Progress report on heavy metal trends at ICP IM sites

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Introduction

Long-range atmospheric transport of heavy metals has increased the exposure to forest ecosystems. Therefore trends of heavy metals have been included within the International Cooperative Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems (ICP IM) to support the Convention on Long-Range Transboundary Air Pollution on Heavy Metals (UNECE 2003). Such evaluations would preferably be based on a catchment concept that provides well-defined boundaries of the systems considering inputs and outputs. Such investigations are comprehensive, but the ICP IM for the UNECE region made it possible to perform Europe-wide comparisons of sites in various climates and exposure to pollution loads. Evaluations of temporal trends within ICP IM have been done in subprogrammes for precipitation chemistry (PC), throughfall (TF), litterfall (LF), runoff water (RW) and soil chemistry (SC). Catchment budgets show an ongoing accumulation of heavy metals and the release (RW) seldom exceeds input (PC + TF + LF) (Aastrup et al. 1991, Ukonmaanaho et al. 2001, Grigal 2002, Bringmark et al. 2013). The build up of heavy metals in soil stores, reflected in SC, are to a large degree dependent on long-term and long-range atmospheric transport (Lundin et al. 2001, Steinnes and Friedland 2006).

Priority heavy metals within CLRTAP and ICP IM are mercury (Hg), lead (Pb) and cadmium (Cd) (Sliggers and Kakebeeke, 2004). Reported data in SC, PC, TF, LF and RW at European sites were evaluated to test for the occurrence of temporal changes/trends in metal concentrations. At Swedish ICP IM-sites (Aneboda, Gårdsjön, Kindlahöjden and Gammtratten) soil samples have been collected with regular intervals over the last decades and were tested for temporal trends in more detail. We showed that heavy metal soil stores and concentrations in both input and release of Pb and Cd were decreasing at Swedish IM-sites. On the other hand, concentrations of Hg in soil, surprisingly still increased. For all priority heavy metals input still exceeded output.

Material and methods

Data reported to the ICP IM Programme Centre at the Finnish Environment Institute (SYKE, Helsinki, Finland) were used for the evaluation of temporal trends. Trends in heavy metal soil concentrations (SC) were evaluated at IM sites across Europe but the annual transport on PC, TF, LF and RW were evaluated only at Swedish IM sites. Temporal trends of heavy metal concentrations were estimated by simple linear regression between sampling year and metal concentrations for each site. Reported SC at IM-sites outside Sweden showed sampling frequency between two and three (at a few occasions four) times between 1994 and 2011. Within soil profiles there were only one value from each soil depth reported at each time, except from Sweden where 6 samples from soil plots (50 * 50 m) taken every 5-10 year.

SC heavy metal concentrations were determined in four soil layers, i.e. litter+organic layer, 0-5 cm depth, 10-20 cm depth, 30-50 cm depth and 50- cm depth and used for the trend analysis. At the four Swedish IM-sites, linear regressions were used to determine temporal trends of soil metal concentrations in three layers, i.e. the FH-layer, and mineral soil at 0-5 cm and 10-20 cm depths.

For SC, Sweden excluded as separately assessed, temporal changes at each IM-site and soil depth were attributed with a symbol indicating either an increase (+) or decrease (-) in metal concentration over time. Strength of the changes were indicated with either one (+/-), two (++ / --) or three (+++ / ---) symbols. Often, the regressions were based on one sample from each of two years. Given the uncertainty for this type of data any changes between the sampling years were given one symbol for the change (+ / -). With more than two years of sampling, or several samples from each soil depth, the goodness of fit (R^2) was used to determine the number of symbols for indication of temporal changes. For regression for temporal changes with $R^2 > 0.7$, the change was given three symbols while temporal changes with $0.3 < R^2 < 0.7$ were indicated with two symbols. Temporal change with an $R^2 < 0.3$, or one sample from each of two years sampling occasions, was indicated with a single symbol (+ / -). The number of increasing (+) and decreasing (-) trends from all IM-sites were counted and summed up for each soil depth. To test for the significance of temporal change in soil metal concentrations the proportion of sites with increasing metal concentration was tested with the exact binomial test (Conover, 1971) with the null hypothesis (H_0 : prop ≤ 0.5) and alternative hypothesis (H_1 : prop > 0.5). This was done to indicate the occurrence of an increasing (H_1) or decreasing (H_0) change of metals for each soil depth.

