LARGE SCALE AIR MONITORING: BIOLOGICAL INDICATORS VERSUS AIR PARTICULATE MATTER

M. ROSSBACH
Institute of Applied Physical Chemistry,
Forschungszentrum Jülich, Germany

R. JAYASEKERA
Department of Botany,
University of Kelaniya,
Kelaniya, Sri Lanka

G. KNIEWALD
Center for Marine Research Zagreb,
Rudjer Bokovi Institute,
Zagreb, Kroatia

Abstract

Biological indicator organisms are widely used for monitoring and banking purposes since many years. Although the complexity of the interactions between bioorganisms 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. Direct 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 uniform matrix characteristics of air particulates as a prerequisite for global monitoring of air pollution will be 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 to 500 g each) from a number of hotels during a period of three to four months by successive vacuum cleaning of used inlet filters from high volume air conditioning installations reflecting average concentrations per three months in different large cities. This approach is expected to be upgraded and applied for global monitoring. Highly positive correlated elements were found in lichen 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 *Usnea spp.* is highest for Cr, Zn, and Fe (400 - 200) and lowest for elements such as Ca, Rb, and Sr (20-10).

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 [1]. 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 [2]. 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 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 [3].

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 [4-8]. 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 [9]. 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. The 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 filter supporting material from such large volume air filtering devices within a period of four to twelve weeks an amount of 300 to 500 g of material 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 mountain rain forest at about 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 [10].

Air dust samples were collected from the air purification device at the Atominstitut in Vienna and from the air conditioning system at the Hilton Hotel in Antananarivo, Madagascar. Vacuum cleaning of the filtering mat yielded enough material to determine inorganic, organic and radio nuclide contaminants. The material was sieved (through 70 mesh) and encapsulated 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 [11].

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 Figures 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 exceed the results from 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. This might cause the distinct difference in grouping of northern and southern hemisphere samples in the discriminant analysis as shown by the dendrogram in Figure 3.

Many highly correlated elements were found and some examples are displayed in Figures 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 Figure 7. Reports of a negative correlation between the two elements could not be found in the literature so far.

3.3. Urban dust

The comparison of results from Austria, Madagascar and the certified reference material NIST 1648 is shown in Figure 8 in logarithmic scale. The NIST material, originating from St. Louis, MO, seems to be highest for As, Se, Br and Ag whereas the material from Madagascar tends to show elevated levels of Na, Rb, Sr, REE, and Th respectively. The origin of the different pattern of trace constituents can be elucidated only after more relevant data are collected and statistically evaluated. The comparison of results from PAH analysis clearly shows a much lower burden of the Madagascar sample compared to Austrian material with such residues from fossil fuel burning (see Figure 9).

3.3. Comparison of results from lichen and dust samples

If the range of concentrations found for various elements in dust and lichen samples is displayed (Figure 10) it becomes obvious that the analytical results differ by nearly two orders of magnitude in the two distinct materials. The ratio of mean concentrations in both materials are shown in Figure 11. Cr, Zn, and Fe are enriched in urban dust by a factor of 200 to 400 and Ca, Rb, and Sr by a factor of 10 to 20 only.

