Deposition of atmospheric pollutants in Switzerland

Chemical analysis of mosses 1990 – 2015

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

Coordinated by the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation, http://icpvegetation.ceh.ac.uk) – a sub-programme under the UNECE Convention on Long-Range Transboundary Air Pollution (LRTAP Convention) – environmental heavy metal deposition has been surveyed in Europe using chemical moss analysis since 1990. In 2015 (following similar studies in 1990, 1995, 2000, 2005 and 2010), 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 using mosses (*Hypnum cupressiforme* or *Pleurozium schreberi*) as accumulative biomonitors. Additionally, a number of countries, including Switzerland, measured polycyclic aromatic hydrocarbons (PAHs) in mosses in 2010 and 2015, and polychlorinated biphenyls (PCBs) in 2015. Alongside Switzerland, 24 western and central European countries, eight Asian countries and Canada took part in the 2015 survey. In 12 countries, including Switzerland, nitrogen content was determined in addition to the metals, and in six countries the level of persistent organic pollutants (POPs) was also measured.

Mosses are a particularly suitable vehicle for this study because they draw water, as well as all nutrients and pollutants, directly from the atmosphere since they don't have 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 approximately 400 to 600 metres above the valley floor but below the tree line were selected. The various samples were collected from forest clearings (rejuvenated areas), moors and Alpine meadows. At each location, five sub-samples were collected.

The moss samples were then processed (removal of pine needles etc., selection of portions of growth from the last three years) and the metals were digested in a microwave oven and subsequently analysed by means of ICP-MS; mercury was analysed using DMA-80; PAHs and PCBs using HPLC/FLD and nitrogen using a vario PYRO cube elemental analyser. For the purpose of quality assurance, blank values, reference material and retained samples were analysed and multiple measurements were carried out.

Metals

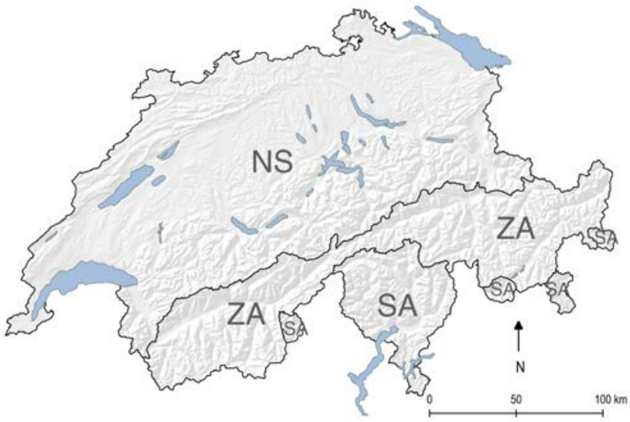
The studies encompassed the following elements: silver (Ag), aluminium (Al), arsenic (As), bismuth (Bi), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), molybdenum (Mo), nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), vanadium (V) and zinc (Zn). In addition, barium (Ba), caesium (Cs), strontium (Sr), thallium (Ti) and uranium (U) were measured in regional composite samples from 1990 to 2015. The concentrations of As, Cd, Cu, Ni, Pb and Zn in moss (medians in central plateau, northern Alps and southern Alps) were compared with the levels of depositions recorded in the NABEL network (locations in Payerne, Rigi-Seebodenalp and Magadino) and the degree of consistency was good. A comparison of temporal changes in Cd, Hg and Pb in mosses with Switzerland's emission of these substances shows parallel declines.

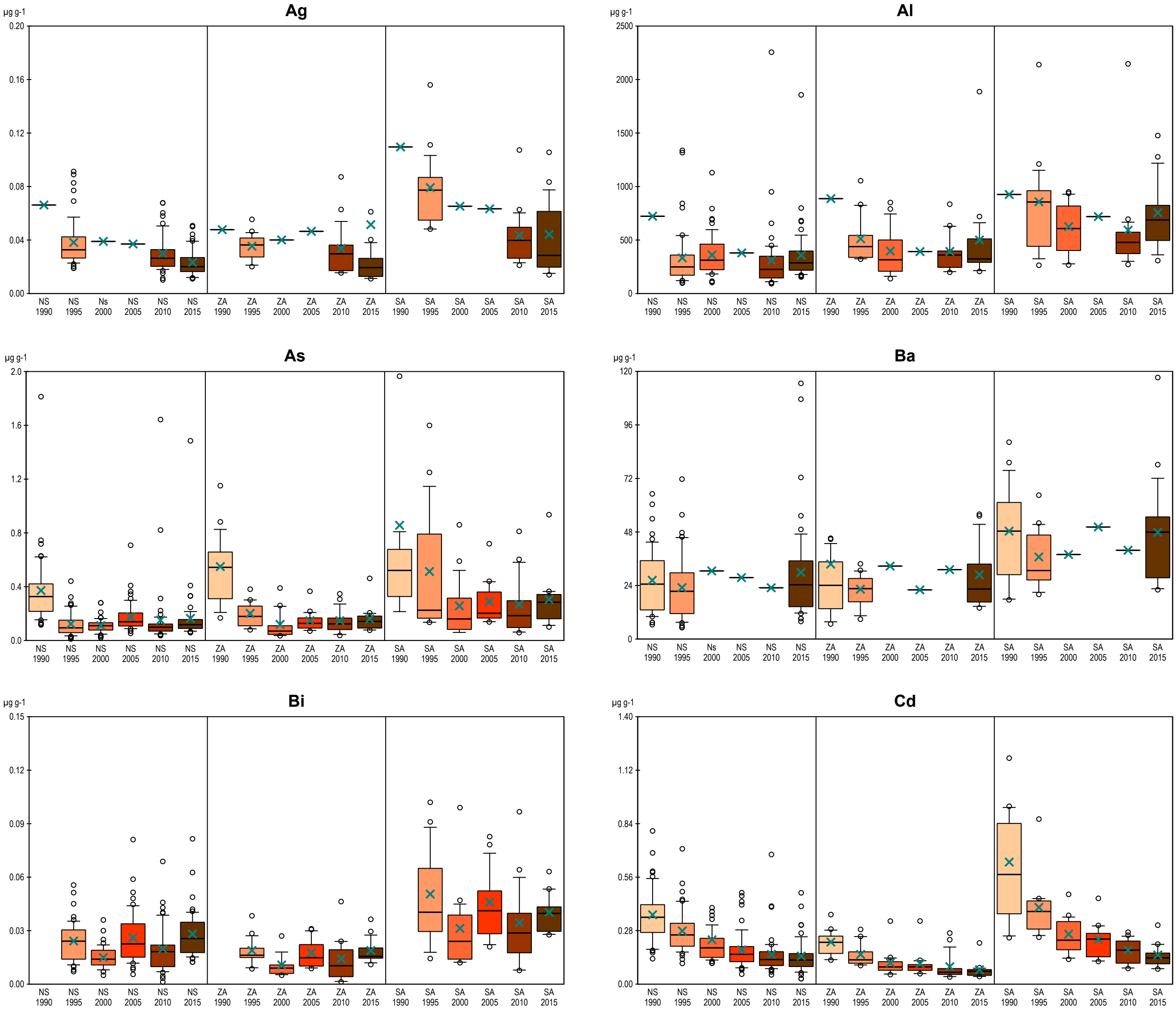
As was the case in the five previous surveys, it was once again apparent in 2015 that the highest medians were for the most part recorded in the southern Alps region (Figure 1). Here, in addition to local emissions, the main contributing factors were high levels of precipitation, the regional topography and long-range transport of pollutants coming from the agglomeration of Milan and the Po Plain. The differences between the Jura, central plateau and northern Alps were mostly minor; they have therefore 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 values are very similar to those recorded in the central plateau. This can probably be attributed to the higher levels of precipitation in the northern Alps and Jura, which result in high depositions. This can have a marked influence on metal concentrations similar to that of urban density in the central plateau. For most elements, the lowest median was recorded in the central Alps. This region is less affected by long-range transport due to its isolated location (high mountains on both sides), and is also less populated.