Results and discussion

Trends in soil metal concentrations Europe, Sweden excluded

Significant changes were estimated from the proportion of symbols (+ and -) in the forest floor layer (litter + organic topsoil) compared to the equal proportion (indicating no change), which revealed the results Hg (2 / 4 = 0.5) , Pb (13 / 21 = 0.62) or Cd (13 / 20 = 0.65) (Table 1). In the upper mineral soil layer (0-5 cm), significant accumulations of Hg (4 / 4 = 1) and Pb (12 / 12 = 1) could be observed over time while the temporal change for Cd was weaker (6 / 9 = 0.67). There were more indications of increasing than decreasing trends on Cd, even though the proportion between increases and decreases at sites were not significant.

Table 1. The proportion of number indicating increasing (+) and decreasing (-) temporal changes in Hg, Pb and Cd soil concentrations

Soil layer, cm	Hg		Pb		Cd	
	+	-	+	-	+	-
Litter + organic topsoil	2	2	13	8	13	7
5	4	0	12	0	6	3
10-20	2	1	9	9	12	7
30-50	0	6	15	13	8	6
50-	1	1	9	6	9	3

Sweden

For Swedish IM-sites Pb concentrations in the forest floor (F+H-horizons) decreased between 1994 and 2011 in site Aneboda, Gårdsjön and Kindla. For Cd, content decreased at Aneboda and Gårdsjön. Mercury concentrations, on the other hand increased over the same period in

Gårdsjön and Kindlahöjden. At Gammtratten there were no resampling done so no time trend in the F+H-horizons could be analysed.

In mineral soil layers, at a depth between 0 and 5 cm, Pb increased in sites Gårdsjön and Gammtratten where also Cd increased as well as in site Kindla. In site Kindla, also Hg concentration increased in the upper mineral soil horizon.

In deeper mineral soil layers (5 - 20 cm), Pb concentrations increased significantly at all Swedish IM-sites (Fig. 1). Hg concentration also showed increased values in the mineral soil at 5 - 20 cm depth in site Kindla. No significant changes in Cd concentrations could be seen in the lower parts of the mineral soil at any site.

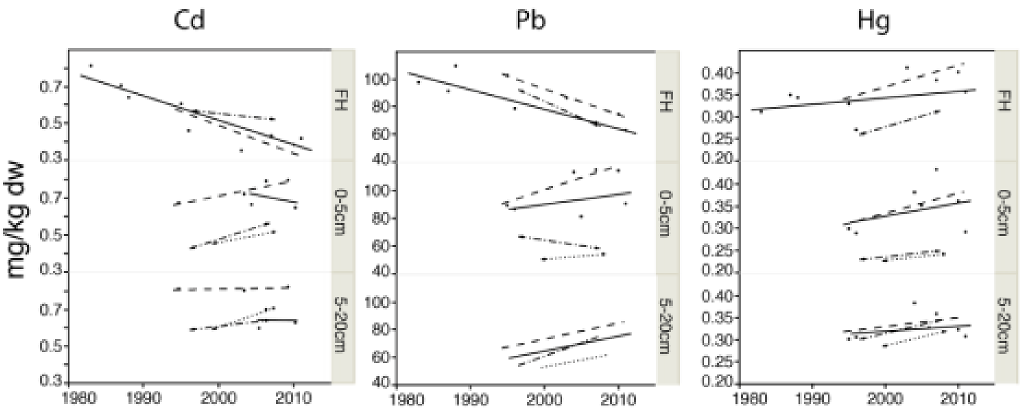

Figure 1. Soil metal concentrations at the four ICP IM sites in Sweden (Aneboda (solid line) , Gammtratten (dotted line), Gårdsjön (dashed line), Kindla (dotdashed line)).

