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Heavy metals, occurrence and monitoring

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Introduction

The most predominant natural sources of heavy metals in the atmosphere are biogenic processes, volcanic dust, soil derived dust, forest fires and sea salt spray. Historically the emission rate has been low due to the low volatile nature of most trace elements. In time with the industrial revolution and invention of high-temperature processes, the rate of emission has substantially increased.

With exception of Hg, most of the atmospheric elements are in particulate form. The various elements are found in different size ranges of the atmospheric particles. Several scientific works refer to about this element distribution among the various size fractions. This is important not only from a health viewpoint, but also because fine particles tend to persist in the atmosphere where they can undergo chemical reactions and they can be transported from their sources over long distances to pristine areas of the environment.

Several international measurement programmes deal with air pollution in rural areas- and one of them are The European Monitoring and Evaluation Programme, for short called EMEP. This program work under the convention for Long Range Transboundary Air Pollution. The three main objects of EMEP is

1. to collect emission data from the parties
2. to measure air and precipitation quality
3. and with support from this information develop models of atmospheric dispersion.

Heavy metals were included in EMEPs monitoring programme in 1999. However, due to co-operation between EMEP and other measurement programmes, EMEP established a database and have been receiving heavy metal data since 1996. So, since then annual data reports on heavy metals have been published in the framework of EMEP.

EMEP has a network of measurement stations. This is a map of locations of the different measurement sites. The stations are generally located distant from local emission sources in order to be representative for a larger region.

At present monitoring of atmospheric content of heavy metals are carried out at 57 stations out of a total of 99. Less than 10 stations measure mercury.

Trace elements are removed from the atmosphere by wet-deposition and dry-deposition. By collecting and analysing precipitation and air samples we obtain information of the supply of heavy metals to the ecosystem. But, a chain is no stronger than its weakest link; effective sampling and analytical techniques are essential in obtaining accuracy and precision in chemical analysis. At present, the sampling, especially of precipitation seems to be the most challenging part.

National laboratories carry out the sampling and analysis within EMEP. To obtain data that are comparable and have sufficient quality, sampling and analysis are attempted harmonised.

Within EMEP it is made a manual for sampling and chemical analysis to guide the participating countries.

There are two different devices for sampling of precipitation- wet-only and bulk.
The wet-only sampler has a lid that cover the funnel whenever the weather is nice. In this way dust fall and windblown debris is prevented to enter the sample container. The lid automatically removes when the rain starts. With such a sampler the sensitivity of the precipitation sensor is of vital importance to assure collection of the very first drops that usually have a high content of particles. The drawback with this sampler is the need for power supply, the cleaning difficulties and the relative high price.

A bulk sampler is easy to clean, need no power supply and is relatively cheep. To prevent leaves and insects to enter the collecting bottle, a sieve with large grid size is placed between the bottle and funnel. Even so, the bulk sampler still tends to give too high metal concentrations due to dust fall and wind blown debris. However, in some areas as for example in Scandinavia, there is practically no difference between the two type of collectors.

Here is a summary of the advantages and drawbacks with both samplers. EMEP recommend the participating countries to use wet-only.

Sampling of particulate phase mercury in air is one of the difficult steps in measurement of atmospheric mercury. In ambient air the particulate fraction of mercury is only 5%, with volatile mercury making up the reminder. This increases the risk of gas to particle conversion and vice versa during sampling. For this reason sampling and analysis of mercury should be considered as an operationally defined method.
At present, for collection of mercury in atmospheric samples, EMEP has adapted the guidelines developed for the network in the measurement programme OSPAR.

Mercury is collected in special precipitation samplers. Also here there is a choice between wet-only and bulk. Field comparisons performed in Sweden have shown no significant difference between wet-only and bulk samplers, but we do not have any information on what kind of sampler that is best in Southern Europe.

Three alternative materials may be used for funnels and collection bottles; borosilicate glass, quartz glass or Teflon. Borosilicate glass is often preferred due to low cost and general availability. To prevent elementary mercury form diffusing into the collected sample and by oxidation to water-soluble forms contribute to the mercury content, a capillary is mounted between the funnel and the collecting bottle. For sampling during all seasons, a heating device is also needed to prevent formation of ice in the system. The sample bottles are also shielded from light to prevent photo-induced reduction of the collected mercury.

Airborne particles are sampled by continuously pumping of air through a filter. Decomposition of the exposed filter followed by a suitable analysis technique will give information of the content of heavy metals in the collected particles.
For sampling of atmospheric particles either high- or low-volume samplers may be used. Most of these samplers provide the possibility to collect either total suspended particle matter or a fraction with a defined cut-off. As mentioned earlier several studies indicate that the mass distribution varies for the different elements, but sampling of the particles less than 10 μm will to a large extend contain the main fraction of long range transported heavy metals. This means that the choice of sampler mainly depends on the

sampling period and particle concentration of at the actual site. For short sampling periods (as daily) at background sites a high volume sampler is usually needed.