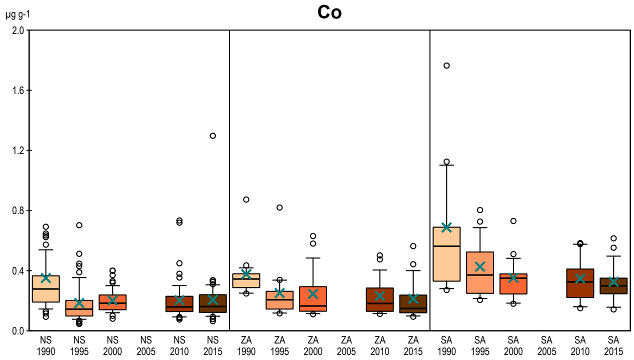
Figure 1

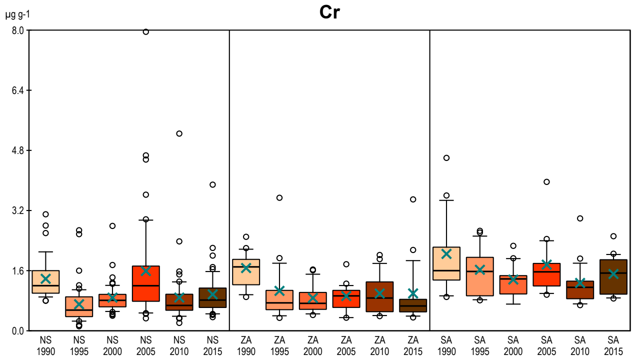
Concentration of surveyed metals depicted as box plots

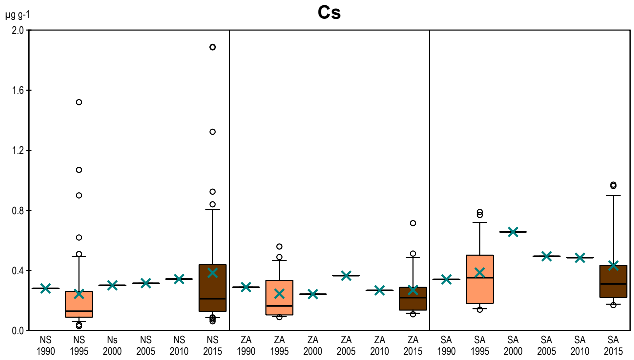
Graph showing metal concentrations measured during the six surveys 1990, 1995, 2000, 2005, 2010 and 2015. The data are grouped into three natural regions of Switzerland: NS: northern Switzerland (Jura, central plateau, northern Alps); ZA: central Alps; SA: southern Alps. Where only the median is shown, it is the result of a composite sample. Concentrations in µg per gram of dry matter.