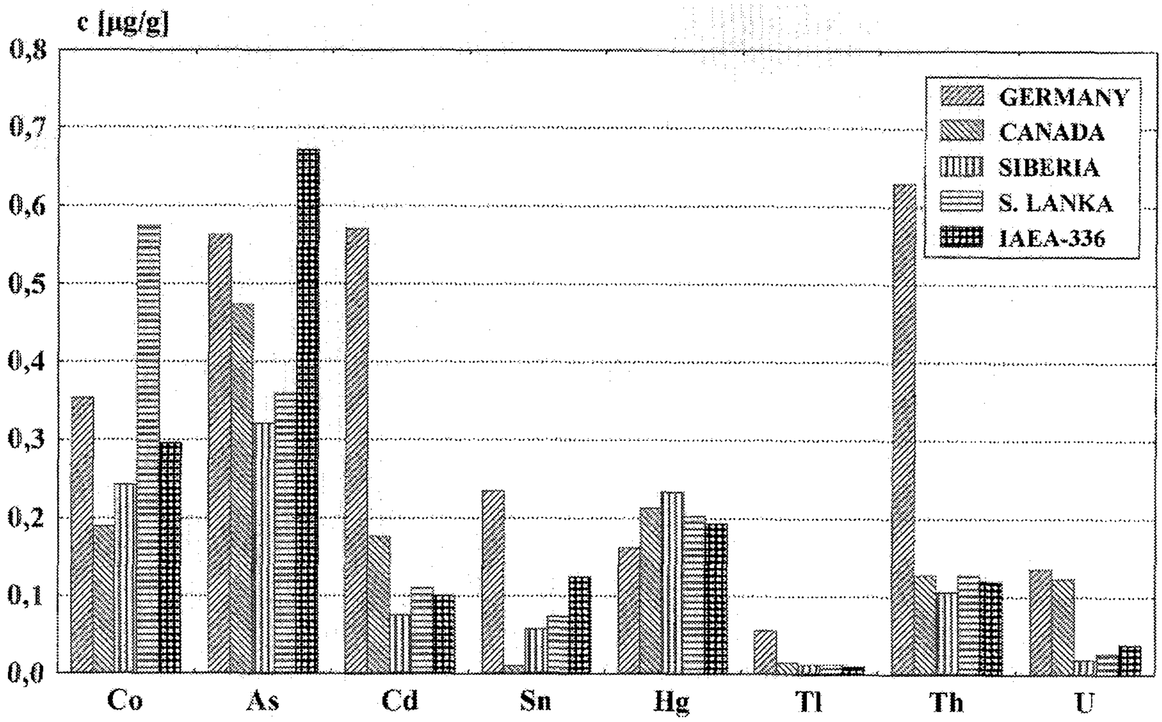

Figure 1: Selected trace elements in lichen (Usnea spec.) from different places of the world.

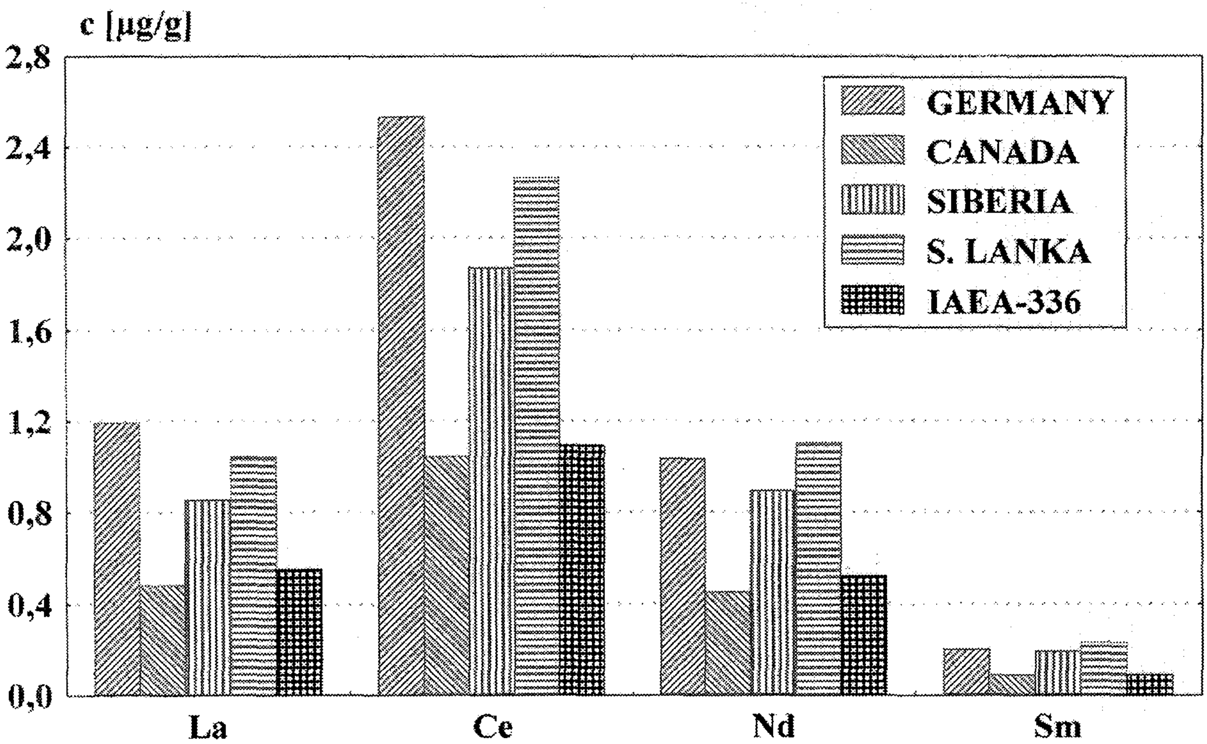

Figure 2: Selected trace elements in lichen (Usnea spec.) from different places of the world.

