> Deposition of atmospheric pollutants in Switzerland

Chemical analysis of mosses 1990–2010

Summary of the publication «Deposition von Luftschadstoffen in der Schweiz»
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> Summary

In 2010 (and following similar studies in 1990, 1995, 2000 and 2005), as a Swiss contribution to the European project, "Monitoring of atmospheric heavy metal and nitrogen deposition in Europe using bryophytes", the atmospheric deposition of various metals, semi-metals (and from 2005 onwards, nitrogen) was estimated in Switzerland using mosses (*Hypnum cupressiforme* or *Pleurozium schreberi*) as accumulative bio-monitors. In some European countries, including Switzerland, in the same year estimates were made of levels of sulphur and polycyclic aromatic hydrocarbons in mosses.

With this study the following objectives were achieved: with the aid of moss analyses it was possible to estimate the regional atmospheric deposition of various elements and to make national and international comparisons. Changes versus previous measurement periods were recorded and were used as the basis for assessing the degree of success of any measures that had been taken with the aim of reducing emissions. Based on the measurement of nitrogen content it was possible to obtain information regarding atmospheric deposition of nitrogen. It was also possible to acquire initial practical experience with the measurement of polycyclic aromatic hydrocarbons in moss. The study also yielded reference data for the National Soil Monitoring Programme (NABO), as well as for other studies.

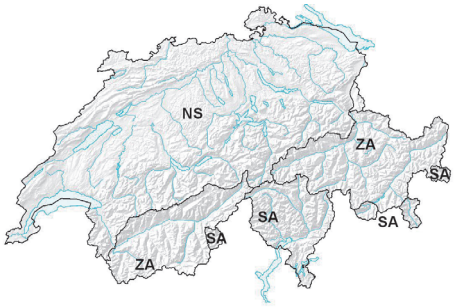
Alongside Switzerland, 26 other European countries participated in the studies in 2010. In addition to the content of metals, the level of nitrogen was estimated in 13 countries, and the sulphur content was measured in 8. Polycyclic aromatic hydrocarbons were included in the analyses in 6 countries. The data recorded in Europe are coordinated by the "Coordinating Centre of the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops" (ICP Vegetation, *http://icpvegetation.ceh.ac.uk/*), which is a sub-programme of the "Working Group of Effects" under the UN/ECE Convention on Long-range Transboundary Air Pollution.

