Trace metal budgets for forested catchments in Europe -Pb, Cd, Hg, Cu, Zn

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Abstract

Input/output budgets for cadmium (Cd), lead (Pb) and mercury (Hg) in the years 1997-2011 were monitored and determined for 14 small forest covered catchments across Europe as part of the Integrated Monitoring (IM) program on effects of long-range pollutants on ecosystems. Metal inputs were considered to derive from bulk deposition, throughfall and litterfall. Outputs were estimated from run-off values. Litterfall plus throughfall was taken as measure of the total deposition of Pb and Hg (wet + dry), on the basis of evidence suggesting that for these metals, internal circulation is negligible. The same is not true for Cd. Excluding a few sites with high discharge, between 74 and 94% of the input Pb was retained within the catchments; significant Cd retention was also observed. High losses of Pb (> 1.4 $mg \cdot m^{-2} \cdot yr^{-1}$) and Cd (> 0.15 $mg \cdot m^{-2} \cdot yr^{-1}$) were observed in two mountainous Central European sites with high water discharge. All other sites had outputs below or equal to 0.36 and 0.06 $mg \cdot m^{-2} \cdot yr^{-1}$,

respectively for the two metals. Almost complete retention of Hg, 86-99% of input, was reported in the Swedish sites. These high levels of metal retention were maintained even in the face of recent dramatic reductions in pollutant loads.

Key words: lead, cadmium, mercury, forested catchment, Europe, deposition, retention.

Introduction

Metals have accumulated in soils and catchments over long time periods; this accumulation is partly responsible for the unnaturally high metal levels encountered at many sites. Such high metal concentrations can have negative influences on biota in soils and on downstream systems along hydrologic pathways in the catchments and beyond (Johanssson et al 2001). It should be noted that the current metal contents of soils are in a great extent reflective of the higher pollution loads of previous decades. Moss surveys conducted in Sweden have shown that the lead (Pb) content of the carpets of forest mosses fell by 85% between 1970 and 1995; similarly, between 1970 and 1990, that of cadmium (Cd) and mercury (Hg) declined by 75% and 70%, respectively (Rühling and Tyler 2001). The changes in the carpets' metal contents were associated with significant reductions of the pollution loads. A long-term study of bulk deposition at rural sites in Denmark demonstrated that Pb levels decreased from about 12 $mg \cdot m^{-2} \cdot yr^{-1}$ in 1973 to about 1.0 $mg \cdot m^{-2} \cdot yr^{-1}$ in 1999, while Cd levels fell from 0.23 $mg \cdot m^{-2} \cdot yr^{-1}$ to 0.04 $mg \cdot m^{-2} \cdot yr^{-1}$ over the same period (Hovmand and Kemp 2007); these changes are comparable in magnitude to those observed in the aforementioned moss surveys. The moss studies showed that the deposition of Pb and of Cd in less polluted areas such as northern Scandinavia fell more or less in tandem with the falling trends in highly polluted areas (Rühling and Tyler 2001). However, no reduction in the Hg load was observed in the northern region in contrast to trends in more polluted areas. Europe-wide data on metals in mosses are available covering the period between 1990 and 2000; they show that with few exceptions, levels of Pb and Cd have fallen throughout Europe, irrespective of their initial absolute levels (Harmens et al 2008).

The relocation of metals such as Pb and Cd from the humus layers to the upper mineral soil and further in the catchments has been observed at sites studied in the IM monitoring program (Ukonmaanaho et al 2001, Eriksson 2002, Kobler et al 2010) and other areas. However, net

losses of metals seldom or never occur on the catchment scale; minerals and organic material in various layers of the soil have a huge capacity for binding and storing metals. The aim of the study reported in this paper was to determine the extent to which metals have accumulated in European forested catchments over the last decade and a half. A few noteworthy cases involving large metal outflows are discussed.

Catchment monitoring with well defined inputs and outputs can provide a lot of useful data on pollution loads in ecosystems. Such investigations are costly, but the international cooperative program on Integrated Monitoring of Air Pollution Effects on Ecosystems (ICP-IM) in Europe makes it possible to perform Europe-wide comparisons of sites with different climates that have been subjected to different pollution loads. The program is one of six environmental monitoring and modelling programs initiated to support the work of the UN ECE Convention on Long-range Transboundary Air Pollution, CLRTAP (Sliggers and Kakeebeke 2004). The aim of ICP-IM is to quantify the effects of regional air pollutants on forest ecosystems. It is a multidisciplinary project based on the monitoring and modelling of well-defined small catchments in natural/semi-natural forest areas; natural/semi-natural areas were chosen to avoid distortion of the results by the local effects of land use such as forestry (Manual for Integrated Monitoring 1998). The study reported herein focused on levels of lead (Pb), cadmium (Cd) and mercury (Hg), all of which are atmospheric long-range pollutants that are readily transported across national borders and were identified as being particularly harmful in the 1998 Aarhus Protocol on Heavy Metals, one of the international agreements on pollution control under the convention. Although copper (Cu) and zinc (Zn) were not identified as being particularly harmful in CLRTAP, their concentrations also exhibit regional patterns (Rühling and Tyler 2001).

