Journal of Hazardous Materials 275 (2014) 72–78

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Use of a moss biomonitoring method to compile emission inventories for small-scale industries

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HIGHLIGHTS

- DSSP method useful for identifying pollution patterns around industrial facilities.
- In the same industrial sector there is no common pattern of pollution.
- Biomonitoring is a tool to compile industrial emissions inventories.

ARTICLE INFO

Article history:
Received 28 December 2013
Received in revised form 25 April 2014
Accepted 27 April 2014
Available online 2 May 2014

Keywords:
Air quality
Cluster analysis
Metals
Pseudoscleropodium purum

ABSTRACT

We used a method of detecting small-scale pollution sources (DSSP) that involves measurement of the concentrations of elements in moss tissues, with the following aims: (i) to determine any common qualitative patterns of contaminant emissions for individual industrial sectors, (ii) to compare any such patterns with previously described patterns, and (iii) to compile an inventory of the metals and metalloids emitted by the industries considered. Cluster analysis revealed that there were no common patterns of emission associated with the industrial sectors, probably because of differences in production processes and in the types of fuel and raw materials. However, when these variables were shared by different factories, the concentrations of the elements in moss tissues enabled the factories to be grouped according to their emissions. We compiled a list of the metals and metalloids emitted by the factories under study and found that the DSSP method was satisfactory for this purpose in most cases (53 of 56). The method appears to be a useful tool for compiling contaminant inventories; it may also be useful for determining the efficacy of technical improvements aimed at reducing the industrial emission of contaminants and could be incorporated in environmental monitoring and control programmes.

1. Introduction

The high degree of industrialization that has taken place in the last century has led to increased emissions of contaminants to the atmosphere. This has led to the search for methods of characterizing and monitoring such emissions, with the aim of minimizing the environmental impact of industrial processes. Biomonitoring of metals and metalloids with terrestrial mosses is recognised as a suitable tool for this type of control.

Atmospheric emission of contaminants can affect small or large areas of land, depending on the source of contamination. Emissions derived from large factories, densely populated areas and agricultural activities generate large-scale contamination processes. Emissions derived from small and medium-sized factories generate small-scale contamination processes. To date, research in which bryophytes are used to study atmospheric contamination by metals and metalloids has addressed both large- and small-scale contamination. Studies of large-scale emissions have focused on evaluating patterns of contamination in sampling networks previously established for large areas, at densities of approximately 1.5 sampling sites 1000 km^{-2} [1]. Research involving small-scale contamination has centred on sources of emission that affect restricted areas [2–5], with the sampling effort involving more than 1 sampling site 1 km^{-2}. However, study of the contaminants produced by various dispersed sources of emission that each generates small-scale contamination over a large area is complicated. When a low

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http://dx.doi.org/10.1016/j.jhazmat.2014.04.061
0304-3894/© 2014 Published by Elsevier B.V.

density of sampling sites is used in a large area, many of the emission sources may be missed if there are no sampling sites nearby [6]. However, studies involving high densities of sampling sites aimed at capturing each dispersed source of contamination are not viable from economic or operational points of view.

One possible solution to this problem is to use the method proposed by [7] for detecting small-scale pollution sources (DSSP). This method enables the contaminants emitted by such sources to be detected by using a very small number samples. The method is based on the shape of the curves that relate the concentrations of metals and metalloids in moss tissues to the distance from the source of emission [2,3,8–12]. According to this relationship, there will be a large difference between the concentrations of the contaminants in a sample of moss collected from close to a source of contamination and in another collected at some distance from the source. However, it is essential to confirm that the difference is actually due to contaminant emissions and not simply to the natural variability in the concentrations of elements in the moss. To ensure this, we can use reference distributions of the differences in the concentrations of each element established using paired sampling points in uncontaminated areas [7]. If the observed differences do not belong to the reference distributions, we can infer that the source is contaminating the surroundings.

The DSSP method is a useful tool for compiling emission inventories such as the European Pollutant Release and Transfer Register (E-PRTR; http://prtr.ec.europa.eu/). This register implements the UNECE (United Nations Economic Commission for Europe) PRTR Protocol of the Aarhus Convention to facilitate access to information about the contamination emitted by the main industrial processing plants in the European Union, Iceland, Norway, Lichtenstein, Serbia and Switzerland. Thus, it includes contaminant emissions to the atmosphere, water and soil of approximately 28,000 factories included in 65 different sectors. However, in most cases the available data are restricted to estimated or calculated values as the number of factories involved is so large that it is not feasible to measure all of the emissions directly. Moreover, in compiling this type of official register and in previous studies of the presence of contaminants in the environment, researchers have tended to associate the emission of certain types of contaminants with particular industrial processes and contaminants, without considering whether all industrial plants dedicated to the same activity emit the same contaminants. The DSSP method may therefore be useful for characterizing the emissions from different types of industries and comparing the results with the data included in the official registers.