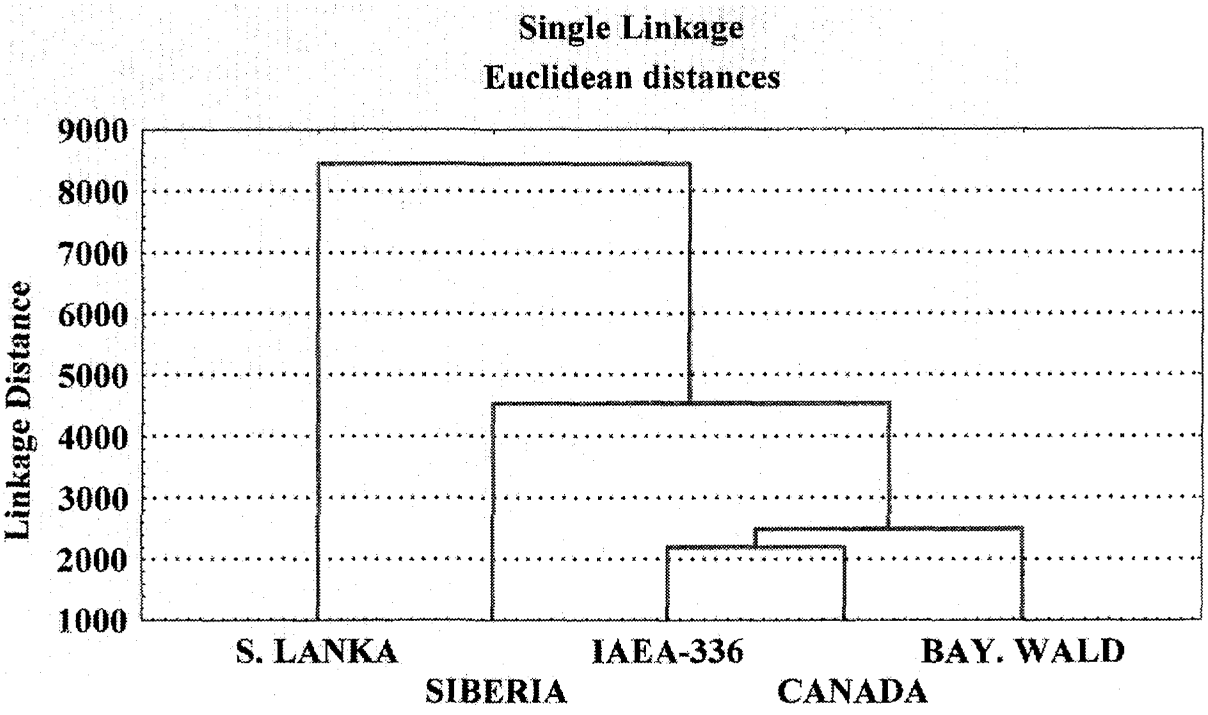

Figure 3: Dendrogram of the discriminant analysis using all elemental results in lichen from various places.