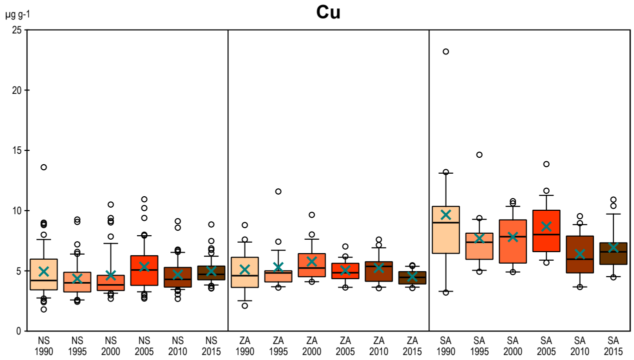


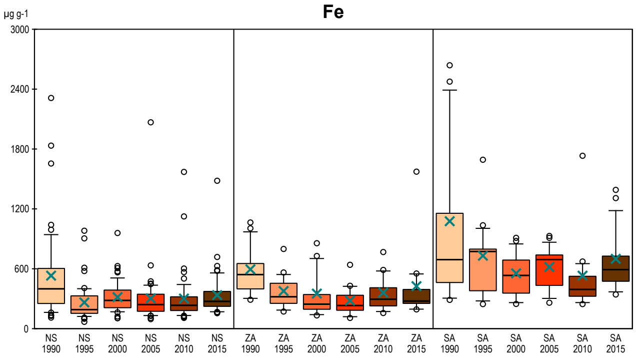


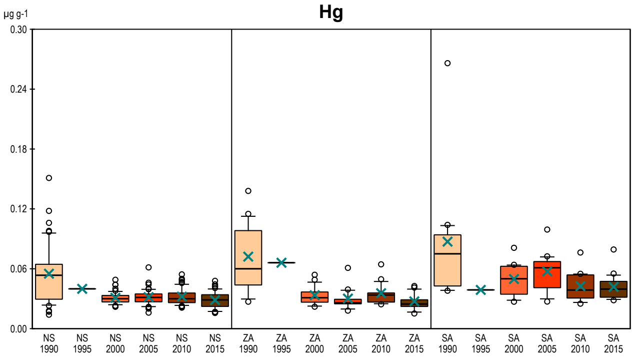

Co
µg g-1
2.0
1.6
1.2
0.8
0.4
0.0
NS 1990 NS 1995 NS 2000 NS 2005 NS 2010 NS 2015 ZA 1990 ZA 1995 ZA 2000 ZA 2005 ZA 2010 ZA 2015 SA 1990 SA 1995 SA 2000 SA 2005 SA 2010 SA 2015

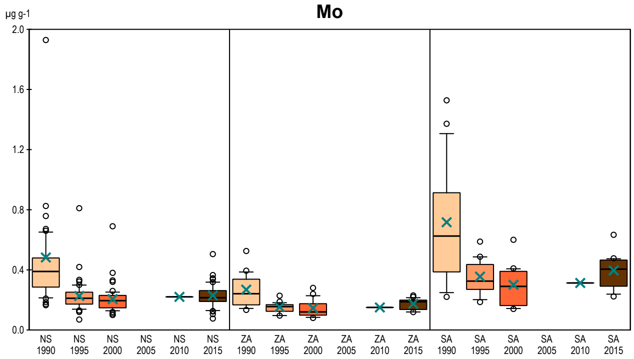

Cr
µg g-1
8.0
6.4
4.8
3.2
1.6
0.0
NS 1990 NS 1995 NS 2000 NS 2005 NS 2010 NS 2015 ZA 1990 ZA 1995 ZA 2000 ZA 2005 ZA 2010 ZA 2015 SA 1990 SA 1995 SA 2000 SA 2005 SA 2010 SA 2015

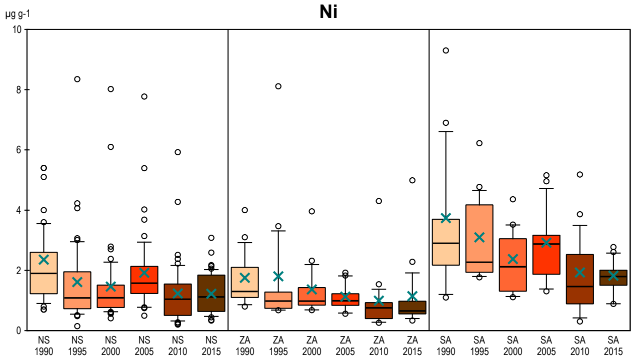

Cs
µg g-1
2.0
1.6
1.2
0.8
0.4
0.0
NS 1990 NS 1995 Ns 2000 NS 2005 NS 2010 NS 2015 ZA 1990 ZA 1995 ZA 2000 ZA 2005 ZA 2010 ZA 2015 SA 1990 SA 1995 SA 2000 SA 2005 SA 2010 SA 2015