Methods

In the Integrated Monitoring program, elemental budgets and balances are calculated by monitoring the relevant fluxes and compartments in small (c. 4 – 100 ha) un-managed forested catchments. The methods by which this is achieved are set out in the Manual for Integrated Monitoring (1998); the accurate assessment of atmospheric inputs into the catchment area and outputs via stream water plays a central role. The most important processes involving metals are illustrated in a flux balance model (Figure 1). Wet and gravitational dry bulk deposition (BD) was monitored using one or two funnel collectors per

site, situated in treeless locations; their contents were usually collected monthly. At sites with regular winter conditions, sack collectors were used to accommodate the winter snowfall. Funnel collectors, numbering c. 10, were used for spatially representative throughfall (TF) sampling under the tree canopies, again with provisions for winter sampling where necessary; samples were usually acquired once per month. Litterfall (LF) was sampled in 6-12 mesh sacks or funnel type collectors with a defined area. Where possible, litterfall sampling was conducted on a monthly basis, but longer intervals were common; during wintertime in particular, sampling was conducted on an occasional basis. The most important litter fraction for monitoring the capture of pollutants is the fine litter (<5mm); which was measured but coarse debris such as stems and large branches were excluded. It should be noted that it was not possible to calculate the litterfall flux of metals for all of the studied sites. Runoff (RW) was collected, often fortnightly, in the outlet streams at weirs, with continuous recording of the water flow. The complicated hydrologic pathways at the Austrian AT01 site necessitated the use of a more specialised approach (see site description).

Individual national institutions were free to use analytical methods of their own choosing, although the IM manual recommends the use of ICP-MS for measuring the Cd, Pb, Cu and Zn contents of water samples. Generally, GFAAS (atomic absorption spectrophotometer using graphite furnace), ICP-OES (inductively coupled plasma - optical emission spectrometry) and ICP-MS (MS: mass spectrometry); both PerkinElmer, were used (ISO 11885, ISO 8288, ISO 15586). Clean sampling procedures were observed. Litter material was analysed by acid digestion of dried samples with HNO_3 followed by AAS and ICP-OES or ICP-MS methods (DIN 38406-6, ISO 5961, ISO 11885). A graphite furnace was used for the AAS determination of Cd levels. Hg in litter samples was determined by acid digestion and cold-vapor-AAS.

For the determination of Hg in aqueous media it is necessary to take extensive precautions during sampling and handling. Precipitation and throughfall samples were protected by adding a few mL of concentrated suprapure HCl to the buckets of the funnel collectors. These samples and samples taken in the streams were transferred to thoroughly acid-cleaned Teflon bottles for transport. Analysis of aqueous Hg was performed using a gold amalgamation method followed by oxidation/ reduction steps and cold vapor atomic fluorescence spectroscopy (Bishop et al., 1998). Hg analysis had a reported detection limit of 0.06 ng L^{-1}.

The Swedish Environmental Research Institute, Gothenburg, specialising in Hg determinations performed the analysis.

The IM manual specifies that individual national laboratories are responsible for designing and implanting their own quality assurance/quality control procedures, although it is required that the rules of good laboratory practise be followed. Certified reference waters and materials were included in sample series for routine quality control. Participation in laboratory intercomparisons (e.g. NIVA, Norway; AQC Quality Consult, Italy, etc.) were carried out and has been organised within the framework CLRTAP and other initiatives. Included heavy metals besides Hg were determined at ppb levels.

The results used in this study were retrieved from the central data base of the international IM program at the Finnish Environment Institute in Helsinki. Measurement of heavy metal levels is optional in the program, so the dataset is heterogeneous in terms of reported sites, metals, subprograms and years. In particular, extensive data on Hg levels is only available for Swedish sites. Results covering the entire period between 1996 and 2011, or from various years within this timeframe, were used. In most cases metal concentrations were monitored for a number of years. In order to perform flux calculations, it was also necessary to retrieve the corresponding data on water flow and litterfall dry mass from the data base.

In many cases, the measured values were below the limits of detection; this significantly reduced the usability of the data, especially for Cd. Occasional monthly values below the detection limit were replaced by values of half the detection limit in the annual sums.

Mean of annual values, coefficients of variation and N (number of years) were reported for each site. One-way ANOVA (JMP 9.0) was applied on annual relative loss from catchments (RW/TF). Three groups IM-sites were tested followed by a Tukey-Kramer test for each pair. To obtain normal distributions and similarity of variances, the values were logarithmically transformed. For Hg at the Swedish sites, correlations were calculated between Hg in TF, Hg in LF and Hg in RW.

Site descriptions

Data from 14 sites in eight countries was examined (Figure 2). However, the available data on heavy metals in different compartments varies from site to site. Country specific site codes are shown in Table 1 and Figure 2. The sites are all small hydrological catchments, which usually have well-defined water divides. Forests dominate the land cover to various extents, although one site (GB01) is primarily covered with shrubs and grass (Table 1). The monitored sites are generally in protected areas with unmanaged forests that have been allowed to develop naturally. The sites' altitudes range from near sea level to mountain locations of up to 1292 meters above sea level. The sites' annual precipitation ranged from 590 to 1650 mm, decreasing moving eastwards and increasing with altitude.

The types of land and soil within the catchment areas varied widely; some consisted of sorted sediments on sedimentary bedrock, others were moraine landscapes on igneous bedrock, and some sites contained extensive peatlands and lakes. Mineral soils dominated most of the sites, but some of those in the UK and Finland included considerable areas of peaty soils. In most cases, the underlying bedrock was mainly granite. However, in Latvia the underlying bedrock is at great depth and consists primarily of sedimentary rocks such as sandstone and limestone. There, above the bedrock, fairly deep layers (3.5 – 8.5 m) of mainly fine sand prevail. Karstic conditions exist in the Austrian site, where the dolomite and limestone cause complicated water flows. At this site, an appropriate water runoff was calculated on the basis of the hydrological balances determined for a catchment area extending beyond the original site and whose hydrology was better defined and controlled. Ideally, the hydrological conditions within catchments should be well-controlled; they should have well-defined water divides and output only via a single stream water discharge location.