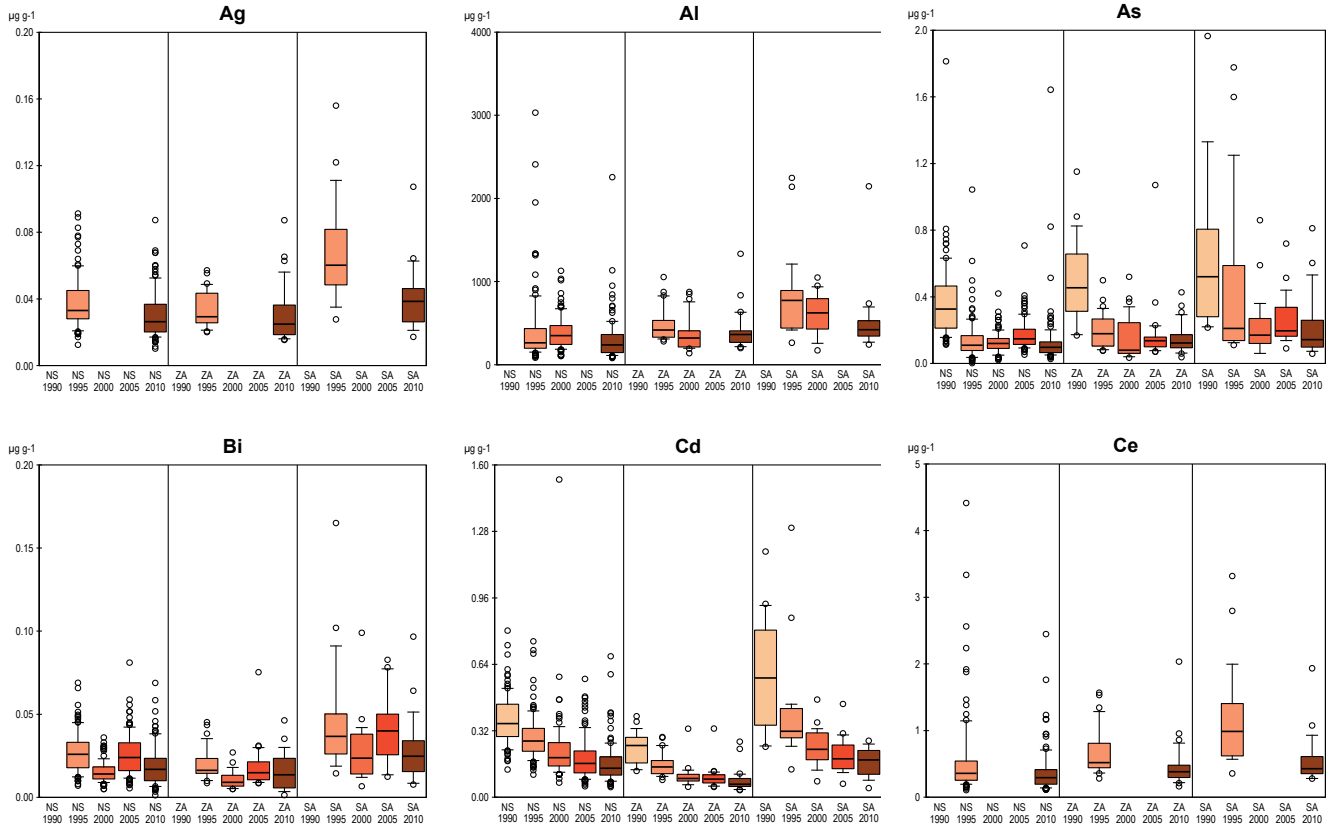
Mosses are a particularly suitable vehicle for this study because they draw water, as well as all nutrients and pollutants, directly from the atmosphere instead of via their roots. Samples were collected at a distance of at least 300 metres from roads and housing developments, since the intention was to record remote pollution levels rather than local peak levels. In the mountains, collection points located at 400 to 600 metres above the valley floor were selected. At each location, 5 sub-samples were collected. The various samples were collected from forest clearings (rejuvenated areas), moors and Alpine meadows. The moss samples were then processed (removal of pine needles, etc., selection of portions of growth of the past three years), digested in a microwave oven and subsequently analysed with the aid of ICP-MS or ICP-AES (Hg with AMA 245, polycyclic aromatic hydrocarbons with HPLC/FLD). For the purpose of quality assurance, blank values, reference material and retained samples were analysed and multiple measurements were carried out.

