Chemosphere 76 (2009) 91–97

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Changes in total concentrations and assessed background concentrations of heavy metals in moss in Lithuania and the Czech Republic between 1995 and 2005

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ARTICLE INFO

Article history:
Received 21 July 2008
Received in revised form 27 January 2009
Accepted 6 February 2009
Available online 6 March 2009

Keywords:
Atmospheric deposition of metals
Lognormal distribution
Variation tendencies
Background concentrations
Effects of local pollution sources

ABSTRACT

Data on concentrations of heavy metals (As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, V and Zn) in moss collected on the lightly industrialized territory of Lithuania and on the highly industrialized territory of the Czech Republic in 1995, 2000 and 2005 is used to separate the background and anthropogenic contributions to heavy metal concentrations in moss. The distribution of the concentration logarithms allowed us to determine a background mode, and to estimate the background concentration of heavy metals from this mode. The method was then applied for an estimation of the contribution of local sources to the total pollution level in both countries. The average concentrations and the background modes of heavy metals in Lithuania and in the Czech Republic were very similar, except in the case of vanadium, where the background concentration was higher in Lithuania than in the Czech Republic. For most elements, the background concentration in moss had a decreasing tendency in Lithuania and in the Czech Republic between 1995 and 2005, though the concentration of Cu and Hg increased in Lithuania. The variability of chromium concentration in moss differed from the remaining investigated elements in the Czech Republic, and it was expressed as a bimodal lognormal distribution. This variability may be due to simultaneous contamination of moss by chromium from soil and from industrial sources of pollution.

1. Introduction

The methodology for using moss for biomonitoring the atmospheric deposition rates of heavy metals was first introduced in Sweden (Rühling and Tyler, 1969). Terrestrial moss bio-indicators accumulate nutrients and heavy metals from atmospheric deposition almost entirely through the surfaces of their above-ground parts. Metals are effectively adsorbed on pectins and on the cell structures of 1–3-year-old moss body segments. For this reason, the concentrations of metals in mosses correlate closely with their atmospheric deposition loads over a given period of time. Many local, national and international moss surveys have been carried out repeatedly in slightly and heavily contaminated areas in northern and central Europe (e.g., Grodzinska, 1978; Berg et al., 1995, 1996; Brown and Brumelis, 1996; Kubin and Lippo, 1996; Rühling et al., 1996; Berg and Steinnes, 1997; Čeburnis et al., 1997, 1999a; Kvietkus et al., 1997; Sucharová and Suchara, 1998, 2004a,b; Čeburnis, 1999; Brumelis et al., 2000). However, some experts call for more effective utilization of the biomonitoring campaigns to reveal the impacts of anthropogenic pollution sources on the environment (Markert et al., 2003, 2008).

Heavy metals find their way into moss from natural geogenic and anthropogenic industrial sources operating locally or from a great distance (Čeburnis et al., 1999b). As environmental scientists, we want to find a method that will make a reliable distinction in moss indicators between natural and anthropogenic contributions of metals, and between contributions of metals coming from local and distant pollution sources. If this can be achieved, biomonitoring surveys will become a highly effective tool for checking environmental pollution.

A lognormal frequency distribution law for the determined concentrations can be used for evaluating the tendencies and the reasons for changes in the background metal pollution of moss. Lognormal distributions (with two independent parameters) play an essential role in human and ecological risk assessments (Ott, 1990, 1995). Many physical, chemical, biological, toxicological and statistical processes tend to create random variables that follow lognormal distributions. For example, the physical dilution of one material with another material, e.g., the mixing of emitted pollutants in the atmosphere or in the surface water in a bay, tends to create non-equilibrium concentrations with lognormal frequency distributions. Respecting the conditions of the Central Limit Theorem, the mathematical process of multiplying a series of random variables will produce a new random variable, which tends to be lognormal in its character regardless of the distributions of the starting variables. Finally, lognormal

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doi:10.1016/j.chemosphere.2009.02.009

distributions are self-replicating under multiplication and division, i.e., the products and quotients of lognormal random variables are themselves lognormal (Limpert et al., 2001; Hadley and Toumi, 2003). Lognormal distributions of elements were adopted for optimizing moss sampling (Aboal et al., 2001) and for determining the background concentration of heavy metals in moss (Šakalys et al., 2004).

The aim of this work was to determine the background values of the concentrations of heavy metals in moss by using the dependence of the concentration distribution density on the concentration value to evaluate the contribution of local sources to the total metal pollution level in the territories of Lithuania and the Czech Republic; and to define tendencies in the changes in the background concentration of heavy metals in moss by comparing the moss analytical data from 1995, 2000 and 2005.

The moss data sets acquired using a standardized methodology in the European biomonitoring campaigns in Lithuania and the Czech Republic – substantially differently industrialized countries – provide plentiful material for comparative studies and for testing the suggested method for estimating the background concentrations of heavy metals in mosses exposed to the effects of differently polluted atmospheres.

2. Materials and methods

2.1. Collection and analyses of moss samples

The moss samples were collected and analyzed in 1995 in the framework of the second European moss survey (Rühling and Steinnes, 1998), and in 2000 and 2005 in the framework of the UN-ECE ICP-Vegetation international biomonitoring programmes (for details see, e.g., http://www.unece.org/env/wge/vegetation.htm and Buse et al., 2003).