Trends in stream water heavy metal concentrations

Temporal trends in stream water metal concentrations were not possible to evaluate for most sites since the extracted part of the reported data covered only short sampling periods at IM-sites outside Sweden (2008-2010) (Fig. 2). At Swedish IM-sites samples were collected and analyzed every month from 1994 to 2013. Cadmium concentrations decreased at site Kindla and for site Gårdsjön while no significant changes were observed at the other two sites. No significant trends could be seen for Pb and Hg at the Swedish sites, except for Hg at site Gårdsjön, where concentrations increased.

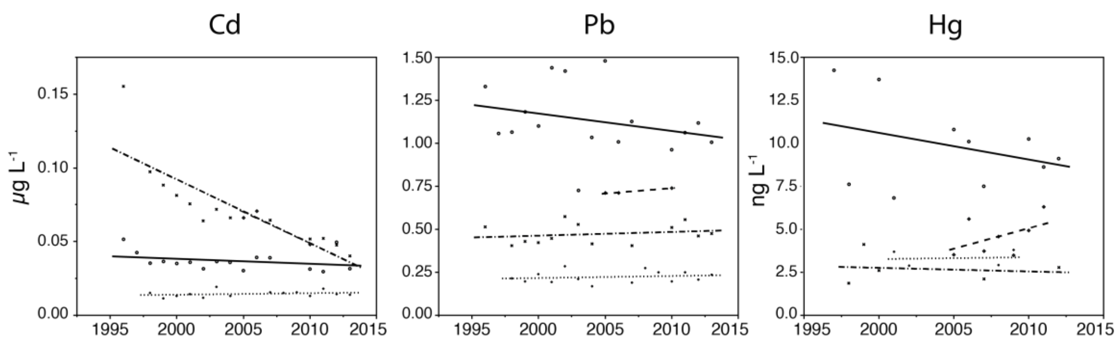

Figure 3.3.5_2. Stream water Cd and Pb (µg L^{-1}) and Hg (ng L^{-1}) concentrations at at the four ICP IM sites in Sweden (Aneboda (solid line) , Gammtratten (dotted line), Gårdsjön (dashed line), Kindla (dotdashed line)).

Trends in heavy metal transport

Annual transport of Pb showed trends that are generally decreasing at Swedish IM sites. On the other hand, trends in Cd and Hg annual transport didn't show any change or only modest decreases. Geographical variation in the observed trends was found with stronger decreasing trends at Gårdsjön (SW Sweden) while Gammtratten (NE Sweden) had smaller or no observed trends. The fact that Gammtratten showed such small changes in the annual transport might be because the levels were already low from the beginning while Gårdsjön receive heavy loads of anthropogenic heavy metal input.

All heavy metals showed exceedence in deposition compared to runoff in the range 4 – 52. The strongest exceedence deposition/ runoff was found for Hg and Pb with deposition (PC+TF+LF) that was 20 times higher than output (RW) at Gårdsjön. At Kindla the highest exceedance were found for Hg with annual deposition rates that was more than 50 times annual runoff transport. The lowest exceedence were found in Cd that ranged between 4 – 12.

Conclusions

Metals in soil and stream water are to a large degree dependent on long-term and long-range atmospheric transport, and the main CLRTAP priority has been on mercury (Hg), lead (Pb) and cadmium (Cd) (Bringmark et al. 2013). Temporal changes in metal concentrations were tested in soil and stream water at European IM-sites. At Swedish ICP IM sites (Aneboda, Gårdsjön, Kindla and Gammtratten) soil and stream water samples have been collected with regular intervals over the last decades and there metal concentrations were tested for temporal trends in more detail. Mainly, slightly decreasing trends were observed and more pronounced at site Gårdsjön.

Pb and Cd concentrations decreased in the forest floor at Swedish IM-sites but accumulated in deeper mineral soil layers. At the European sites, there were different trends observed in the forest floor but accumulations of Cd and Pb were observed in the mineral soil layers also at IM-sites outside Sweden. Despite decreases in Hg deposition, Hg concentrations in the forest floor increased at all Swedish IM-sites.

In stream water, temporal trends of metal concentrations were not obvious, even though Cd concentrations showed decreases in Swedish streams. Large exceedances were found in deposition compared to runoff for all metals indicating an ongoing accumulation of heavy metals in the catchment despite efforts to decrease anthropogenic emissions to the atmosphere.

References

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