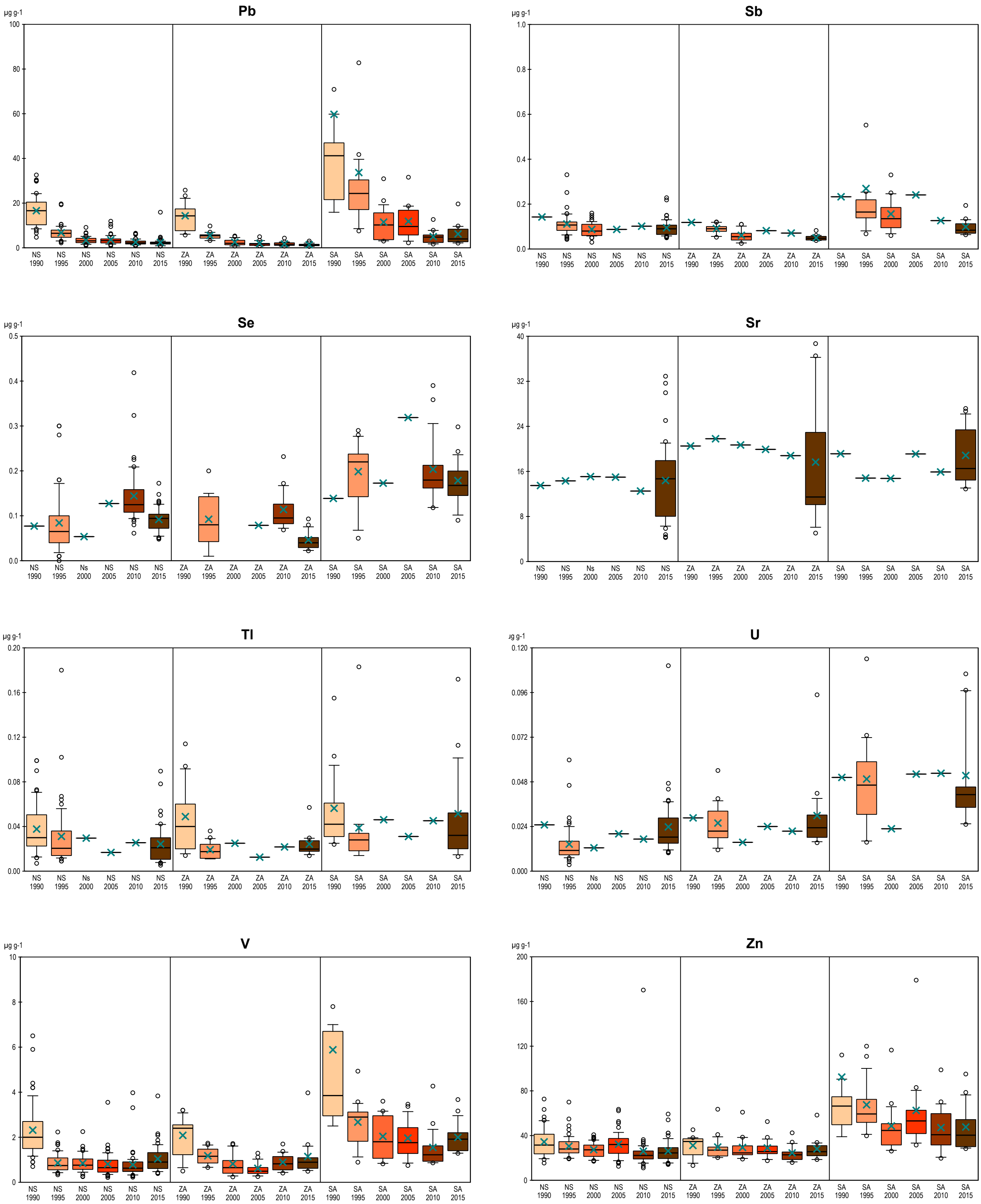

Cu
µg g-1
25
20
15
10
5
0
NS 1990 NS 1995 NS 2000 NS 2005 NS 2010 NS 2015 ZA 1990 ZA 1995 ZA 2000 ZA 2005 ZA 2010 ZA 2015 SA 1990 SA 1995 SA 2000 SA 2005 SA 2010 SA 2015


Fe
µg g-1
3000
2400
1800
1200
600
0
NS 1990 NS 1995 NS 2000 NS 2005 NS 2010 NS 2015 ZA 1990 ZA 1995 ZA 2000 ZA 2005 ZA 2010 ZA 2015 SA 1990 SA 1995 SA 2000 SA 2005 SA 2010 SA 2015


Hg
µg g-1
0.30
0.24
0.18
0.12
0.06
0.00
NS 1990 NS 1995 NS 2000 NS 2005 NS 2010 NS 2015 ZA 1990 ZA 1995 ZA 2000 ZA 2005 ZA 2010 ZA 2015 SA 1990 SA 1995 SA 2000 SA 2005 SA 2010 SA 2015


Mo
µg g-1
2.0
1.6
1.2
0.8
0.4
0.0
NS 1990 NS 1995 NS 2000 NS 2005 NS 2010 NS 2015 ZA 1990 ZA 1995 ZA 2000 ZA 2005 ZA 2010 ZA 2015 SA 1990 SA 1995 SA 2000 SA 2005 SA 2010 SA 2015


Ni
µg g-1
10
8
6
4
2
0
NS 1990 NS 1995 NS 2000 NS 2005 NS 2010 NS 2015 ZA 1990 ZA 1995 ZA 2000 ZA 2005 ZA 2010 ZA 2015 SA 1990 SA 1995 SA 2000 SA 2005 SA 2010 SA 2015


Pb
Sb
Se
Sr
Tl
U
V
Zn
μg g-1
NS 1990 NS 1995 NS 2000 NS 2005 NS 2010 NS 2015
ZA 1990 ZA 1995 ZA 2000 ZA 2005 ZA 2010 ZA 2015
SA 1990 SA 1995 SA 2000 SA 2005 SA 2010 SA 2015

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 petroleum products has become cleaner. These efforts to reduce emissions are clearly reflected in the moss concentrations, with only a few exceptions. Figure 2 shows the temporal trend of the standardised median of the measured metals grouped according to their behaviour over time.

Top: Ag, Al, Co, Fe, Mo, Sb and Zn have fallen since 1990 (–54 %, –42 %, –45 %, –36 %, –49 %, –42 % and –31 %, respectively), although the decreases were not always continuous. Only Cu shows a more or less unchanged development since 1990 (–9 %).