Results

Deposition and litterfall

Pb and Cd are pollutants that are subject to long range transport through the atmosphere and thus have regional distribution patterns. They are deposited in forests as aerosols and via precipitation. The mean annual bulk deposition of Pb determined at the different sites in the years between 1996 and 2011 varied from 0.5 mg m^{-2} yr^{-1} to 2.4 mg$\cdot m^{-2}\cdot yr^{-1}$ (Table 2).

Extremes of this range were both observed at Czech sites, with the maximum occurring at the lowland site and low values at the highland site. Low values of BD were encountered in Fennoscandian sites in margins of polluted regions. The amount of Pb deposited by either TF or LF alone was sometimes greater than, sometimes less than, and sometimes equal to the total BD. The beech forest at AT01 had relatively low TF compared to the spruce stand at that site. However, the combined TF+LF at the sites where it was available was always considerably greater than the BD. In the Baltic region, some sites (LV01, LT03) exhibited rather high loads of Pb measured either as BD, TF or LF. DE01 was recovering from an earlier storm and consecutive massive bark beetle attack and was in a stage of regrowth in spruce stands after the die-off (Heurich et al 2010). At this site, the metal flows in the TF and LF were measured in some of the remaining intact mature stands; this could result in overestimation of the flow because the undeveloped canopies that cover much of the catchment area would be less able to capture these metals.

The mean annual bulk deposition of Cd for different sites was found to range from 0.015 $mg \cdot m^{-2} \cdot yr^{-1}$ to 0.24 $mg \cdot m^{-2} \cdot yr^{-1}$. The quantity of Cd deposited by TF was mostly higher than that deposited via BD; in some cases similar or even lower. The beech stand at AT01 had low cadmium TF. Comparatively high levels of Cd deposition via both BD and TF were observed at the high-altitude DE01 site (Table 2). At the site also LF showed high values. Cd fluxes in the LF were in some cases of similar magnitudes as those of the TF sometimes less, but the resulting TF+LF values were exceeding BD except for the beech stand.

The mean annual bulk deposition of Cu ranged from 0.5 to 3.0 $mg \cdot m^{-2} \cdot yr^{-1}$ at different sites; that for Zn varied between 1.4 mg m^{-2} yr^{-1} and 20 $mg \cdot m^{-2} \cdot yr^{-1}$. A large scale geographical gradient of deposition was discernible especially for Zn with low Fennoscandian values and high central European. In most cases, the deposition of Cu and Zn via TF was greater than that via BD. The total flux of TF+LF to the forest floor was even larger. However, for Cd, Cu and Zn, some of this flux may take part in the inner circulation in forests and is only partly deposition.

Metals in stream flows

Annual water discharges varied greatly between the sites; this in turn affected the metal transport. High-altitude grassland and forested mountain sites subjected to high amounts of

237 precipitation and low evapotranspiration (AT01, DE01, GB01, Table 1) had annual water
238 discharges between 800 mm to 1400 mm. Continental Eastern European lowland sites had
239 rather low precipitation and thus, annual stream water discharges reached only 50-300 mm
240 (sites CZ01, FI01, FI03, LV01, LV02, LT01, LT01, LT03). The Swedish sites and the Czech
241 highland site CZ02 were intermediary, with annual stream water flows of 310-557 mm. The
242 pronounced differences in the stream flow characteristics of adjacent sites in the Bohemian
243 Massif have been described by Kram et al (2008); site DE01 had a water discharge of 992
244 mm, while that at CZ02 was 557 mm and the lowland site CZ01 had a discharge of only 57
245 mm during the years examined. The forest at DE01 consists in part of young spruce stands
246 regenerating from a bark beetle attack; this site thus has a greater degree of stream water
247 runoff than might otherwise be expected.
248
249 At most sites, the mean annual stream water flux for Pb was found to be in the range 0.04-
250 0.36 $mg \cdot m^{-2} \cdot yr^{-1}$. However, at the CZ02 and DE01 sites, both of which are at high elevations
251 on the Czech-German border, the Pb fluxes were as high as 1.8 $mg \cdot m^{-2} \cdot yr^{-1}$ and 1.4 $mg \cdot m^{-2} \cdot yr^{-1}$
252 , respectively (Table 2). In the time period of our investigation, 1996-2011, 74-94% of the
253 deposited Pb as estimated by Pb in TF was retained in the catchments. The CZ02 and DE01
254 sites were exceptions to this rule; at CZ02, the outflow was greater than that deposited via TF
255 but most likely not with LF included that could be estimated to c. 1 $mg \cdot m^{-2} \cdot yr^{-1}$. This would
256 resemble conditions at the fairly close-by site DE01, where the total quantity deposited by the
257 TF + LF was significantly greater than that in the runoff (Figure 3). At the Finnish site FI03
258 and the two sites in northern Sweden, the runoff transport of Pb was very low. A somewhat
259 larger export occurred at the southern Swedish site SE14 (Figure 4), in which the soil organic
260 matter content was rather high (Löfgren et al., 2011).
261
262 The geographical patterns of relative Pb release from catchments were analysed by comparing
263 annual RW/TF ratios in three groups of IM sites in which this variable was available, i.e.
264 group A; DE01 CZ02, group B; SE14, SE15, SE16 and AT01 and group C; CZ01, LV01 and
265 LV02. Based on logarithmically transformed data, the differences between groups were
266 evident (ANOVA and Tukey-Kramer test, $p < 0.001$). The mean RW/TF values were 1.0,
267 0.26 and 0.06 for the groups A, B and C, respectively.
268
269 The range of mean annual Cd flux in streams at eleven sites was 0.003-0.06 $mg \cdot m^{-2} \cdot yr^{-1}$ and
270 was not sensitive to differences in the water discharge (Table 2). Effluxes were low at FI01,

FI03 and LT01 geographically located in the east and somewhat higher at SE15 and LV02. Very high Cd outflows were observed at CZ02 and DE01 and low outflow at alkaline AT01 in spite of large water discharge at all three sites (Table 2, Figure 3). There was a wide span of retention in the catchments ranging from 92% of Cd deposited by TF at LV01 to no retention at CZ02, DE01 and SE15 (Table 2, Figure 5).