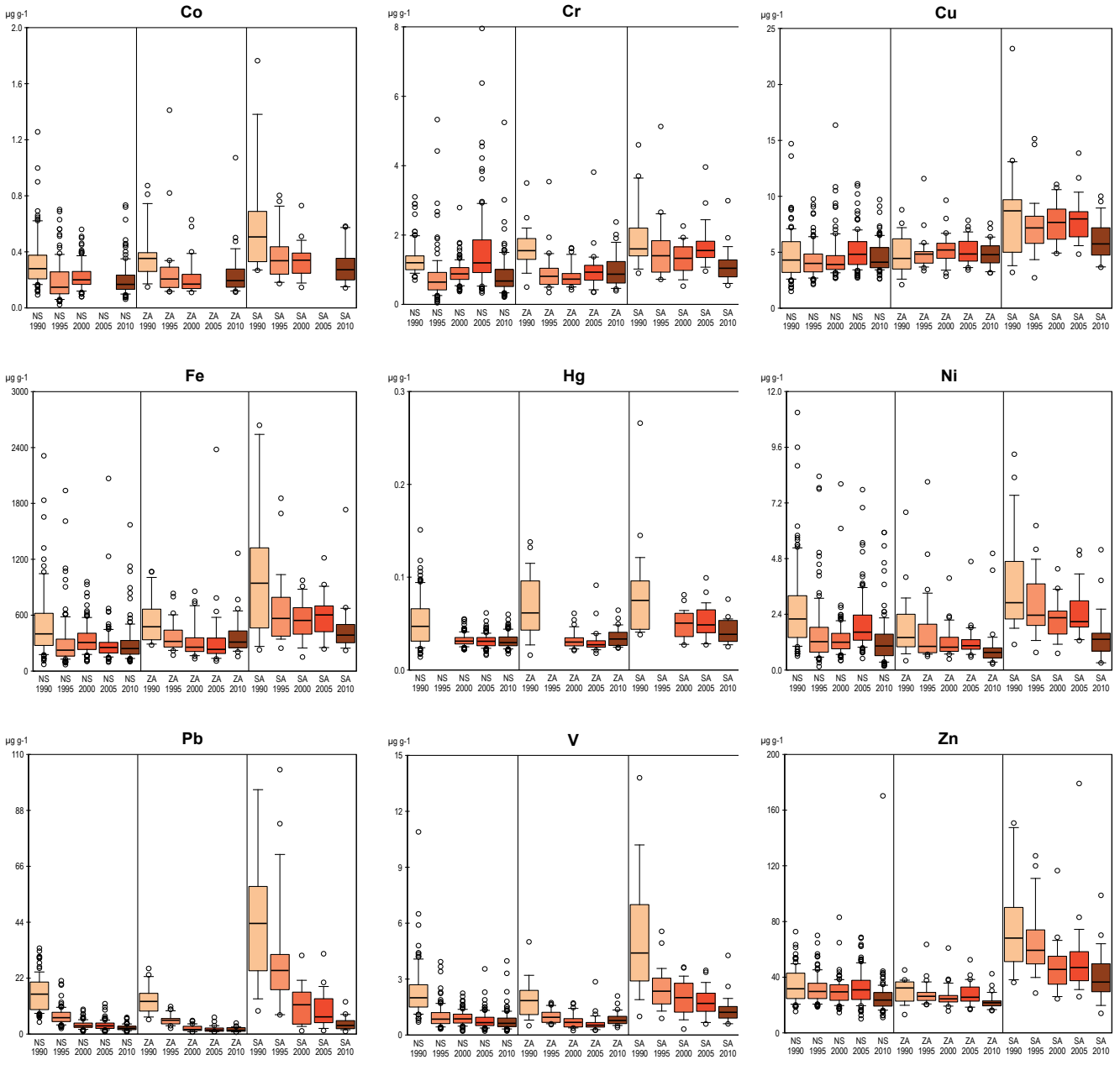
Metals

Fig. 1 > Concentration of heavy metals in µg/g dry matter

Depiction of heavy metal concentrations measured during the five study periods (1990, 1995, 2000, 2005 and 2010). The data were broken down into three natural regions of Switzerland: NS = northern Switzerland (Jura, central plateau, northern Alps); CA = central Alps; SA = southern Alps).