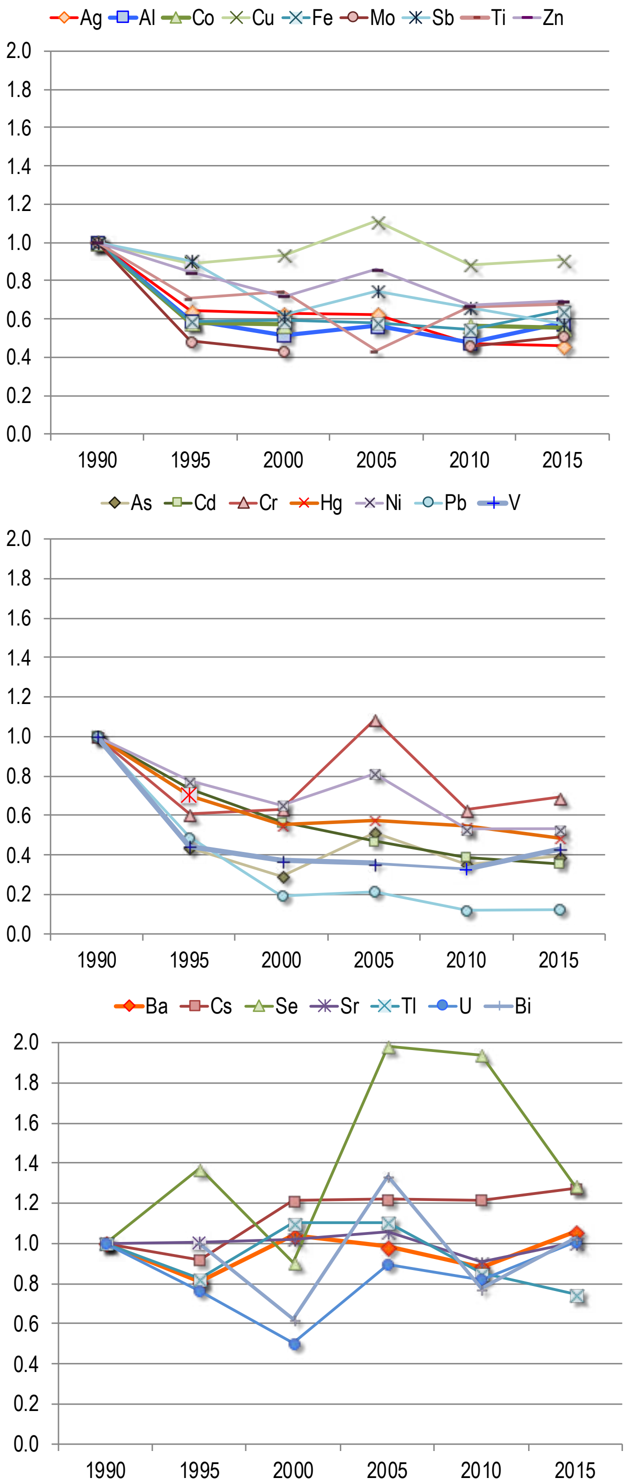
Middle: As, Cd, Cr, Hg, Ni, Pb and V have also fallen since 1990, with the concentrations decreasing by more than half in most cases (–62 %, –65 %, –31 %, –51 %, –47 %, –88 % and –57 % respectively). The sharpest and most continuous decrease was recorded for Pb.

Bottom: The median concentrations of Ba, Cs, Se, Sr, and U remained in the same range or increased slightly over the six surveys (+6 %, +27 %, +29 %, 0 % and 1 % respectively). Tl shows a decline (–32 %). The concentrations of Se and U fluctuated sharply over the six surveys. A possible explanation is that the values for these elements were low.

Figure 2

Trend in metal concentrations in the period from 1990 to 2015

Graphs showing metal concentrations measured during the six surveys 1990, 1995, 2000, 2005, 2010 and 2015. The values were standardised to the concentrations recorded in 1990.

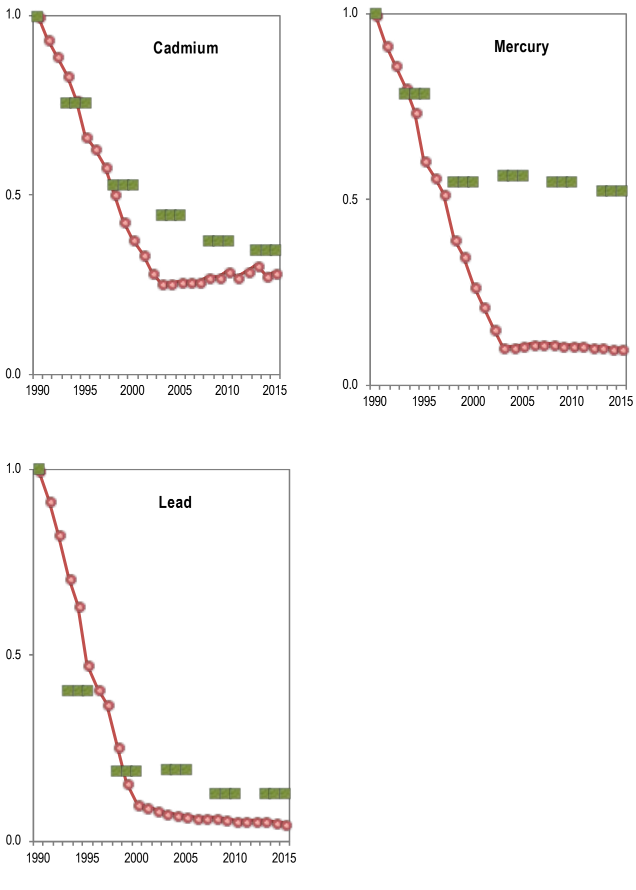


For Cd, Hg and Pb, specific measures to reduce emissions have been implemented in recent decades. These include the renovation of waste incineration plants (mainly Cd) and crematoriums (Hg) as well as the introduction of unleaded petrol. The resulting reduction in emissions is clearly reflected in the measured concentrations in moss (Figure 3), except for Hg, for which the emission reduction after 2000 cannot be seen in mosses. This could be due to the evaporation of existing mercury from soil or long-range transport.

Figure 3

Comparison with emissions in the period from 1990 to 2015

Graph showing the measured concentrations of Cd, Hg and Pb in moss and emissions in Switzerland, standardised to the values of 1990. Circles = emissions, bars = moss concentrations.



Source of emissions data: Swiss emission inventory, FOEN 2017

In order to obtain an overview of the overall level of heavy metal pollution, the elements As, Cd, Cr, Ni, Pb and V are presented cumulatively (Figure 4, Figure 5). These elements are mainly anthropogenic, are toxic in small quantities and were measured in all six surveys. The values were standardised to their geometric average for the six surveys, added together for each location and shown in proportion to the spot size. On the maps we can clearly see the highest concentrations in southern Switzerland, as well as the Switzerland-wide decline over the last 25 years (Figure 5). For the elements As, Co, Cr, Hg, Pb, Tl and V, it can be assumed that the anthropogenic influence decreased between 1995 and 2015. An indication of this is the increased correlation of these elements with aluminium, which in Switzerland is predominantly emitted by geogenic sources, with anthropogenic sources only secondary.

Figure 4

Overall pollution in Switzerland with toxic, anthropogenically influenced heavy metals

The levels of toxic, mainly anthropogenically influenced elements (As, Cd, Cr, Ni, Pb, V) were standardised and added together. The chart shows the median levels of overall pollution for the six surveys 1990, 1995, 2000, 2005, 2010 and 2015, standardised to 1990.

