Large scale air monitoring: lichen vs. air particulate matter analysis

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Abstract

Biological indicator organisms have been widely used for monitoring and banking purposes for many years. Although the complexity of the interactions between organisms and their environment is generally not easily comprehensible, environmental quality assessment using the bioindicator approach offers some convincing advantages compared to direct analysis of soil, water, or air. Measurement of air particulates is restricted to experienced laboratories with access to expensive sampling equipment. Additionally, the amount of material collected generally is just enough for one determination per sampling and no multidimensional characterization might be possible. Further, fluctuations in air masses have a pronounced effect on the results from air filter sampling. Combining the integrating property of bioindicators with the world wide availability and particular matrix characteristics of air particulate matter as a prerequisite for global monitoring of air pollution is discussed. A new approach for sampling urban dust using large volume filtering devices installed in air conditioners of large hotel buildings is assessed. A first experiment was initiated to collect air particulates 300–500 g each from a number of hotels during a period of 3–4 months by successive vacuum cleaning of used inlet filters from high volume air conditioning installations reflecting average concentrations per 3 months in different large cities. This approach is expected to be upgraded and applied for global monitoring. Highly positive correlated elements were found in lichens such as K/S, Zn/P, the rare earth elements (REE) and a significant negative correlation between Hg and Cu was observed in these samples. The ratio of concentrations of elements in dust and \textit{Usnea} spp. is highest for Cr, Zn and Fe (400–200) and lowest for elements such as Ca, Rb, and Sr (20–10). © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Air pollution monitoring; Lichen; Air particulate matter; Global monitoring

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1. Introduction

Bioindicators are organisms or organs of such organisms that respond to a certain level of pollution by a change in their life cycle or accumulation of the particular pollutant. They reflect, contrasting to direct analysis, complex effects of harmful substances, as such organisms not only show synergistic effects of a sum of parameters, but also reflect a time-integrated picture of the history of their life span (Arndt et al., 1987). Another advantage is the selective uptake of such substances, as an organism exposed to an environmental pollutant, either through air or direct uptake, absorb the bioavailable fraction only, and hence reflect readily the portion of the substance which might be hazardous to man as well.

Bioavailability is generally accepted as the extent and the rate of absorption of matter and its availability at the site of reaction (Marquardt and Schäfer, 1995). Chemicals can be accumulated in organisms via the direct uptake from the surrounding medium (e.g. air, water) by gills, skin, stomata, etc. or by ingestion of particle-bound chemicals (bioconcentration, or bioaccumulation) as well as via a food chain following various pathways along different trophic levels (biomagnification). These processes will not always manifest themselves as direct adverse effects, e.g. mortality, but complex phenomena may occur, e.g. reduced fertility, malformation of offsprings, decoloration of leaves and dwarf growth, which constitute a risk potential for humans and the environment (Franke et al., 1994).

Many examples are known where indicator organisms or communities have been used to assess environmental quality by phenomenological description of their appearance, shape or behavior (Arndt and Schweizer, 1991; Ellenberg, 1991; Schubert, 1991; Streubing et al., 1991; Pinelalloul et al., 1996). More interesting with respect to monitoring, however, is the analysis of the concentration of a particular substance accumulated by the organism and the assessment of trends following environmental input or exclusion of this material. Early recognition of compositional disturbances of our environment sometimes can only be achieved using the accumulation and magnification properties of food chains by sensitive and accurate analysis of parts of these bioindicators. Long-term specimen banking programs, as the one going on since 1985 at the Environmental Specimen Bank of Germany at the Research Center in Juelich, help to maintain continuity in sampling, processing of samples and the analysis of hazardous substances in order to elucidate such trends (Schwuger, 1997). Carefully selected biological indicators for such programs assure a meaningful data interpretation and could even serve as pieces of evidence in future trials as for the responsibility in a certain case of pollution or the effect of a legislative action.

The main criteria for the selection of bioindicators include the wide-spread availability, some information about the dose/response relationship and the accumulation properties of the species.

A more serious aspect in the selection of any indicator organism is its selectivity for the absorption of environmentally interesting substances. It should have a certain tolerance and respond more or less linearly to the increase or decrease of that substance’s concentration. If a lethal threshold concentration in the environment is exceeded no further material can be sampled for investigation. Therefore, well adapted and dominant biological specimens should be preferred to more occasional species even if they accumulate to a lower extent. Additionally, nature conservation aspects should not be violated.