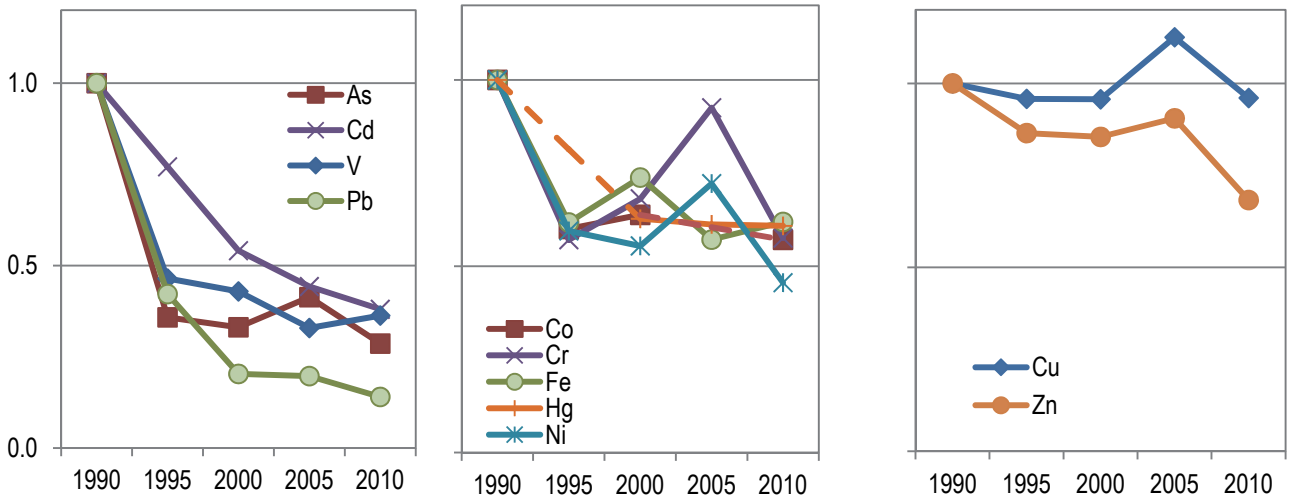


The studies encompassed the following elements: silver, aluminium, arsenic, bismuth, cadmium, cerium, cobalt, chromium, copper, iron, mercury, nickel, lead, selenium, vanadium and zinc. In the case of arsenic, cadmium, copper, nickel, lead and zinc it was possible to compare the concentrations in moss (medians in central plateau, northern Alps, southern Alps) with the levels of deposits recorded in the NABEL network (PAY, RIG, MAG), and the degree of consistency was high.

As was the case in the previous four measurement periods, it was once again apparent in 2010 that the highest medians for all depicted elements were recorded in the southern Alps region (fig. 1). Here, in addition to local emissions, the main contributing factors were high levels of precipitation, the regional topography and long-distance road transport originating from the agglomeration of Milan. The differences between the Jura, central plateau and northern Alps regions were mostly minor, therefore, they have been grouped together in this chapter as a single zone (northern Switzerland). Despite the lower urban density in the northern Alps and Jura regions, the readings are very similar to those recorded in the central plateau. This is probably attributable to the higher levels of precipitation in the northern Alps and Jura, which result in high depositions and can have a pronounced influence on heavy metal concentrations similar to that of urban density in the central plateau. For most elements, the lowest median was recorded in the central Alps (Fig. 1), which is less exposed to long-distance road transport because of its more isolated location.

Fig. 2 > Trend in heavy metal concentrations in the period from 1990 to 2010

Depiction of heavy metal concentrations measured during the five study periods (1990, 1995, 2000, 2005 and 2010). The data were standardised to the concentrations recorded in 1990.



In the period from 1985 to today, numerous industrial facilities both in Switzerland and abroad have either been closed down or renovated, and the combustion of oil products has become cleaner. This reduction in emissions is clearly reflected in the concentrations in moss (Fig. 2). The above graphs show the standardised median for the measured heavy metals distributed according to their behaviour over the course of time.

> Left: concentrations of arsenic, cadmium, vanadium and above all lead have fallen sharply since 1990 (by 71%, 62%, 64% and 86%, respectively).
> Centre: concentrations of cobalt and mercury have also fallen, though not quite as sharply (by 43% and 39%, respectively). Levels of chromium, iron and nickel were

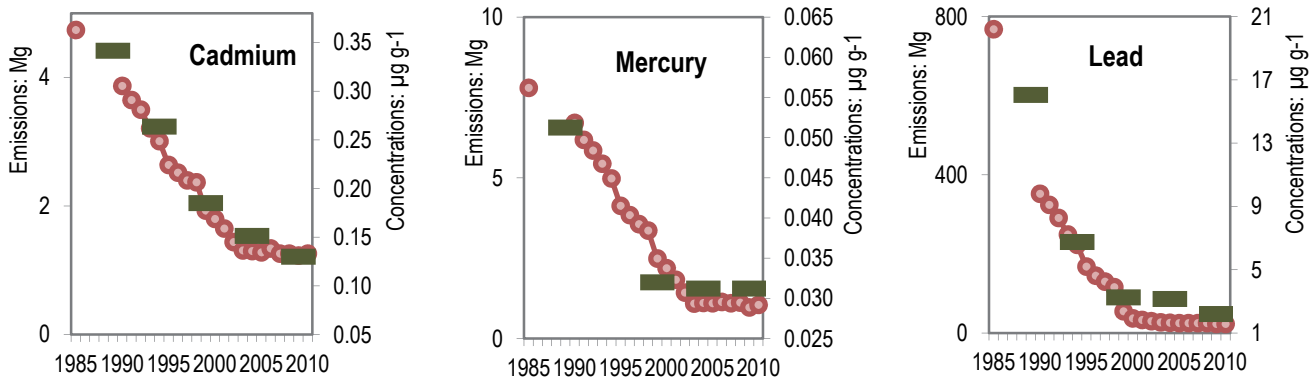
also lower in the later periods versus 1990 (down by 42%, 38% and 54%, respectively), but increases have been recorded again in the meantime.