In Lithuania, 133 moss samples were collected in 1995, 138 samples in 2000 and 146 samples in 2005. In the Czech Republic, 195, 250 and 283 moss samples were collected in 1995, 2000 and 2005, respectively. The sampling procedure is described in greater detail in Čeburnis (1999) and in Čeburnis et al. (1999b). Samples were collected of two moss species, *Hylocomium splendens* and *Pleurozium schreberi*, which are the most widespread species on the Lithuanian territory. The collection density was not lower than two samples per 1000 km^2. Most of the samples (90%) in the Czech Republic comprised *P. schreberi* moss species, while *Scleropodium purum* (6%), *Eurhynchium angustirete*, *Brachythecium rutabulum* and *Brachythecium salebrosum* made up the rest of the collected samples. The density of sampling was two samples per 800 km^2. To avoid possible local pollution, moss was collected at a distance of about 300 m from main roads and settlements, and at a distance of 100 m from minor roads and farmlands. An area of 50 × 50 m was chosen for gathering one collective sample, and from this area moss subsamples were taken at 5–10 sites. The sampling plots were situated in the middle of canopy gaps to avoid throughfall effects. Three upper moss body segments aged 1–3 years were taken for analysis.

The analysis of heavy metals in moss collected in Lithuania was performed at the Institute of Physics in Vilnius. The moss samples were dried at room temperature for about a week and then dried at 40 °C for 24 h. About 1.5 g of dry moss was weighed into ceramic crucibles, with 15 mL of high purity concentrated nitric acid poured in. The crucibles were covered with concave glass and heated for 3 d, gradually increasing the temperature from 40 °C to 115 °C until about 5 mL of solution was left. The digestates were quantitatively converted to volumetric flasks and diluted with deionized water to 50 mL. The concentration of the metals was measured using the Zeeman 3030 Atomic Absorption Perkin–Elmer spectrophotometer. The modifiers ($NH_4H_2PO_4 + Mg_2NO_3$) and $PdNO_3$ were used for determining Pb, Cd and As, respectively. The analytical methods used are described in greater detail in Čeburnis (1997, 1999) and Čeburnis et al. (1999b). Mercury determination was performed using the GARDIS-3 Atomic Absorption Mercury Analyzer (Kvietkus et al., 1997). The laboratory kept to all elementary internal and external quality assurance rules. NIST 1575 and NIST 1547 standard reference materials were used to check the calibration procedure. Comparisons of the determined element concentrations in the moss standards (M1, M2, M3, H1, H2, H3) were presented, for example, in Čeburnis (1997) and Steinnes et al. (1997). The same standards were used during the biomonitoring campaigns in 2000 and 2005.

Approximately 0.5 g of dry (40 °C) homogeneous samples was differentially weighed in Teflon PFA pressure-relief type digestion vessels in the laboratory at Pruhonice. Digestion of the samples in nitric acid (Merc, suprapure) and hydrogen peroxide (Merc, suprapure) was performed in a CEM (MARS 5) assembly. After digestion, the samples were diluted to the defined volume of 50 mL with deionized water. The heavy metal concentrations in the samples were determined by means of AAS, Spectr 300A VARIAN and ICP-MS, PE Elan 6000 in 1995, in 2000 and in 2005. The contents of mercury were measured directly in the powdered moss samples, in parallel, from three weights, using an AMA 254 (Altec) Mercury Analyzer. Standard reference NIST Pine Needles 1575, AQCS Hay V-10, CRM Sea Lettuce 279, CRM Plankton 414 and others, and international interlaboratory moss standards S3, DK2, DK3, M2 and M3 were analyzed in parallel to control the analytical results in the biomonitoring campaigns in 1995, 2000 and 2005. The analytical results for the reference materials, the values of the detection limits of the methods and the share of crucial steps of the biomonitoring procedure in the uncertainties of the analytical results are available, for example, in Sucharová and Suchara (1998, pp. 40–41 and 2004c, p. 23) and in Sucharová et al. (2008, pp. 13–14 and 95–96).

2.1.1. Introduction of mathematical equations and their application

The lognormal concentration distribution is described by the following equation:

$$p(\ln C) = \frac{1}{\sigma_{\ln}\sqrt{2\pi}} e^{-\frac{(\ln C - \ln C_m)^2}{2\sigma_{\ln}^2}}, \quad (1)$$

where $p(\ln C)$ is the dependence of the distribution probability density on $\ln C$, C is the argument (in our case the numerical value of the heavy metal concentration in moss), C_m is the value corresponding to the $p(\ln C)$ maximum of the argument and $\sigma_{\ln}$ is the standard deviation of $\ln C$.

The above equation can be expressed as:

$$p(C) = \frac{1}{\sigma_{\ln} C\sqrt{2\pi}} e^{-\frac{(\ln C - \ln C_m)^2}{2\sigma_{\ln}^2}}, \quad (2)$$

where $p(C)$ is the dependence of the distribution probability density on C.

The average of the concentration is:

$$\overline{C} = C_m \exp\left(\frac{\sigma_{\ln}^2}{2}\right). \quad (3)$$

The standard deviation of the concentration C is:

$$\sigma^2 = C_m^2 \cdot e^{\sigma_{\ln}^2}(e^{\sigma_{\ln}^2} - 1). \quad (4)$$

Eqs. (3) and (4) show the relation between the parameters of the lognormal distribution when the arguments are C and $\ln C$.

When processing the experimental data, the whole range of investigated concentration logarithm values was divided into