Finally analytical aspects as to the possibility to produce a homogeneous sample by milling, grinding or sieving or the digestion properties of the material should be mentioned. If a particular organ of an organism should be targeted (e.g. liver or kidney of mammals or fish) proper dissection and separation from adhering material is mandatory.

The analysis of air particulate matter in principal does not raise any serious problems to the analyst, particularly when nuclear analytical methods are available. Here the sampling of adequate amounts of material is the critical factor. Filters for air dust sampling can introduce contamination especially when small volume samplers are used. Multidimensional characterization
of air filter materials is hardly possible as the few milligrams collected are consumed in one analytical run. The interest in organic, inorganic and radioisotope analysis from the same sample urged us to look out for high volume sampling facilities which might be available in many places around the world to be used for the collection of large amounts (up to 500 g) of air particulate matter. Air conditioning in large hotels is one possible source for the collection of adequate quantities of material suitable to be used for air quality assessment. By simply vacuum cleaning of the inlet filter supporting material from such large volume air filtering devices within a period of 4–12 weeks an amount of 300–500 g of particulate material from urban environment can be collected. By appropriate selection of the hotels a more or less world-wide net of sampling stations, — both urban sites as well as holiday resorts at remote places — can be used for sampling.

2. Materials and methods

Usnea spp., a fruticose lichen hanging from trees in bundles of thalli is abundant in almost all continents and remote areas of the world having moderately humid climate. Particularly in elevated mountainous regions it can be found and collected without risk of contamination from the host tree. As lichens possess no roots they totally rely on nutrient uptake from air constituents (wet or dry). Samples of Usnea were collected in Siberia, near Lake Baikal and in Calgary, Canada, in boreal forests and in Sri Lanka in a montane rain forest at approximately 1200 m above sea level. In the Bavarian Forest, Germany, a sample was taken by the local forestry personnel, air dried and sent to the laboratory in Juelich, where the milling and analysis of all the samples were performed.

All samples, including the reference material IAEA 336 were acid digested and analyzed using a PE ELAN 5000 ICP-MS and a PE Optima-500 ICP-AES system. The analytical parameters and settings used are described elsewhere (Amer et al., 1997). Air dust samples were collected from the air purification device at the Atominstut in Vienna, from the air conditioning system at the Hilton Hotel in Antananarivo, Madagascar, as well as from the Hilton in Dresden, München and Düsseldorf, Germany. Vacuum cleaning of the filtering mat yielded enough material to determine inorganic, organic and radio nuclide contaminants. Prior to analysis the air dust samples were sieved and only the fine fraction (< 63 μm) was encapsulated into Suprasil® quartz ampoules for neutron irradiation with 10^{13} N cm^{-2} s^{-1} at the research reactor DIDO in Juelich. INAA was performed according to the procedure described in Rossbach et al. (1993).

Quality control of analytical results was
achieving by processing IAEA-336 (lichen) for the lichen samples with all the techniques used (ICP-OES, ICP-MS and INAA) and NIES No. 8 (vehicle exhaust) for the air dust samples by INAA. Results are compared to the given values in Tables 1 and 2. Particularly for the INAA derived values for some elements (e.g. Se, Mo, Cd) deviation from the given values occur but this might be due to bad statistics (mean value composed of only three to four single results). Generally the agreement with the given values seem, however, to be satisfying.

3. Results and discussion

3.1. Lichen

From the many elements determined in the lichen Usnea spp. only a few can be presented and discussed here for lack of space. In Figs. 1 and 2 some environmentally relevant elements are displayed. It can be seen that for Cu, Zn, Cd, Sn, Pb and Th concentrations in the sample from Bavarian Forest far exceeds the concentrations found in the other samples. Only Ba is higher in the Canadian lichen and Hg tends to be highest in the Siberian sample. Co as well as some rare earth elements (not shown here) are highest in the sample from Sri Lanka. The tree diagram as shown in Fig. 3 was derived using normalized to the mean of all samples values. The linkage distance for the sample from the Bavarian forest indicates that this sample is strongly separated from the rest, due to the elevated concentrations compared to the other four samples.