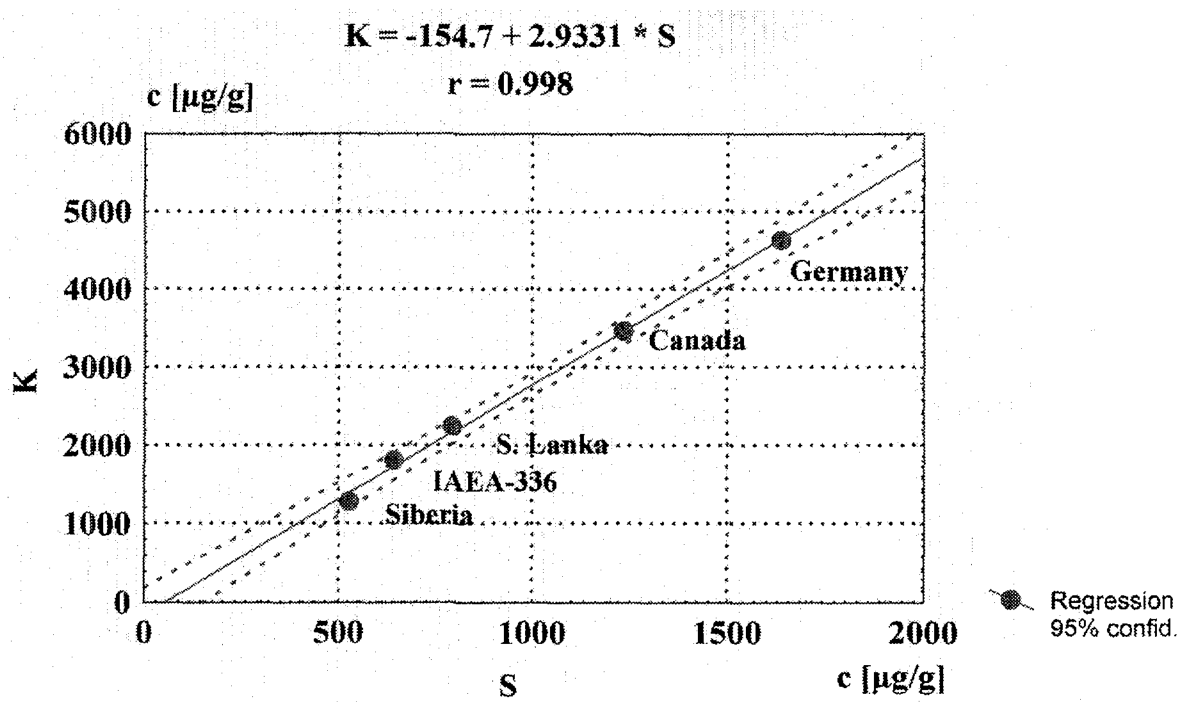

Figure 4: Correlation of K and S in lichen from various places of the world.

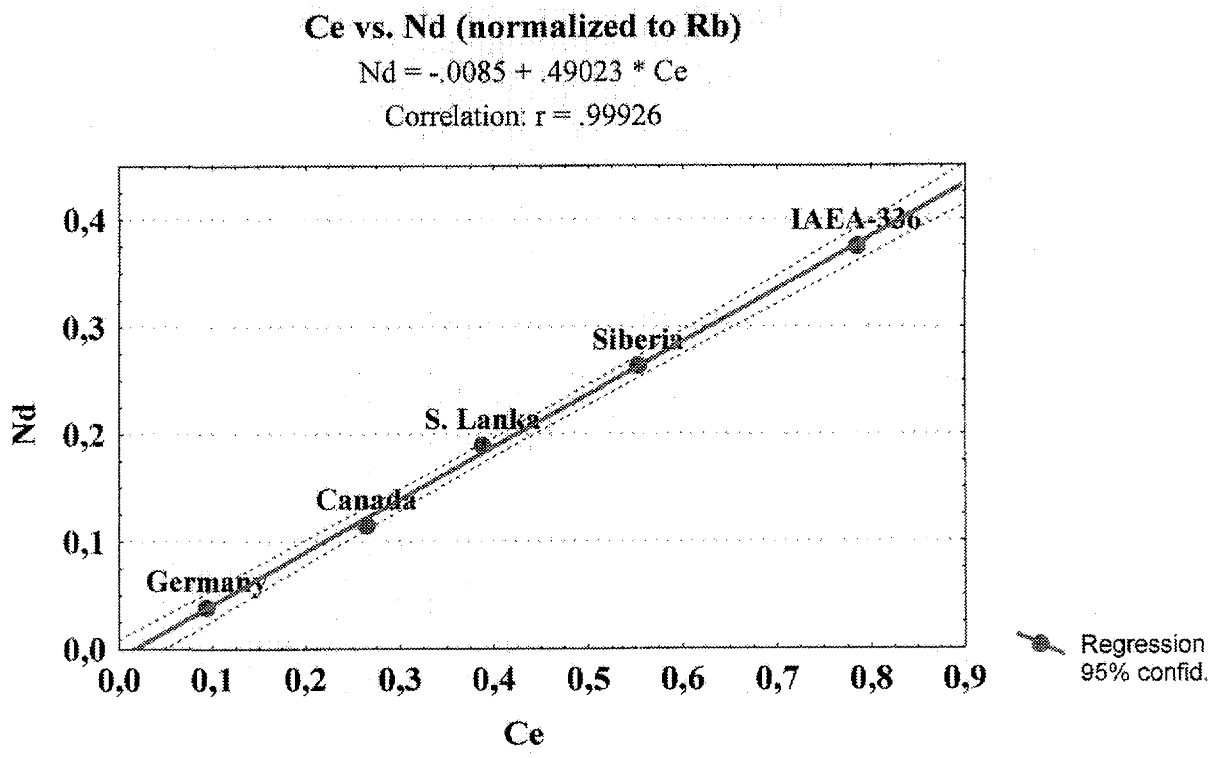

Figure 5: Correlation of normalized (Rb) lichen data for Ce and Nd.