> Right: The mean concentrations of copper remained more or less constant throughout the five measurement periods, and zinc concentrations only began to decline significantly in the period between 2005 and 2010 (by 32%).

For cadmium, mercury and lead, specific measures to reduce emissions have been taken in the past few years, including the renovation of waste incineration plants (above all, Cd) and crematoria (Hg), and the introduction of lead-free petrol, and the impacts of these measures are clearly reflected in the respective concentrations in moss (Fig. 3).

Fig. 3 > Comparison between concentrations and emissions, 1990 to 2010

Depiction of measured Cd, Hg and Pb concentrations in moss and emissions in Switzerland: red circles = emissions / green bars = moss concentrations.



Source (emissions): 1985: Swiss Federal Statistical Office – Swiss Statistical Encyclopaedia, 1990–2010: FOEN 2102

In a European comparison, somewhat lower levels were recorded in Switzerland for almost all elements. Similar concentrations were often recorded in Austria, while in Norway, concentrations of cadmium were significantly lower and those of mercury were considerably higher. Copper and zinc levels were highest in Germany, while concentrations of most of the other elements were at their highest in the Czech Republic. Throughout Europe, there has been a reduction in concentrations of almost all elements in the past 20 years.

In order to obtain an overview of the overall level of pollution with heavy metals, those elements that are primarily emitted anthropogenically were measured in all five periods and were depicted in accumulated form on a series of maps (Fig. 4). For this purpose the levels for As, Cd, Cu, Pb and Zn were standardised to their geometric average for the five periods, added together for each location and shown in proportion to the spot size. From the maps we can clearly identify the “problem region” (southern Switzerland), as well as the reduction during the past 20 years, and in particular in the period between 1990 and 1995 (see also Fig. 5).

Fig. 4 > Overall pollution with heavy metals in Switzerland

Depiction of overall pollution during the five measurement periods (1990, 1995, 2000, 2005 ad 2010). The levels for anthropogenically influenced elements (As, Cd, Cu, Pb, Zn) were standardised and added together. The spot sizes are roughly proportional to the level of pollution.