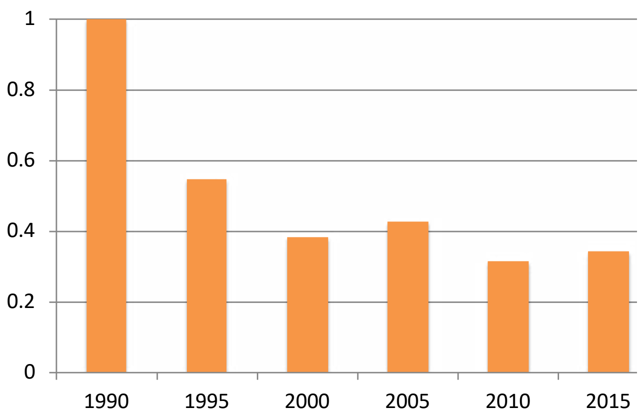
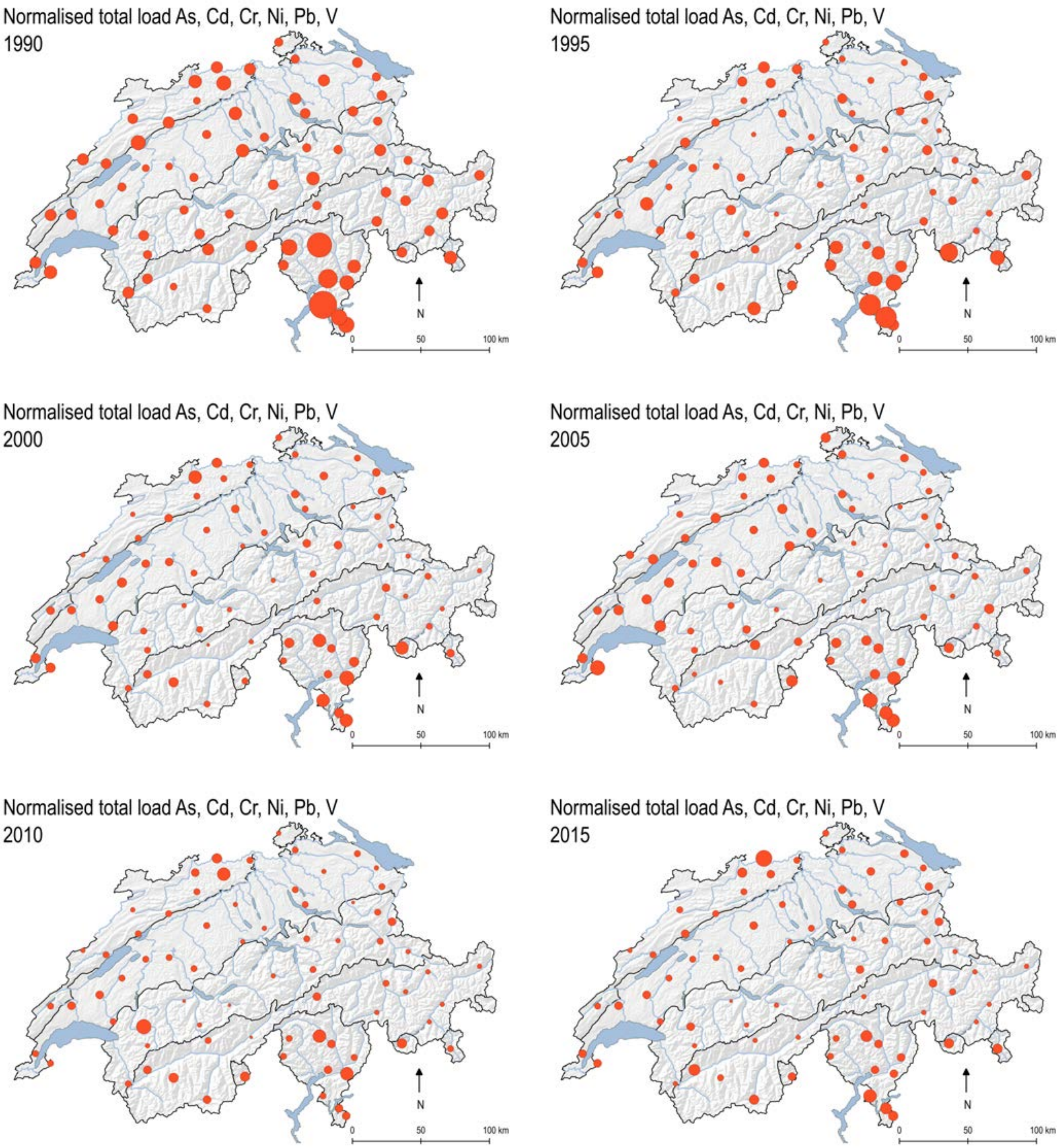


Figure 5

Overall pollution in Switzerland with toxic, anthropogenically influenced heavy metals

Map of total pollution for the six surveys 1990, 1995, 2000, 2005, 2010 and 2015. The levels of toxic, mainly anthropogenically influenced elements (As, Cd, Cr, Ni, Pb, V) were standardised and added together. Spot sizes are proportional to the pollution level.



Compared with a number of other European countries, lower levels of virtually all elements were measured in Switzerland. Similar concentrations were often found in Austria and levels were often lower in Norway, except for mercury where they were much higher than in Switzerland. Germany had the highest levels of copper and zinc, while the Czech Republic recorded the highest values for most other elements. High levels were often also found in Slovenia. Across Europe, the levels of almost all elements have declined over the past 25 years.

Nitrogen

Nitrogen concentrations have barely changed since 1995, but if anything have tended to increase slightly (Figure 6).

In the 2015 survey, the regional distribution of nitrogen was similar to that of metals, with the highest median values measured in southern Switzerland, and the lowest concentrations in the central Alps. Unlike metals, relatively low values were also found in the northern Alps (Figure 7). The highest level measured in the study was found in the central plateau, which is hardly surprising given the intensive agriculture in this region.