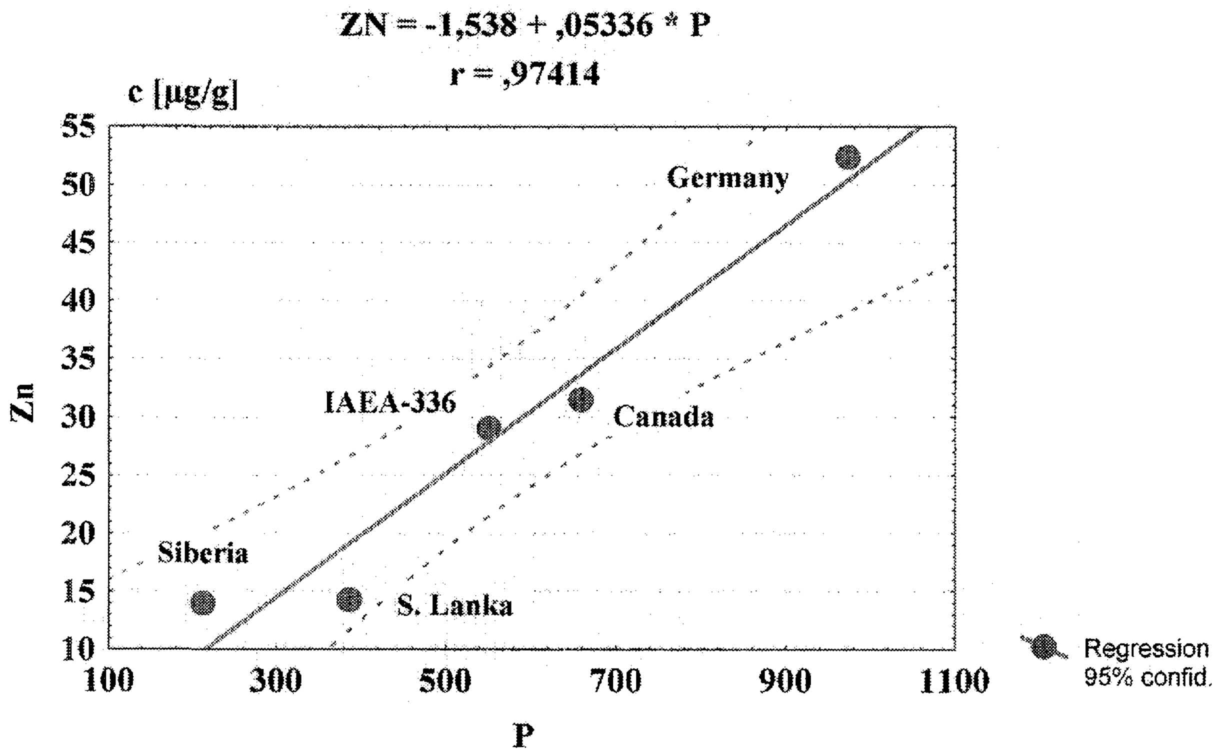

Figure 6: Correlation of Zn and P in lichen from various places of the world.