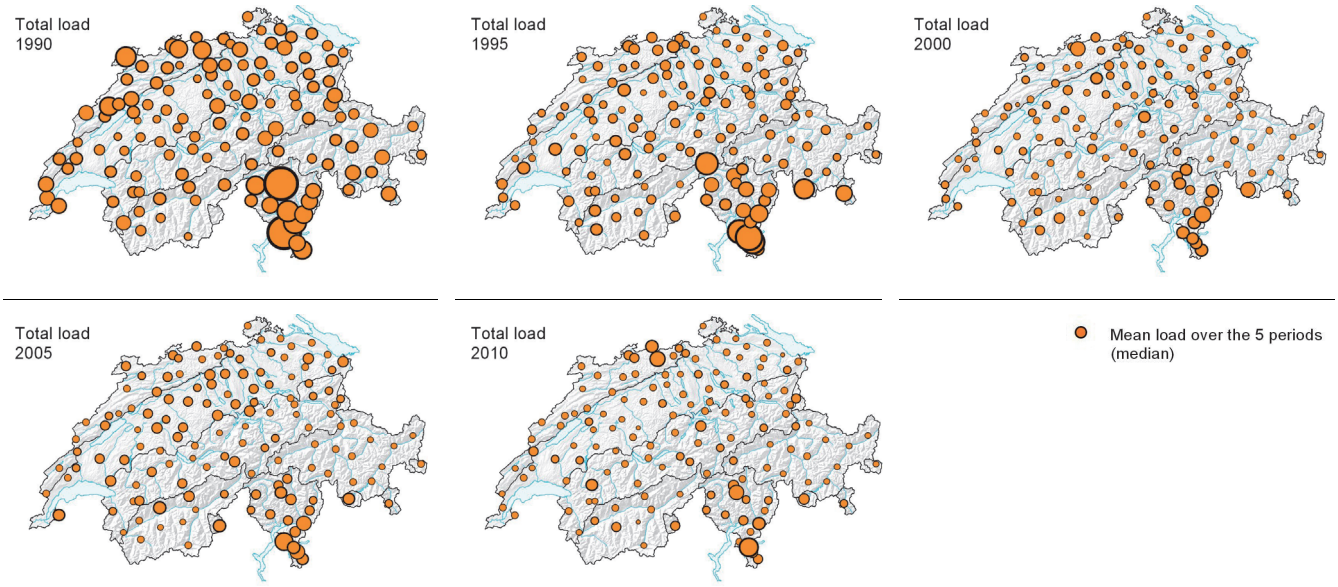
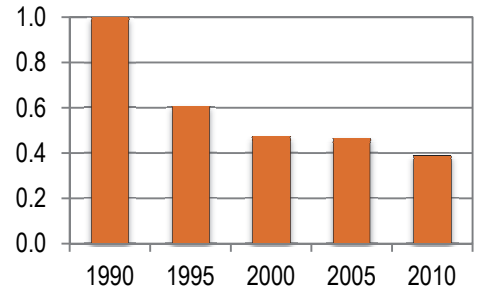


Fig. 5 > Overall pollution with heavy metals in Switzerland

The levels for anthropogenically influenced elements (As, Cd, Cu, Pb, Zn) were standardised and summed up. The diagram shows the median levels of overall pollution for the five measurement periods (1990, 1995, 2000, 2005 and 2010), standardised to 1990.



Nitrogen

In the case of nitrogen a slight increase was recorded between 1995 and 2005, followed by a slight decrease between 2005 and 2010 (Fig. 6). Higher levels were also recorded in southern Switzerland, while the lowest median was noted in the northern Alps (Fig. 7). A comparison between concentrations of nitrogen in moss and in depositions from precipitation shows a strong correlation (Fig. 8).

Fig. 6 > Nitrogen – comparison between three periods (1990, 2005 and 2010)

Depiction of median, maximum and minimum levels for each of the 16 locations. The blue line indicates the natural nitrogen content in mosses.

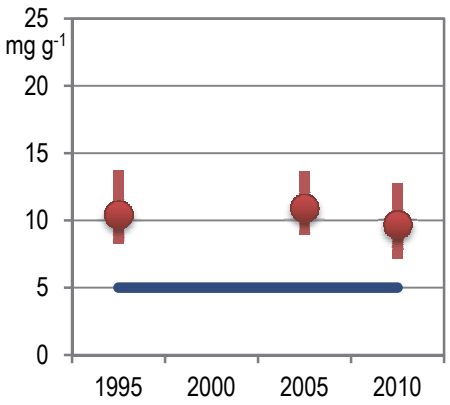


Fig. 7 > Nitrogen concentrations in the five natural regions (2010)

Depicted as box plot, divided into the five natural regions: J = Jura, M = central plateau, N = northern Alps, Z = central Alps, SA = southern Alps.