Figure 6

Comparison of nitrogen concentrations in the four surveys 1995, 2005, 2010 and 2015

Measured nitrogen concentrations depicted as box plots. Only the locations that were surveyed in all four surveys are included (n = 10). The green line represents the natural nitrogen content in moss (5 mg g⁻¹).

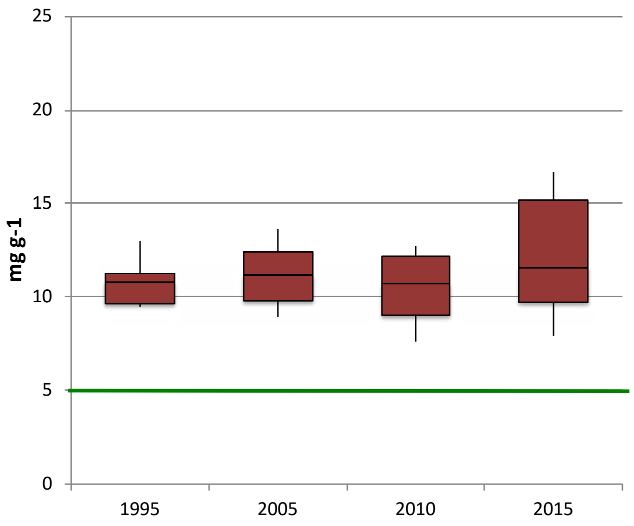
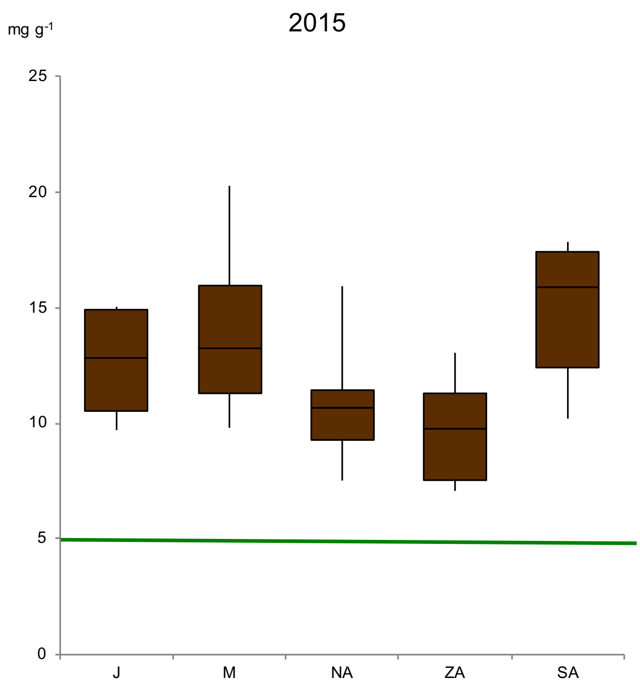


Figure 7

Nitrogen concentrations in the five natural regions (2015)

Depicted as a box plot, divided into the five natural regions: Jura (J, n = 7), central plateau (M, n = 17), northern Alps (NA, n = 15), central Alps (ZA, n = 10) and southern Alps (SA, n = 6). The green line represents the natural nitrogen content in moss (5 mg g⁻¹).



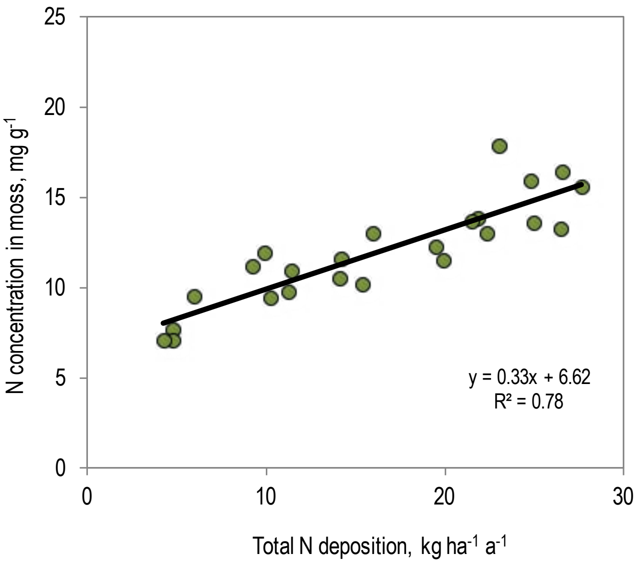
In 2014, Switzerland's total nitrogen deposition was measured in the context of a Switzerland-wide project. To this end, nitrogen components in the air were measured using active and passive sampling techniques for calculating total deposition (Seitler et al. 2016)[1]. These data were compared to the nitrogen concentrations in moss in the vicinity of the monitoring sites at 24 locations and a strong correlation was found (Figure 8).

1 Seitler E., Thöni L., Meier M. 2016: Atmosphärische Stickstoff-Deposition in der Schweiz 2000 bis 2014. FUB – Forschungsstelle für Umweltbeobachtung , Rapperswil. 105 p.

Figure 8

Comparison with total nitrogen deposition at 24 locations

Comparison of nitrogen concentration in moss with total nitrogen deposition (ammonium and nitrate in precipitation, gaseous ammonia, nitrogen dioxide, nitric acid as well as ammonium and nitrate in aerosols).



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

PAHs – polycyclic aromatic hydrocarbons

Fourteen different PAHs were analysed in moss samples from 22 locations throughout Switzerland. Figure 9 shows the total of these 14 substances in map form. We can see that some locations have higher values, mostly in the regions of Basel, Lake Constance, the western central plateau and southern Ticino. Inner Alpine regions tend to have lower concentrations, but there are no clear differences in the overall concentrations within the individual natural regions. If we compare the PAH concentrations with the values from the 2010 study, we see that PAH pollution has declined in some locations and stayed the same in others (Figure 10). The regional differences detected in 2010 seem to be disappearing. However, it should be noted that the proportions of the particular PAHs at the individual locations vary widely.