The retention of Cd was tested on logarithmically transformed RW/TF data for the same groups of IM sites as for Pb. The Tukey-Kramer test showed that group B and C did not differ ($p=0.35$), while group A differed significantly from groups B and C ($p < 0.001$). Mean RW/TF values were 2.3, 0.15 and 0.08 in respective group.

The sites Cu exports varied significantly, ranging from 0.04 $mg \cdot m^{-2} \cdot yr^{-1}$ to 0.95 $mg \cdot m^{-2} \cdot yr^{-1}$; the British moorland site GB01 exhibited a particularly large Cu outflow (Table 3). Strong retention on the catchment scale was commonplace, reaching 80-97% of TF. Large quantities of Zn were transported in the runoff at CZ02 and GB01 (Table 3); at the other sites, the amount of Zn exported was between 0.3 $mg \cdot m^{-2} \cdot yr^{-1}$ and 3.5 $mg \cdot m^{-2} \cdot yr^{-1}$. Zn was heavily retained in the catchments to a degree of 38-96% of deposited Zn in TF.

Mercury at Swedish sites

Hg levels were monitored at Swedish sites during special one year campaigns that moved from site to site with one repetition. Additionally, in some years, Hg levels in the litterfall and stream water were measured. The mean annual BD values for sites SE04, SE14, SE15 and SE16 were 7, 6, 5 and 2.4 $\mu g \cdot m^{-2} \cdot yr^{-1}$, respectively (Figure 6). This corresponds with the gradient for several pollutants throughout Scandinavia with the highest levels in the south-west, represented by SE04, and the lowest in the north (SE16). The Hg flows in TF and LF followed this pattern (Figure 6). The four sites had average annual Hg deposition by TF of 17, 14, 12 and 4 $\mu g \cdot m^{-2} \cdot yr^{-1}$, respectively, corresponding values by LF at 39, 23, 12 and 8 $\mu g \cdot m^{-2} \cdot yr^{-1}$. Determinations of Hg in TF were made 2 to 6 years at the different sites and for Hg in LF 8 to12 years. Correlation analysis of annual values showed that Hg flows in TF and LF were correlated ($p = 0{,}024$, $n = 11$). There was a very pronounced enrichment of both TF and LF compared to BD, which indicates very large dry deposition (Steinnes and Andersson, 1991). There were north-south gradients for deposition and litterfall but no such gradient for

runoff amounts, which were remarkably similar from site to site, annual values being on average 1.7-2.7 $\mu g \cdot m^{-2} \cdot yr^{-1}$. Measurements of Hg in RW were performed from 2 to 14 years at the sites. Correlation analysis of annual values showed that Hg in RW had no significant relation to the Hg deposition using Hg in LF as proxy ($p = 0.52$, $n = 23$). The degree of retention in the catchments was 86-99% of the amount deposited by TF+LF.

Discussion

Metal deposition in forest ecosystems

Metals can be deposited by both wet and dry means (Figure 1); the latter primarily involve particle capture. In open field situations, the amount deposited is equal to the gravimetric bulk deposition, but interception becomes much more important in forested sites. We are of the opinion that for some metals the combined input from throughfall and litterfall can be used as a rough estimate of the total deposition, at least in situations involving high air pollution. This approach has been adopted for Hg by various authors (Schwesig and Matzner 2001) and is valid if one assumes that the uptake from the soil by trees and internal circulation are negligible. There is evidence that roots have barriers to the uptake of toxic metals such as Hg (Godbold 1994, Grigal 2002). The transportation of Hg in the xylem sap has been shown to be small compared to the amount deposited by litterfall (Bishop et al 1998). For Pb, an isotope study in two boreal spruce/pine ecosystems showed the root uptake to be 2-14% of the total wet deposition (Klaminder et al 2005); its share of the total deposition would be even lower. A pot experiment with spruce plants using spiked Pb showed that only 2% of the Pb in the plants originated from the soil, with the remainder originating from deposition (Hovmand et al 2009).

As a consequence of the evidences mentioned above, it could be concluded that internal circulation of Hg and Pb is very limited. It is therefore reasonable to use TF+LF as an estimate of total deposition of these elements. However, some earlier studies on the metal budgets of soil-plant systems have suggested that plants take up significant quantities of Pb, Cd, Cu, Zn and other metals from the soil, on the basis of metal budgets with independent input estimates not involving LF and TF (Bergkvist 1987, Ukonmaanaho et al 2001). In one of the studies, the total deposition was estimated by assuming that the easily-determined ratio

of dry to bulk deposition for Na could be used to approximate the same ratio for other elements. This approach relies on the assumption that the capture of heavy metal particles proceeds via similar mechanisms to those involved in the capture of Na salts. Using this method, Ukonmaanaho et al (2001) calculated that the external input to Finnish IM sites was much lower than TF + LF. It is undoubtedly true that the LF and TF in part reflect various internal fluxes for some metals and that simply estimating the total deposition by summing them can result in overestimation. However, the use of BD as estimation of total input will give too low values and we consider the estimation with TF+LF being closer to the truth. Internal circulation of at least Pb and Hg could be neglected.