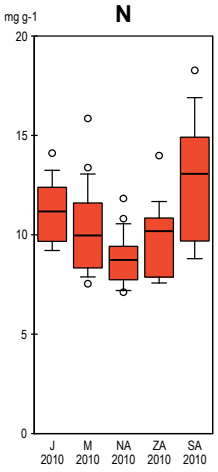
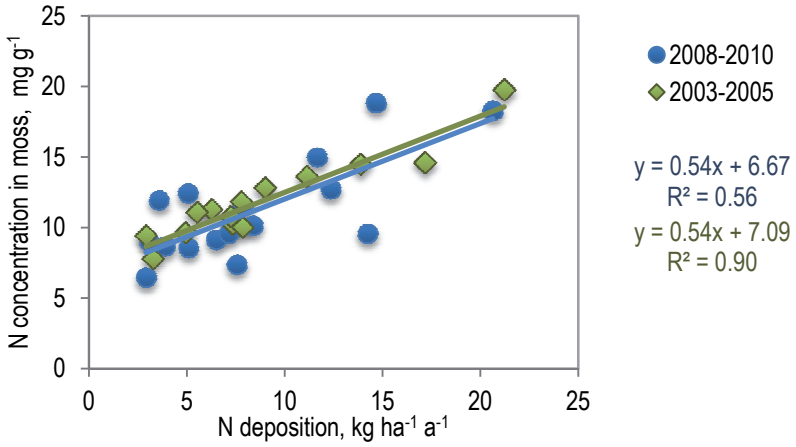


Fig. 8 > Comparison with nitrogen depositions from precipitation (2005 and 2010)

Here a comparison was made between nitrogen concentrations in moss and loads of N as ammonium and nitrate ("bulk") recorded in the vicinity of the moss collection location.



Source: Nitrogen in precipitation, calculated by WSL, IAP, FUB

Sulphur

The sulphur concentration in moss was higher in southern Switzerland than in the central and northern regions, and the same applied to the levels attributable to precipitation. The concentration in moss fell sharply after 1990 (Fig. 9) in southern Switzerland, but not in the other regions, despite significant reductions in sulphur levels in precipitation since 1990. By contrast with nitrogen, the comparison with sulphur deposition in precipitation revealed only a very weak correlation (Fig. 10). Following these measurements it is not clear to what extent the sulphur concentration in moss can be included in the estimate of sulphur deposition.

Fig. 9 > Sulphur concentration in moss (1990 and 2010)

Depiction of heavy metal concentrations measured during the two periods, 1990 and 2010, in the form of a box plot. The data were broken down into three natural regions of Switzerland: NS = northern Switzerland (Jura, central plateau, northern Alps); ZA = central Alps; SA = southern Alps.

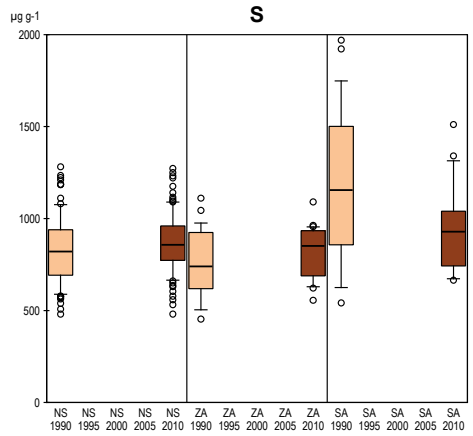
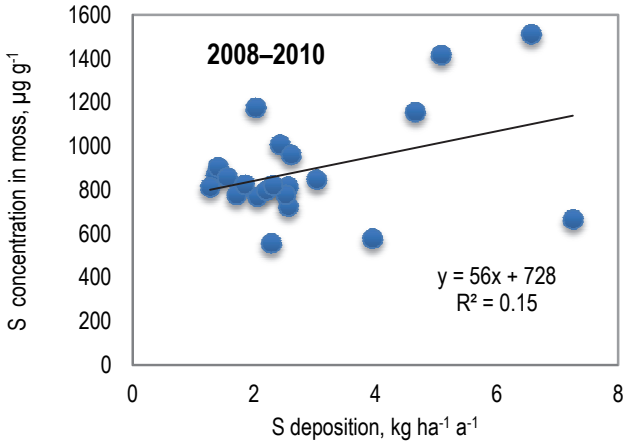


Fig. 10 > Comparison with sulphur deposition from precipitation

A comparison was made between sulphur concentration in moss and the sulphur deposition designated as "bulk" or "wet only" (as sulphate) measured in the immediate vicinity.