Figure 9

Total PAH concentrations in Switzerland

Map of the total of 14 PAH components in the moss samples collected in 2015. The values are indicated in ng g^{-1} TS. Spot sizes are proportional to the concentrations in moss.

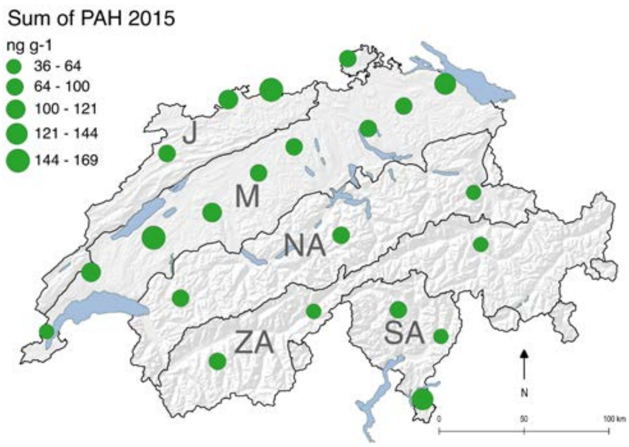
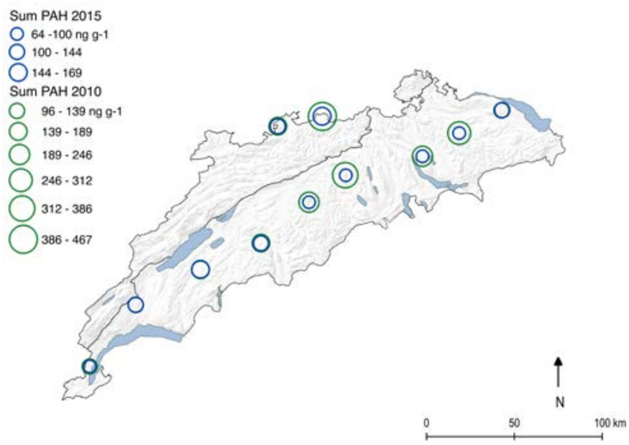


Figure 10

Comparison of total PAH concentrations in 2010 and 2015

Map of the total concentrations of the 9 PAHs that were measured in 2010 and 2015. Only the locations that were included in both surveys are taken into account. The values are indicated in ng g^{-1} TS. Spot sizes are proportional to the concentrations in moss.



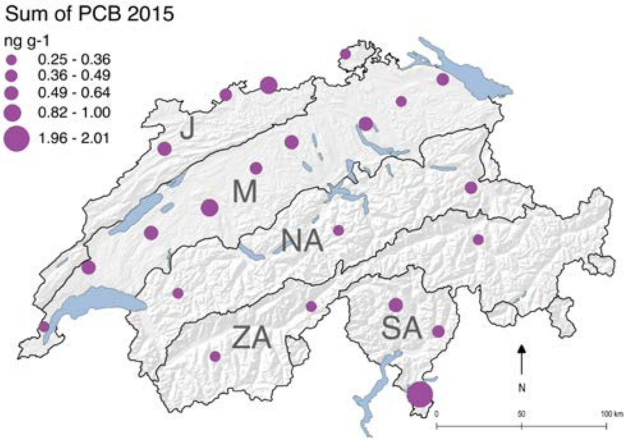
PCBs – polychlorinated biphenyls

PCBs were measured at the same 22 locations as PAHs. The concentrations of all measured PCBs were relatively close to the detection limit of the method used. Values from samples taken from the northern and central Alps were lowest; intermediate values were measured in the central plateau and the Basel region; and the highest value was detected in southern Ticino (Figure 11). Unfortunately, there are no comparable studies for the given time period to place the levels of PCBs in Swiss moss in a broader context. However, PCB concentrations in Switzerland are similar to those in Germany, but are significantly higher than those in Norwegian moss.

Figure 11

Comparison of total PCB concentrations in 2015

Map of the total PCB concentrations measured in 2015. The values are indicated in ng g^{-1} TS. Spot sizes are proportional to the concentrations in moss.



Conclusions

This report shows the spatial distribution and temporal trends of concentrations of metals, nitrogen and POPs in Switzerland's moss. Pollution from Ag, As, Cd, Hg, V and particularly Pb has sharply and significantly declined in the last 25 years (decrease of between 51 % and 88 %), and the concentrations of Al, Co, Cr, Fe, Mo, Ni, Sb, Tl and Zn have also decreased (by between 31 % and 49 %). These values show that emission reduction measures are effective. The concentrations of Bi, Cu and Se have not declined over time, but hardly any abatement measures for these elements have been taken either. Levels of Ba, Cs, Sr and U have barely changed, but the concentrations in moss are mainly of natural origin. With regard to spatial distribution, it should be noted that irrespective of the element, in all surveys the highest values were usually recorded in southern Switzerland and the lowest in the central Alps.

The analysis of nitrogen (N) in moss allows conclusions to be drawn regarding nitrogen pollution in ecosystems, although nitrogen concentrations have changed little since 1995. For nitrogen too, levels are highest in the southern Alps and much lower in the northern and central Alps. Compared with 2010, PAH concentrations in moss have mostly fallen. These decreases were also detected in PM10 measurements in independent studies. Unfortunately, PAHs have only been surveyed using the moss method since 2010, so no conclusions can yet be drawn for longer periods of time.

Thanks to this study, it was possible to estimate the regional atmospheric deposition of various elements and compounds with the aid of moss analysis, and to make comparisons with other European countries. The changes compared to previous surveys were used as a basis to gauge the success of measures to reduce emissions. The survey also provides reference data for the Swiss Soil Monitoring Network (NABO) and for further studies. The methods used can be recommended to monitor the success of measures to reduce emissions.