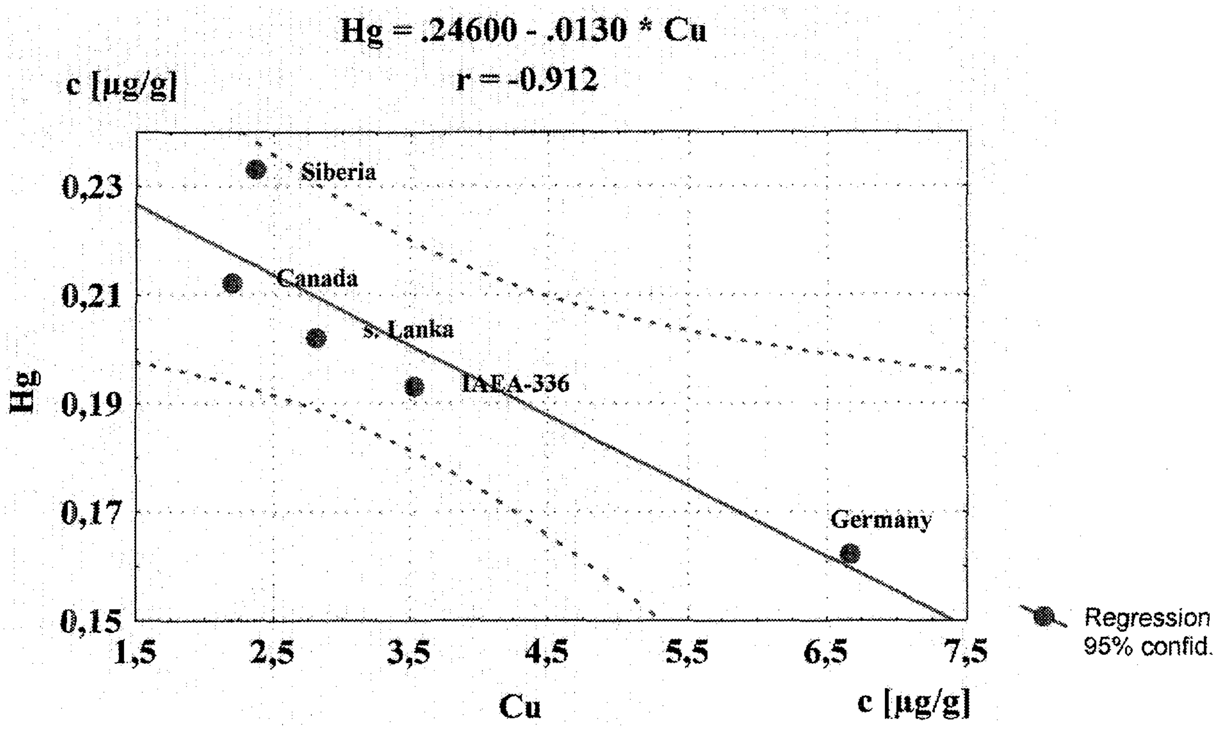

Figure 7: Negative correlation of Hg and Cu in lichen from various places of the world.

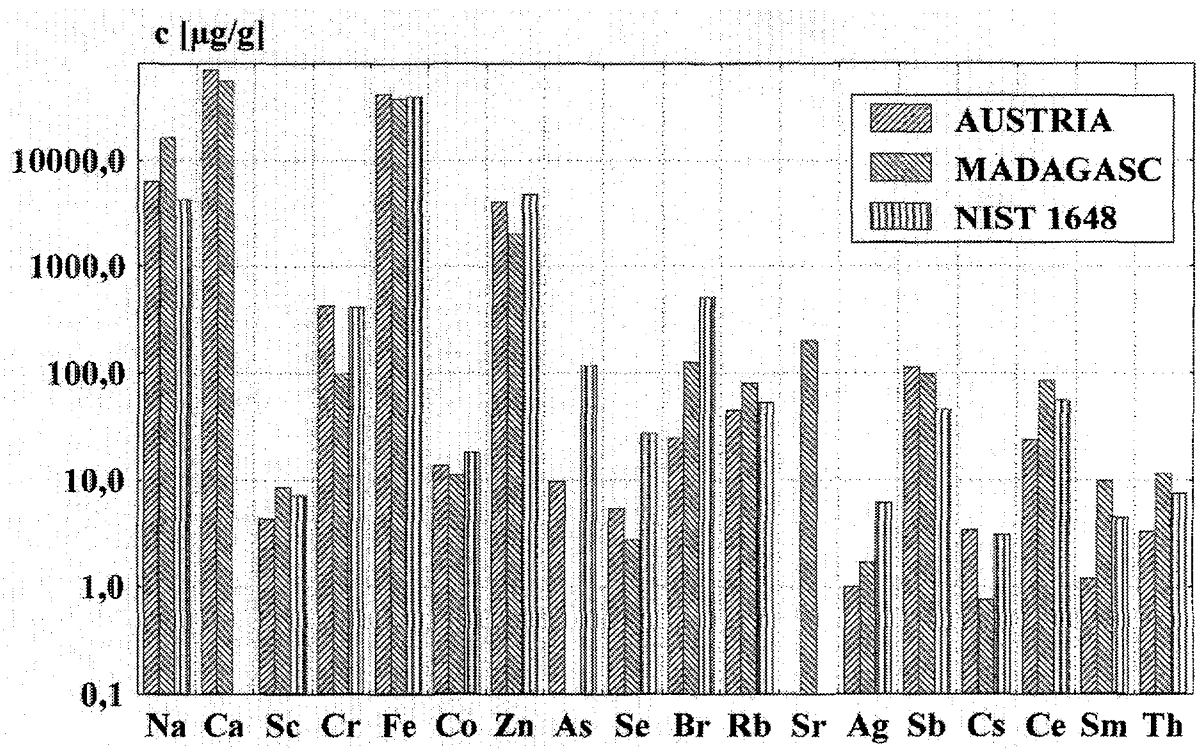

Figure 8: INAA results in large volume air dust samples from Austria, Madagascar and the USA.