Source: Sulphur in precipitation, measured by WSL, IAP, FUB

Polycyclic aromatic hydrocarbons

13 polycyclic aromatic carbons were analysed at 14 locations in the central plateau (SW-NE transect) and at 6 locations in the Basel region. Figure 11 shows the total of these 13 components in map form. As we can clearly see, the concentrations in the western section of the central plateau are lower than in the more densely populated central and eastern sections, and these are mostly lower than those in the Basel region where there is a major chemicals industry. The comparison with 9 polycyclic aromatic hydrocarbons in PM10 at NABEL stations and 13 polycyclic aromatic hydrocarbons in the soil of NABO locations, in each case within a radius of a few kilometres, shows a strong correlation (Fig. 12).

Fig. 11 > Total of polycyclic aromatic hydrocarbons in the central plateau and the Basel region

Depiction of the total of 13 polycyclic aromatic hydrocarbon components in the moss samples collected in 2010. The figures are indicated in µg g^{-1} TS. The spot sizes are roughly proportional to the concentration in moss.

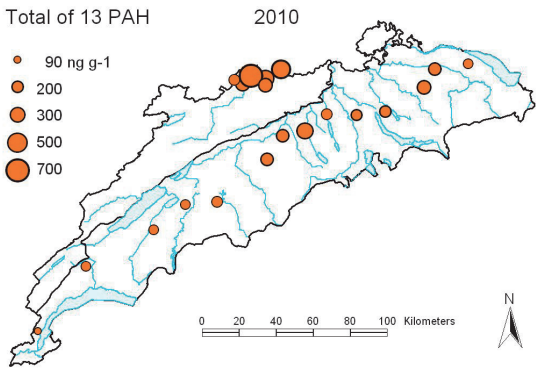
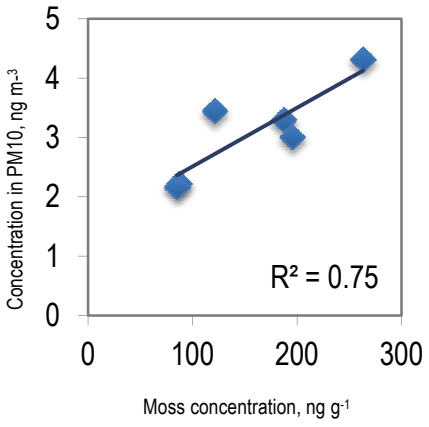
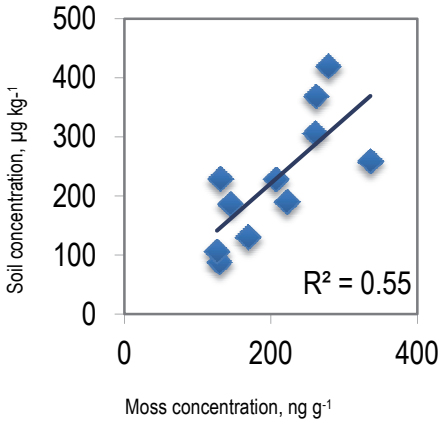


Fig. 12 > Total for polycyclic aromatic hydrocarbons: moss compared with PM10 and soil

Total of 9 polycyclic aromatic hydrocarbons: comparison of levels in moss with those in PM10 at NABEL stations in the vicinity of the moss collection points.



Total of 13 polycyclic aromatic hydrocarbons: comparison of levels in moss (2010) with those in soil (1995–1999) at NABO stations in the vicinity of the moss collection points.



Source of PM10 figures: Gehrig 2011. Source of soil figures, Desaules et al. 2009

Conclusions

This study demonstrates once again that, using the relatively favourable moss analysis method it is possible to fairly accurately estimate both regional differences as well as the trend in deposition over the course of time for a broad variety of metals and for nitrogen. In this way it has been possible to document the impacts of measures aimed at reducing emissions. The applied method can therefore be used for carrying out success controls in the area of environmental protection. Mosses are also suitable for monitoring levels of polycyclic aromatic hydrocarbons.

For a repeat of the study in 2015 less sites would be sufficient for heavy metals. Within these sites, the calculation of nitrogen concentrations can support the implementation of a success control concerning measures taken in the future with the aim of reducing nitrogen oxide and ammoniac emissions, and it is also possible to monitor the trend in polycyclic aromatic hydrocarbon immissions with the aid of moss analyses.