The dominating tree species within a site will affect element capture and the relative contributions of LF and TF to the total deposition. The deciduous beech at the Austrian AT01 site had lower fluxes of Pb and Cd in TF than was observed for spruce at the same site. Clearly, this is partially due to seasonal differences in the two species' canopy cover, but it should also be noted that the standing biomass of the beech stands at AT01 is comparatively low, and this might also be relevant. The LF/TF ratios for Hg at Swedish sites differed substantially between sites, from 1.0 in the central Swedish SE15 to 2.8 in the southern SE04 site. In the latter case, at relatively high Hg load, the LF pathway accounted for the main part of the deposition.

The summed TF and LF flows can be substantially greater than the incoming bulk deposition, BD (Tables 2 and 3). This was the case for Pb, Cd, Cu and Zn in coniferous stands at the Swedish, German, Latvian and Austrian sites, for which sites metal fluxes in the LF could be determined. It is less reasonable to approximate the total deposition of Cd, Cu and Zn as TF+LF, due to the possible internal circulation of these elements, although the assumption remains acceptable for Pb and Hg. Forest cover has a profound impact on metal deposition. For Hg at the Swedish sites, the total deposition measured as Hg in TF+LF was 8, 6, 5 and 4 times higher than BD at SE04, SE14, SE15 and SE16 respectively, showing a very sharp enrichment by canopy capture. It is important to assess the total atmospheric input when considering the formation and fate of large metal stores in the soil. However, since TF and LF could not be determined for all sites, it was sometimes necessary to use TF or BD as measures of the metal input and this would most probably lead to underestimation of total input.

It is of interest to compare the measured deposition at IM sites to the official estimates made by EMEP, the UN program for monitoring and evaluation of the long range transmission of air pollutants in Europe. EMEP uses a model-based mapping procedure for deposition, which is driven by a massive input of spatially defined data on meteorological and geophysical conditions and on human metal emissions. The estimated Pb deposition for the year 2000 amounted to 0.5-1 $mg \cdot m^{-2}$ in large parts of Europe, with levels in Central Europe reaching up to 5 $mg \cdot m^{-2}$ (EMEP 2004). These values are consistent with the bulk deposition measured at IM sites (Table 2). The deposition levels for Pb seemed to remain about the same in 2008 (EMEP 2010). The BD and TF values at IM sites were in the same range as EMEP values for Pb (Table 2), but the combined TF+LF fluxes were higher.

The EMEP estimated of the total deposition of Cd in Scandinavia and Germany in 2008 to be between 0.01 $mg \cdot m^{-2}$ and 0.1 $mg \cdot m^{-2}$, with higher values in some Eastern European areas (EMEP 2010). This is lower input as compared to estimations with TF+LF and the possible internal component of its circulation makes Cd less suitable for the comparison. The deposition of Hg in Scandinavia and Germany was estimated to range from 0.007 $mg \cdot m^{-2}$ to 0.02 $mg \cdot m^{-2}$ along a north-south gradient, with even higher levels in other parts of Europe. Our assessments of TF+LF of Hg in Swedish forest sites were clearly larger than the EMEP deposition estimates for Hg (Figure 6).

High-altitude locations are particularly exposed to metal pollution, which often originates from very distant locations (Zechmeister 1995). This is primarily due to their high levels of precipitation, although they may also be more prone to particle deposition than lowland sites. The humus layer at DE01, which is in the Bavarian forest mountains of Central Europe, had a very high Pb content of 260 $\mu g \cdot g^{-1}$ at high altitudes which decreased on moving downslope (Beudert unpublished). This is consistent with substantial historical deposition due to altitude. However, the current deposition values for this site were not exceptional. An altitude gradient of Pb in the humus layer was also observed in the rather steep topography of the SE15 site at Kindla (Eriksson 2002), which was subject to relatively high bulk deposition of Pb (Table 2).

Catchment balances

Looking at the input/output balances for Pb and Cd calculated from the input and output data (Table 2, Figures 3, 4 and 5), it is evident that most of the sites exhibit very high retention of

deposited metals, with a few remarkable exceptions. Disregarding DE01 and CZ02, the average outflow of Pb was 16% of the input by throughfall (TF) for the coniferous sites; it should be noted here that TF is only a part of the total deposition. For Cd corresponding output was 26% of TF, but SE15 with high output of Cd was also excluded from the average. Cd is considered to be more mobile than Pb in soils (Bergkvist, 2001); it is more soluble and is subject to cation exchange, whereas Pb is tightly bound to the soil organic material (SOM) and its mobility dependent on that of the SOM. High retention of Pb and Cd has been observed in numerous catchment studies, often with the addition that Pb is retained to a larger degree than Cd (Lindberg and Turner 1988, Johnson et al 1995, Aastrup et al 1995, Ukonmaanaho et al 2001, Minarik et al 2003, Watmough and Dillon 2007). The period examined in this study was one of dramatically lowered pollution loads, but this did not affect the general pronounced retention of these elements. Consequently, on the catchment level, the stores of Pb and Cd in soils continue to accumulate. Huang et al (2011) recently reported that the deposition and outflow of Cd in a Bavarian forest catchment were almost in balance, which is a first case that was attributed to a reduction in the load. Model calculations involving soil processes in catchments in semi-natural moorlands have demonstrated that the changes in the abundance of loosely sorbed Cd and Zn may occur over timescales of decades to centuries, while for Pb, the changes will occur over centuries or millennia (Tipping et al 2006). This does not mean that no improvement is possible. The relocation of Pb, Cd and other elements in soils have been reported in many cases (Friedland et al 1992, Bergkvist 2001, Eriksson 2002, Watmough et al 2004, Johnson and Richter 2010, Kobler et al 2010). In combination with reduced deposition, this lowers the metal burden on the biologically important top-soils. The reduction of these more available stores may also cause decreases in the outflow to aquatic recipients (Watmough and Dillon 2007).

