoma de Barcelona”. The studied herbarium specimens were collected in Spain (mostly Northeast rural regions). The older specimens had been fumigated with DDT and most specimens had been submitted to temporary freezing temperatures as conservation procedures. We sampled material from four different decades. For the last one we sampled specimens already collected and stored for more than 5 years to avoid possible initial processes of decomposition and make all samples comparable. The same locations and seasons for each species were sampled throughout the period of study. When no samples from the same geographical location could be found throughout the century, the closest possible geographical location was sampled. Leaves from the same terminal position of the herbarium specimens were analysed to avoid, as much as possible, variability due to leaf age and position and to light exposure during growth. Analyses from 1 to 8 different herbarium specimens were conducted for each vascular plant species at each sampling decade. Analyses from 1 to 9 different herbarium specimens were conducted for each bryophyte species at each sampling decade. Each analysis was conducted with 3–6 bulked leaves (40–60 for bryophytes) of the same stage of development. It must be noticed that while foliage from vascular species represents a single year, the bryophyte foliar material is from several years due to bryophytes slow growth. The drying procedure was similar for all specimens. They had been herbarium pressed when collected, and prior to the current analyses they were freed by hand of extraneous materials adhered to the leaves by using plastic tweezers and disposable plastic gloves, washed with deionised water, oven-dried at 60 °C to constant weight (dry weight), and ground to a fine powder in a mill.

2.2. Elemental analysis

Leaf concentrations of P, K, S, Ca, Mg, Si, B, Al, Fe, Na, Mn, Zn, Pb, Ti, Sr, Ba, Cd, Co, Cu, Mo, Ni, V and Cr were measured on sub-samples (about 100 mg) of ground leaves. Samples were digested in a microwave Whirlpool AVM 635 using open fluorinated ethylene propylene flasks (Nalge Company, Rochester) with an acid solution of 2:1 nitric and 60% perchloric acids. Once samples were efficiently oxidised (0.5 cm³ remaining), they were diluted with 20 ml of 3% perchloric acid. Flasks were stoppered and shaken by hand for thorough homogenization. The sample solution was poured into a polystyrene sample cuvette, placed in an autosampler carousel and analysed for the above-mentioned 23 elements by inductively coupled argon plasma emission spectrometer (ICAP–AES) Polyscan Thermo Jarrel ASH Model 61 E. Quality control was ensured by a reference sample every 10 samples analysed. Readings were accepted when reference samples (Pine needles, NIST 1575) were within a 5% range of known values for macroelements and 10% range for microelements. Operational blanks consisted of 2 ml of the acids reacted without any sample material.

2.3. Data treatment and statistics

Statistical analyses were conducted using a one-way ANOVA with sampling decade as the main effect, and using the Tukey’s significant difference at the 0.05 level between species means for the periods 1920–1930, 1940–1950, 1960–1970 and 1985–1995, after testing for normality and homogeneity of variance. Changes relative to 1920–1930 values for each species of vascular plant and to 1940–1950 values for each species of bryophyte were used in the data analysis to standardise the variability due to species genetic differences and to focus on the environmental variability. Regression models of the studied variables across the decades were conducted with species mean values, and therefore with values having known associated variance. Thus where a model
I regression was not strictly appropriate, a model II regression with the reduced major axis method was used (Sokal and Rohlf, 1995).

Multivariate principal component analyses were conducted with the different element concentrations as variables. They were conducted on both the matrix of correlations and the matrix of covariance, i.e., without and with correction by mean, respectively. Statistical analyses were conducted using the statistical program package SYSTAT 5.2 (SYSTAT, Evanston, IL, USA).

3. Results and discussion

We found significant and progressive increases in vanadium (V) concentrations both in bryophytes and vascular plants (Fig. 1). Vanadium concentrations of vascular plants in 1985–1995 were 350% greater than in 1920–1930, and they also were 72% greater in 1985–1995 than in 1940–1950 in bryophyte species (Fig. 1). Vanadium is primarily released into the global environment through the combustion of fossil fuels both from industry and from domestic and electric utilities (Nriagu and Pacyna, 1988; Nriagu, 1996). Vanadium is thus a proxy tracer of increasing oil pollution in Spanish terrestrial ecosystems. This increase seems quite global as it has also been found in other natural archives like coral reefs of oil polluted areas such as the Caribbean sea (Guzmán and Jarvis, 1996), and also in lake sediments of apparently pristine areas such as Finland (Simola et al., 1991).