However, there are certain limitations to the proposed method, as the following conditions must be fulfilled for correct application of the technique: (i) each source of contamination must be isolated from other possible sources; (ii) the distance between the closest sampling site and the source of contamination must be small enough to capture the contamination gradient; (iii) the moss samples must represent the temporal variability inherent in the concentrations of contaminants in moss [13,14]; and (iv) the sampling sites must be arranged in the direction in which the decrease in the concentrations in the moss is most evident. If the above conditions are not fulfilled, the method will not be capable of detecting the existence of contamination (false negatives), although it will not detect contamination that does not exist (false positives).

The main aims of the present study were as follows: (i) to determine any common qualitative patterns of contaminant emissions for individual industrial sectors, (ii) to compare any such patterns with previously described patterns, and (iii) to compile an inventory of the metals and metalloids emitted by the industries considered.

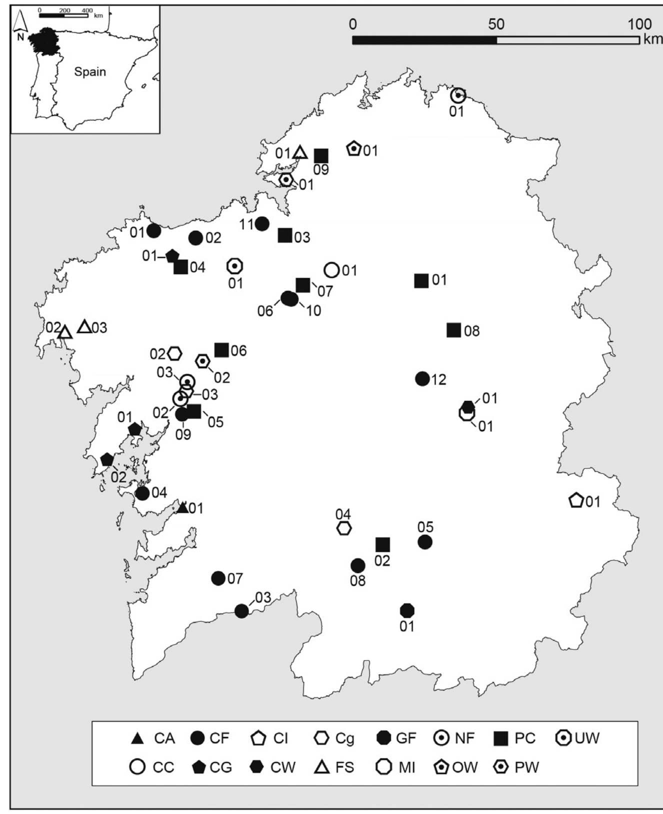

Fig. 1. Location of the moss *P. purum* SS in the surroundings of the different factories classified in several industrial sectors (see legend for Table 1).

2. Material and methods

2.1. Sampling

Samples of *Pseudoscleropodium purum* (Hedw.) M. Fleisch were collected in Galicia (NW Spain), between 1999 and 2008, at sampling sites (SS) in the surroundings of 43 different factories (some were sampled during the course of several years) that are potential sources of contamination. The factories represent 26% of the factories in the region that are included in the E-PRTR, and they are categorized into 14 industrial sectors: chlor-alkali plants (CA), ceramic factories (CF), cogeneration plants (CG), chemical industries (CI), chemical industries with cogeneration (CC), cement works (CW), ferrous-smelters (FS), glass factories (GF), mineral industries (MI), non-ferrous smelters (NF), waste oil treatment (OW), paper and wood productions with cogeneration (PC), paper and wood productions (PW) and urban waste incinerators (UW) (Fig. 1). Table 1 includes detailed information about the factories studied, including the industrial sector, year in which sampling was carried out, distance of sampling point from the focal point of emissions, the products manufactured and the annual production.

The samples of moss were collected following the method proposed by [7]. Briefly, the SS were arranged along two polar radii from the focal point of emission. One transect followed the direction of the prevailing wind in Galicia (NE-SW) and the other was arranged perpendicular to this (NW-SE), with the aim of detecting any anisotropy in the dispersal of the contaminants. Samples were collected from two SS on each radius; one of the SS was located as close as possible to the focal point of emission and the other at a distance of between 970 and 1250 m from the first, as recommended in the method (Table 1). Whenever possible, the samples were collected in open areas or small clearings in forests, although not next to trees, and areas close to main roads and centres of