The retention of Cd and Pb at the Scandinavian sites was less extensive than the extreme values observed in some eastern European sites such as LV01, LV02 and CZ01. The differences in retention between groups of sites were highly significant (ANOVA). For the eastern European group the strong retention is partly due to the very small water discharge. Two of the mountainous sites, AT01 and DE01 had very large water discharge volumes (Table 1); notably, the losses of Pb and Cd from the German DE01 site were almost equal to the input from throughfall (Table 2, Figure 3). However, the total deposition (here defined as TF+LF) would exceed the outflow even at DE01. The situation at AT01 is more complex because of its unusual soil conditions and the irregular hydrological flow paths within its

limestone bedrock. While the levels of Pb and Cd in the topsoil decreased at this site, the magnitude of this decrease was considerably greater than the amount detected in the filtered seepage water and in the runoff. This may be due to particulate transport of trace metals, which would hence inflate the catchment budgets (Kobler et al 2010).

The Cd runoffs observed at the SE15 site were greater than those at other Fennoscandian sites even though all of these sites had similarly acidic soils. The high runoffs in SE15 are attributed to its shallow soils and rapid through-flow.

Hg binds especially strongly to organic matter in soils and its transport is highly dependent on the movement of the organic material. The use of TF+LF as a measure of the total deposition is thus particularly well-justified for this metal. The Hg input and output data for Swedish IM sites (Figure 6) indicate that its outflow on average is 1-14% of the total input. Similar results have been reported for other Fennoscandian sites in studies using LF as a measure of the total input (Lee et al 1998). Larssen et al (2008) reported somewhat lower retention, which can be attributed to relatively low Hg deposition and very shallow soils at the site of that study in Norway. Lower but still substantial retention, 30%, was also reported from a German site with a higher pollution level (Schwesig and Matzner 2001). All of the Swedish sites examined in this work exhibited similar Hg runoffs within the range of 1.7 $\mu g \cdot m^{-2} \cdot yr^{-1}$ to 2.7 $\mu g \cdot m^{-2} \cdot yr^{-1}$, with no correlation to deposited quantity.

Some of the uncertainties of catchment studies have been discussed by Larssen et al (2008). Elemental analysis and the usually well-defined output by stream discharge are considered less of a problem than up-scaling from point measurements for deposition and terrestrial data. However, annual differences in runoff amounts are sometimes large. The degree of forest cover under which LF and TF occur is important and the delineation of catchment areas is crucial. However, clear trends that are probably strong enough to override any potential uncertainties are apparent in the metal retention data presented in this paper.

The CLRTAP protocol focuses on three heavy metals - Pb, Cd and Hg - as highly toxic long-range pollutants. However, there are a number of less hazardous metal pollutants, such as Cu and Zn, both of which were examined in this work. The outflows of these metals were also found to be much smaller (10%) than the inputs, as measured by the TF or BD (Table 3). Sites DE01 and CZ02 were exceptions to the general pattern observed for Zn, since their outputs

were not greatly lower than their TF inputs; Cu levels at these sites were note measured. SE15 exhibited localised enhancements of Zn output that were probably driven by the acidity of its shallow soils, as was observed for Cd. The British grassland site GB01, which has peaty soils, and the Latvian site LV01 had rather large Cu flows, 25% of the input in TF or BD. A similarly high Cu output was also observed at the Swedish SE15 site, which was probably due to this site's shallow soils and rapid through-flow.

Conclusions

Budget calculations for the heavy metals Cu, Zn, Pb, Cd and Hg at 14 catchment sites in Europe covering north-south and east-west geographical gradients showed mainly large retention values. This would mean accumulation of the metals primarily in the catchment soils. Large differences in amounts of metal deposition and in hydrologic budgets were accounted for. A few sites with high precipitation, such as at high altitudes, exhibited higher outflow and lower retention but at these sites also metal loads were high.

In recent years, the deposition of Pb, Cd and Hg has declined significantly. Current loads are only a small fraction of those experienced in previous decades. Despite this, there is still found a pronounced metal retention in most forested catchments. However, a mobility of Cd and, to lesser extent Pb would relocate these metals within the soil profile, which might reduce the strain on biota that fulfil important ecosystem functions in the upper soil layers. Especially Hg was found to show high retention and would be bound tightly to organic matter in the soil.

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Table 1. Descriptions of the IM sites examined in this work and compiled into regions based on similar P and R. P – average annual precipitation during the period over which metal concentrations were measured; RW- annual runoff during the period over which metal concentrations were measured. All sites were forested except for GB 01.