Many highly correlated elements were found and some examples are displayed in Figs. 4–6. Potassium correlates to sulfur in our samples at a very high significant level as does Nd to Ce and Zn to P also. The only negative correlation we found is between Hg and Cu as shown in Fig. 7. Reports of a negative correlation between the two elements in Usnea or other biological samples could not be found in the literature so far.

3.2. Dust samples

Results obtained from INAA investigation are displayed in Fig. 8. Some of the elements, such as Fe, Co, and Sb appear to be quite comparably concentrated in all the five samples whereas elements, such as Cr, Zn, Se and Cs are lowest in the material from Madagascar. Na, Br, the rare earth elements and Th, however, are highest in Madagascar. The sample from München exhibits an extraordinarily high Ag concentration. Unfortunately not all elements could be determined in all the dust samples, hence comparison of elements
Fig. 1. Selected trace elements in lichen (*Usnea* spp.) from different places of the world.

such as Ca, As, Se, Rb, Sr and Th cannot be fully exploited.

Organic contaminants were determined in the dust samples from Austria and Madagascar (see Fig. 9). The comparison of PAHs in the sample from Vienna and Antananarivo shows clearly that all species are present in higher concentrations in the Austrian sample and the pattern of PAHs in Madagascar is shifted more to the less volatile compounds compared to the Austrian sample.

3.3. Comparison of results from lichen and dust samples

If the range of concentrations found for various

Fig. 2. Selected trace elements in lichen (*Usnea* spp.) from different places of the world.
in the two distinct materials. The ratio of mean concentrations in both materials are shown in Fig. 11. Cr, Zn and Fe are enriched in urban dust by a factor of 200–400 and Ca, Rb and Sr by a factor of 10–20 only.

4. Conclusion

In a world of increasing communication and transportation facilities, collection of lichen samples from remote areas around the globe seems to be feasible. Sampling of air dust could be strongly facilitated by implementation of existing air conditioning installations from large hotels. These two materials seem to be complementary from several point of views:

Fig. 3. Dentogram of the discriminant analysis using all elemental results in lichen from various places.

Fig. 4. Correlation of K and S in lichen from various places of the world.

Fig. 5. Correlation of normalized (Rb) lichen data for Ce and Nd.

Fig. 6. Correlation of Zn and P in lichen from various places of the world.

Fig. 7. Negative correlation of Hg and Cu in lichen from various places of the world.
Lichen can be collected in remote, far from point source pollution areas only and, hence, represent air quality of natural reserve areas. Air dust from air conditioning systems of large hotels in the first place represent the air quality of large cities and is indicating more realistically what is inhaled by a large proportion of human population.

- Air dust as a mixture of soot, soil and aerosols in varying proportion is very much influenced from weather conditions and collection procedures whereas lichens absorb constituents from wet and dry precipitation more or less constantly during their entire life cycle. The contaminants and nutrients are embedded into a biological matrix. Excretion is negligible.
- Dust concentrations can be directly related to m³ of air (using the capacity and throughput of the air conditioning system) whereas concentrations found in lichen can only be quali-
tatively related to the surrounding air masses. Although the argument of ‘the bioavailable fraction of trace elements determined in bioindicators’ is frequently cited, it seems somewhat questionable if this can be applied in the case of lichen.

- Lichen as well as air filter dust samples can be used for the assessment of organic and radionuclide air pollution. These two groups of contaminants are of increasing importance in air quality monitoring programs.

The combination of both, the biomonitoring approach as well as the use of air particulates for air quality monitoring opens the opportunity to assess and evaluate air quality from various locations and regions around the world. Whereas lichens seem to reflect the background levels from remote areas influenced only by long-range transport of trace contaminants, the dust samples, however, if taken from the city centers, reflect the highly contaminated, densely populated areas. Only the combination of these informations will give a full picture of the span of concentrations and the magnitude of burden in the vicinity of point source emission. Further experiments to expand the applicability of this approach are in progress.

Acknowledgements

Sincere thanks are due to the technical officer at the Hilton Hotel at Antananarivo, Madagascar and the IAEA, Seibersdorf Laboratory for providing the dust samples. Mrs C. Mohl and Mrs H. Schüsseler are gratefully acknowledged for ICP-MS and ICP-AES analysis of the lichen material.

References