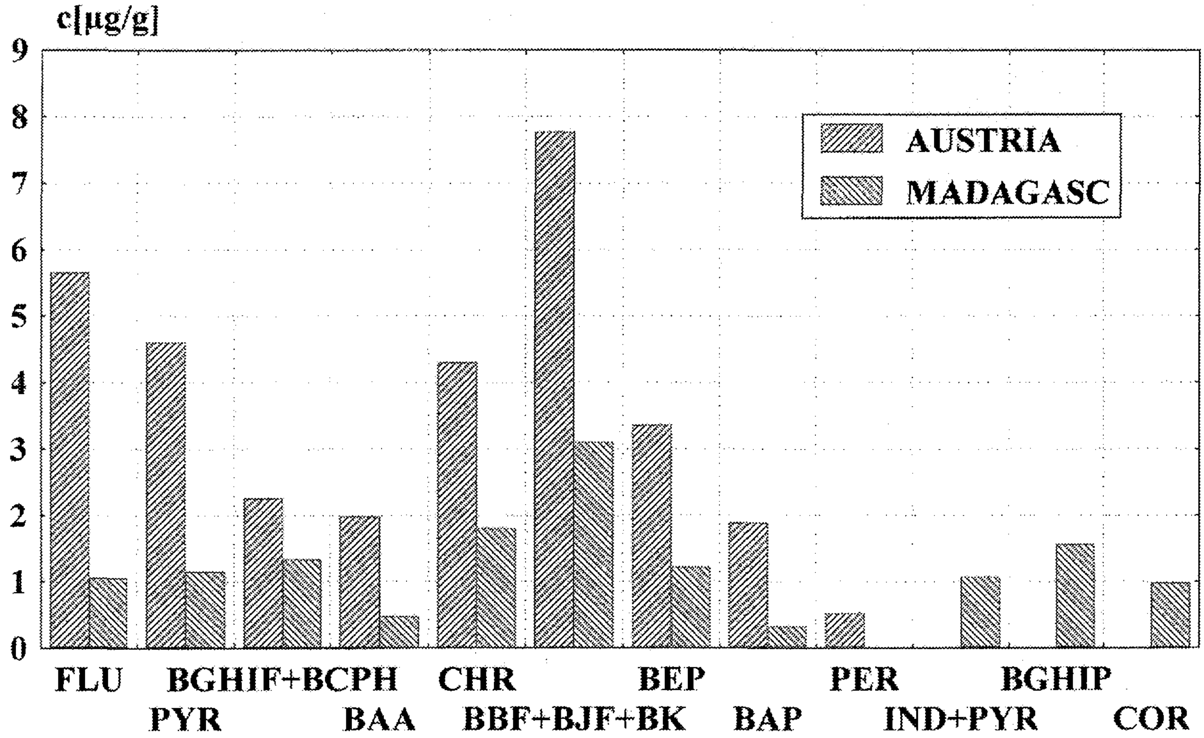

Figure 9: PAH analysis of large volume air dust samples from Austria and Madagascar. (FLU = Fluoranthen, PYR = Pyren, BGHIF+BCPH = Benzo[ghi]fluoranthen + Benzo[c]phenanthren, BAA = Benz[a]anthracen, CHR = Chrysen, BBF+BJF+BK = Benzofluoranthen[b+j+k], BEP = Benzo[e]pyren, BAP = Benzo[a]pyren, PER = Perylen, IND+PYR = Indol + Pyren, BGHIP = Benzo[ghi]perylen, COR = Coronen).