IM site	Vegetation	Area, km^2	Altitude, m	P mm	RW mm
SE04	Norway spruce dominated	0.04	114-140	1059	564
SE14	Norway spruce dominated	0.20	210-240	773	310
SE15	Norway spruce dominated	0.20	312-415	934	430
SE16	Mixed forest, Scots pine, Norway spruce	0.45	410-545	983	496
FI 01	Norway spruce dominated.	0.30	150-190	635	211
FI 03	Scots pine dominated	4.64	165-214	626	347
LV01	Mixed forest, Scots pine, birch, Norway spruce	6.65	6-16	757	203
LV02	Mixed forest, Scots pine, Norway spruce	0.27	184-192	695	233
LT 01	Scots pine, Norway spruce	1.02	159-189	760	87
LT03	Scots pine, Norway spruce	1.47	147-180	788	146
CZ 01	Norway spruce dominated	0.29	487-543	650	57
CZ 02	Norway spruce	0.27	829-949	986	557
DE 01	Norway spruce, beech	0.69	787-1292	1540	992
AT 01	Mixed forest, beech dominated, Norway spruce etc	0.90	550-950	1650	1255
GB 01	Heather and fescue grassland	9.98	225-1111	1143	816
Regionalisation					
Low P, R	FI01, LV01, LV02, LT01, LT03, CZ01	1.67	189 - 218	718	145
Mean P,R	FI 03, SE 04, SE 14, SE 15, SE 16	1.11	242 - 311	864	429
High P, R	CZ 02, DE 01, AT 01, GB 01	2.96	598 - 1075	1348	897

Note: The nation codes are: AT-Austria, CZ-Czech republic, DE-Germany, FI-Finland, GB-United kingdom, LT-Lithuania, LV-Latvia and SE-Sweden.

Table 2a. Flows of lead (Pb) in bulk deposition (BD), throughfall (TF), litterfall (LF) and stream water (runoff-RW) at ICP IM sites for parts of the period 1996-2011 ($mg \cdot m^{-2} \cdot yr^{-1}$). Coefficient of variation – CV and number of values (years) – N.

Lead, Pb, mg m^{-2} yr^{-1}

IM site	BD	CV	N	TF	CV	N	LF	CV	N	RW	CV	N
SE 14	1,03	11	5	1,36	66	2	1,32	37	6	0,28	90	2
SE 15	0,82	61	5	0.76	51	4	0.80	38	11	0.20	33	10
SE 16	0.56	94	4	0.47	58	2	0.38	66	8	0.09	45	9
FI 01	0.63	25	14	-	-	0	-	-	0	0.12	36	10
FI 03	0.54	30	15	-	-	0	-	-	0	0.04	31	11
LV 01	1.53	49	11	1.55	58	14	0.61	-	1	0.12	50	7
LV 02	0.99	39	13	0.72	43	15	-	-	0	0.06	88	9
LT 01	-	-	0	-	-	0	0.91	56	6	0.09	-	1
LT 03	-	-	0	-	-	0	1.94	30	4	0.24	-	1
CZ 01	2.43	86	14	1.21	46	13	-	-	0	0.07	83	12
CZ 02	0.63	28	8	0.65	24	9	-	-	0	1.75	139	9
DE 01	1.36	23	6	1.82	38	6	1.40	-	0	1.40	49	9
AT 01, spruce	0.81	89	12	1.48	123	10	0.36	3	2	0.36	62	7
AT 01, beech	0.81	89	12	0.63	86	10	0.38	2	2	0.36	79	7

Table 2b. Flows of cadmium (Cd) in bulk deposition (BD), throughfall (TF), litterfall (LF) and stream water (runoff-RW) at ICP IM sites for parts of the period 1996-2011 (mg.m-2.yr-1). Coefficient of variation – CV and number of values (years) – N.

Cadmium, Cd, mg m^{-2} yr^{-1}

IM site	BD	CV	N	TF	CV	N	LF	CV	N	RW	CV	N
SE 14	0.036	25	5	0.045	64	2	0.065	25	6	0.012	25	10
SE 15	0.024	34	5	0.032	29	4	0.027	25	11	0.035	41	10
SE 16	0.015	37	4	0.021	43	2	0.025	28	8	0.007	43	10
FI 01	0.025	23	11	-	-	0	-	-	0	0.004	109	8
FI 03	0.027	44	12			0			0	0.003	38	3
LV 01	0.082	38	9	0.205	80	12	0.055	-	1	0.017	64	5
LV 02	0.075	41	12	0.084	46	13	0.017	-	1	0.062	73	9
LT 01	-	-	0	-	-	0	0.069	29	4	0.006	54	2
LT 03	-	-	0	-	-	0	0.050	56	2	0.014	31	3
CZ 01	0.107	61	12	0.073	57	12	-	-	0	0.010	139	10
CZ 02	0.037	26	6	0.033	38	7	-	-	0	0.149	53	7
DE 01	0.236	74	6	0.248	69	6	0.11	-	0	0.224	70	9
AT 01, spruce	0.039	60	7	0.072	58	7	0.010	6	2	0.02	-	5
AT 01. beech	0.039	60	7	0.029	24	7	0.006	10	2	0.02	-	5

Table 3a. Flows of copper (Cu) in bulk deposition (BD), throughfall (TF), litterfall (LF) and stream water (runoff-RW) at ICP IM sites for parts of the period 1996-2011 ($mg \cdot m^{-2} \cdot yr^{-1}$). Coefficient of variation – CV and number of values (years) – N.