For sampling of atmospheric particles EMEP recommend weekly samples. This is mostly due to cost. For weekly sampling low-volume samplers may be used.

For high volume samplers Quartz filters are recommended to assure sufficient air flow through the entire sampling time. For low-volume samplers filters made of teflon, cellulose or quartz may be used.
Generally, what is important is to use filters that give as low blind values as possible and allow constant flow rate during the entire sampling period.

For sampling of total gaseous mercury in air there is two options, you can use gold trap or monitor. The basic principle for sampling of total gaseous mercury is amalgamation with gold, both in manual- and automatic methods.
Also here EMEP has adapted the guidelines developed within OSPAR.

Gold traps comprise 10 –12 cm quartz glass tubes filled with gold adsorbent. For sample collection two of these gold traps are placed in series. With this arrangement a breakthrough of mercury is detected with a significant mercury amount on the second trap. Sampling flow rate in the range of 0.1-0.5 litre per minute for 12-24 hours is normally adequate.

Here is a list of quite commonly used techniques for analysis of heavy metals. Here is the number of laboratories reporting results to EMEP that uses these techniques. The techniques marked in red are the once that EMEP recommend. ICP-MS is a powerful analytical tool for multielement analysis, particularly in cases that involve a large number of samples. It is a sensitive technique, which is required since the concentration of heavy metals in precipitation typically is a few nanogram per millilitre.

In order to ensure data comparability, interlaboratory tests are organised every year. Here is a summary of the results from last years round. In these plotts the median value of the reported results are compared to the expected value. It is chosen to differentiate between EMEP laboratories and other participants. These samples contained the metals in concentrations usually found in rural areas in Scandinavia. I sort of like to see the EMEP laboratories have relative good control on analysis of low concentration samples. These samples, contained the metals in concentrations usually found in rural areas in central Europe. As you can see there good agreement between median values and expected values for both laboratory groups.

I will show you some maps of heavy metal concentration over Europe. The yearly precipitation mean concentrations (represented as coloured dots on the map) are calculated from daily, weekly or monthly reported values as precipitation-weighted averages. Average air concentrations are arithmetic averages of the reported values.

This map presents the annual averages of lead in precipitation collected in 1999. As we can see the lowest concentrations are found in northern Scandinavia, Iceland, Ireland and Portugal, where the annual averages are below 1 µg Pb pr litre. What we also can see, is an increasing gradient eastbound, with a peak at the Czech stations. In this area values like 5-6 µg Pb pr litre are measured.

This is a map presenting cadmium in precipitation. The lowest values are found in the Nordic countries. An increasing southbound gradient can be seen, with the highest values reported from the Belgian and Czech stations. The high values found at the Belgian station are most probably due to emissions from the Hoboken smelter. Overall the emissions of cadmium have decreased in Europe in recent years, but not to the same extent as lead.

As can be seen from this slide, few stations are monitoring heavy metals in air. This map presents the annual averages of lead in air in 1999. Concentrations below 1ng Pb pr m^3 can be seen at Svaldbard, Iceland and Greenland. The highest values are reported from Belgium. In addition, relatively high concentrations of lead in aerosols are reported from the Slovakian sites.

Here is cadmium in aerosol presented. The lowest concentrations are measured in Svaldbard and Norway. The highest values are measured in Belgium and relatively high values are reported from the Slovak stations.

These plots show temporal trends for lead in aerosol from stations that have reported data for at least six years. Several countries in Europe have reduced their emissions of lead which can be seen from the Danish and German stations. A marked seasonal variation in the lead level can be seen at the station on Spitzbergen, with highest concentration during the Arctic winter.

Detailed information about national atmospheric deposition patterns and location of significant trace element emission sources requires a very extensive sampling network. However, it is obvious that it is not possible to have samplers placed in every valley. In cases where detailed information is required mosses used as biomotors may give additional information.

Biomotors may be defined as “organisms that can be used for the recognition and quantitative determinations of antrophogenically induced environmental factors”. Why use moss? Mosses, especially the carpet forming species obtain most of their nutrition directly from precipitation and sedimentation of airborne particles. The mosses have reduced cuticle and this means that ions retained on their surface have direct access to the exchange sites in the cell walls. In addition the risk for uptake of heavy metals from the ground is negligible due to underdeveloped root system.

The moss called “ Hylocomium splendens” have been commonly used in Scandinavia. In Norway this moss is present everywhere and it is easy to distingwish from other moss species. This moss also has very close-set leaves, which leads to an effective filtering of airborne particles. Another advantage is that the annual growth increments are easily identified, making it easy to tell the age of the segment. In Norway, more than 600 moss samples have been collected from all over the country round every 5 th year since 1977.

As can be seen from this maps the level of lead in moss is highest in the southern part of Norway and decreases gradually to the north, which is atypical of elements associated with long-range atmospheric transport. However, local maxima can be seen in the Oslo area and a few other urban districts. In addition, these maps show that the concentration of lead transported to Norway has gradually decreased since 1977.