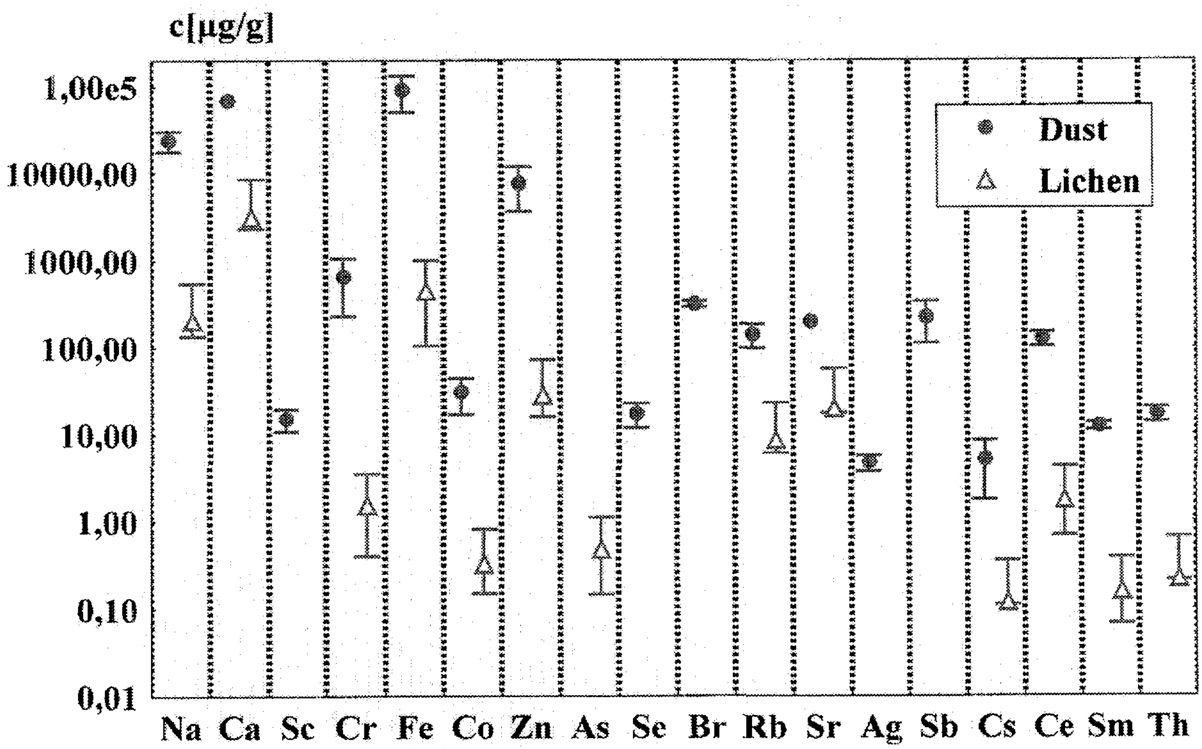

Figure 10: Range of element concentrations determined in lichen and dust samples in logarithmic scale.

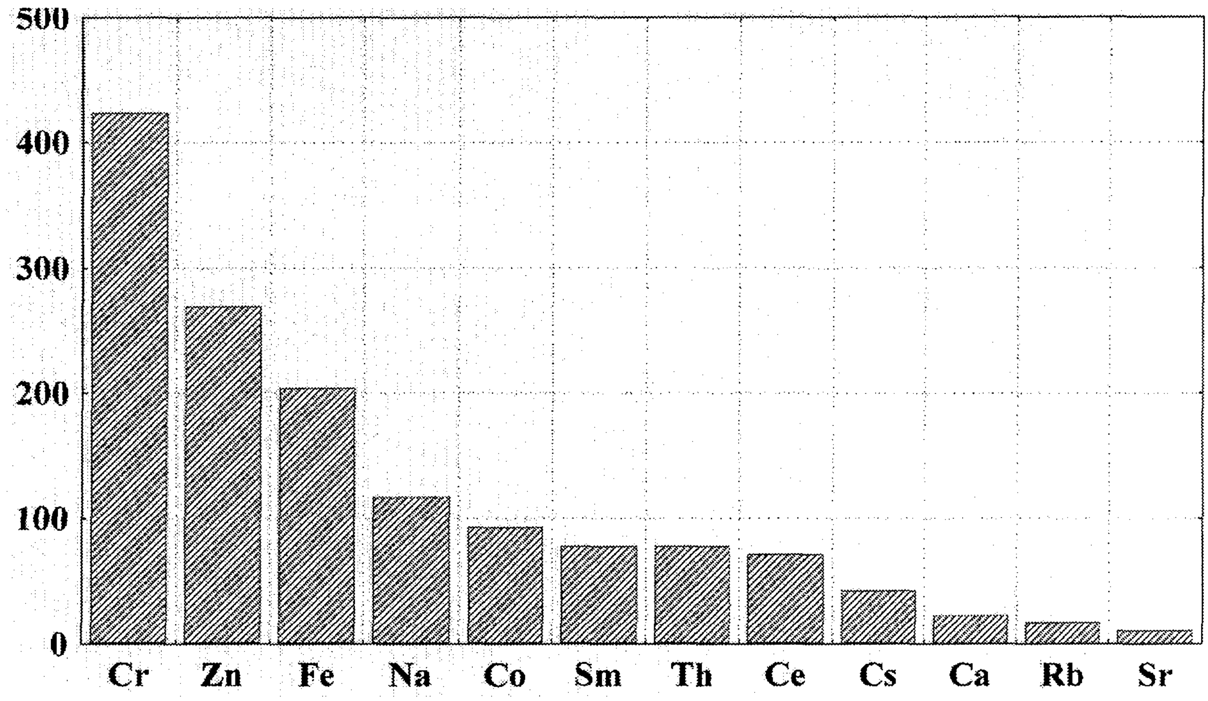

Figure 11: Ratio of mean concentrations in dust and lichen materials.

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:

- 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 m^3 of air (using the capacity and throughput of the air conditioning system) whereas concentrations found in lichen can only be qualitatively 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 our findings 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.

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