Zn concentrations also increased both in bryophytes and vascular plants (68% and 24% respectively, Fig. 1). The main source of Zn emissions is Cd–Zn production (Nriagu and Pacyna, 1988). Cd concentrations of vascular plants also increased over the last century almost 300% in the last decades relative to the first ones (Fig. 1). Cd is used in paints and plastics, as well as in batteries. The main sources of its emissions are municipal waste incineration, non-ferrous metal production, iron and steel production, and fossil fuel combustion. These Cd sources act mainly as area sources, making it generally more widely dispersed than other heavy metals with more important point sources.

While V concentrations started to increase slightly in the 1960s and increased exponentially in the later decades, Cd and Zn began to increase by the beginning of the century, although Cd concentrations in bryophytes began to decrease in the later decades (Fig. 1). The maximum metal concentrations in 1960–1970, and subsequent decreases in later decades were also found in vascular plants for Cr, Ba and Sr and in bryophytes for Cd, Al, Fe, Na, Pb, Ba, and Ti (Figs. 1 and 2). A similar pattern was found for Sr, Al, Zn and Cu in a previous study that we also conducted in Spanish herbaria (Peñuelas and Matamala, 1993), in a study of plant Pb and Cd concentrations conducted in England (Jones et al., 1992) and in several other studies such as that of Herpin et al. (1997) conducted on herbarium moss material from Germany. There is also sedimentary evidence of similar profiles for several of these heavy metals such as Cu, Pb, Zn and Cd in the NE of USA, Switzerland and Greenland (Boutron et al., 1991; Owens and Cornell, 1995; Candelone et al., 1995; von Gunten et al., 1997). The increases early in the century correlate to the growth of industrial activities, whereas the decrease after 1960–1970 seems caused by the introduction of more stringent restrictions and improved methods of preventing releases of pollutants to the environment, e.g., those that concern the use of unleaded gas. For
example, European current emissions of Pb and Cd are about 65% below the peak levels of 1965 (EEA, 1998). Bryophytes seemed better suited to biomonitor these changes (Figs. 1 and 2) because of their dependence on aerial sources.

Although the concentrations of the other analysed elements (Mo, Pb, Ti, Fe, Al, Mn, Cu, Na, Ni, Mg, K, Ca, Co, S, and P in vascular plants and Ca, Mg, Sr, Cr, Mn, Co, Cu, Mo, and Ni in bryophytes) did not significantly change throughout the century, although there is a need for closer studies on mechanistic relationships between the accumulation of the different elements and the environmental conditions, and although the amount of metals potentially available to plants in any given locality depends on various atmospheric and micro-environmental factors that can result in considerable spatial variation (Market, 1993), it is clear that there was an overall change in plant elemental concentrations throughout the different decades of the century as indicated by multivariate principal component analysis. The principal components 1 and 5, based on the correlation matrix of the different element concentrations, accounted for 32% and 5% of the total variance, respectively. The first principal component clearly separated vascular plants from bryophytes while the fifth principal component allowed separation of the different decades (Fig. 3) showing different overall plant elemental concentrations in the different periods of the twentieth century. Thus, the historical process of industrialization can be followed by the results for heavy metal pollution obtained from herbarium samples dating from the different decades of twentieth century.

Human alteration of metal cycles represents an ongoing global change of which we are certain. The plant chemical changes presented here constitute new evidence of this alteration at the regional level. They also indicate that added anthropogenic metals are retained, at least in part, in the terrestrial ecosystems of rural regions of Spain which, although not pristine, are not immediate to very highly industrialised or urbanised areas. Important consequences on ecological processes at all levels of organisation, from single organisms to the globe may be foreseen, including, possible effects on human health, unless legal regulations are also effective with these metals whose concentrations are still increasing.
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