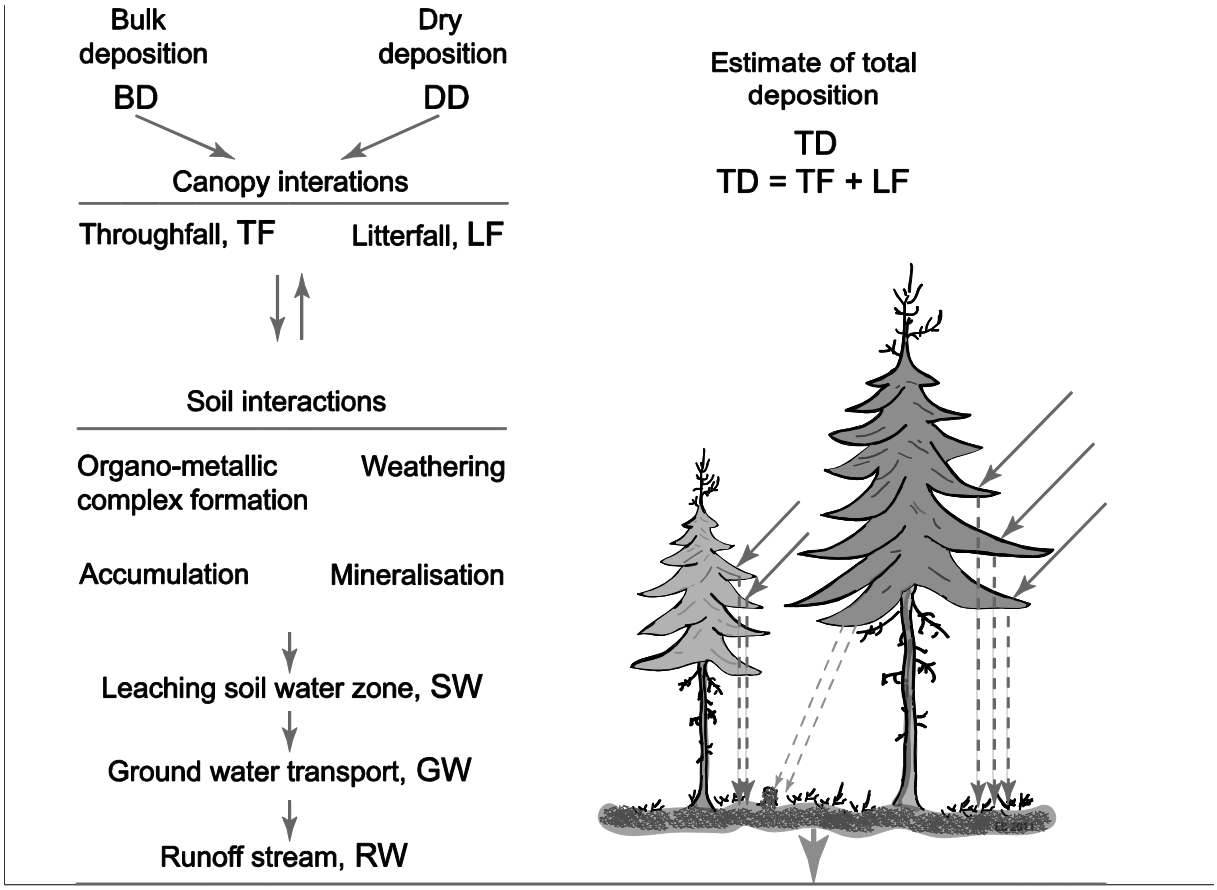
Copper, Cu, mg m^{-2} yr^{-1}

IM site	BD	CV	N	TF	CV	N	LF	CV	N	RW	CV	N
SE 14	1.18	20	5	1.48	95	5	1.32	23	10	0.20	38	13
SE 15	0.60	31	5	1.19	78	4	0.55	30	11	0.10	41	10
SE 16	0.46	36	4	0.69	53	2	0.38	29	9	0.14	50	10
FI 01	0.58	28	14	1.40	52	4	-	-	0	0.05	41	11
FI 03	0.60	41	15	1.43	-	1	-	-	0	0.04	34	11
LV 01	1.43	46	11	2.30	57	14	0.47	-	1	0.42	47	7
LV 02	1.81	39	14	3.33	65	15	0.24	-	1	0.09	55	7
LT 01	-	-	0	-	-	0	0.86	23	6	0.17	71	7
LT 03	-	-	0	-	-	0	1.23	21	4	0.41	78	5
GB 01	2.99	58	4	-	-	0	-	-	0	0.95	14	3

Table 3b. Flows of zinc (Zn) in bulk deposition (BD), throughfall (TF), litterfall (LF) and stream water (runoff-RW) at ICP IM sites for parts of the period 1996-2011 (mg.m-2.yr-1). Coefficient of variation – CV and number of values (years) – N.

Zinc, Zn, mg m^{-2} yr^{-1}

IM site	BD	CV	N	TF	CV	N	LF	CV	N	RW	CV	N
SE 14	8.67	26	5	9.5	128	5	28.1	30	10	1.39	37	13
SE 15	3.95	42	5	10.9	47	4	11.6	26	11	3.5	42	10
SE 16	3.37	47	4	6.4	64	2	11.6	31	9	1.0	46	10
FI 01	2.4	27	14	13.4	63	6	-	-	0	2.1	87	12
FI 03	1.8	38	17	1.4	-	1	-	-	0	0.3	35	11
LV 01	1.4	46	11	20.0	40	13	12.9	-	1	3.3	74	7
LV 02	14.8	73	14	15.6	44	14	11.9	-	1	0.8	40	11
LT 01	-	-	0	-	-	0	20.7	31	6	1.1	66	7
LT 03	-	-	0	-	-	0	16.3	23	4	2.8	52	5
CZ 01	15.3	87	13	13.7	49	14	-	-	0	0.5	68	10
CZ 02	19.9	36	8	14.9	28	7	-	-	0	9.3	25	4
GB 01	17.7	27	3	-	-	0	-	-	0	5.7	7	3



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677 **Fig. 1**. Processes involving metals in forest catchment. Uptake from the soil to the vegetation
678 via the roots is not shown, and is not significant for Pb and Hg.

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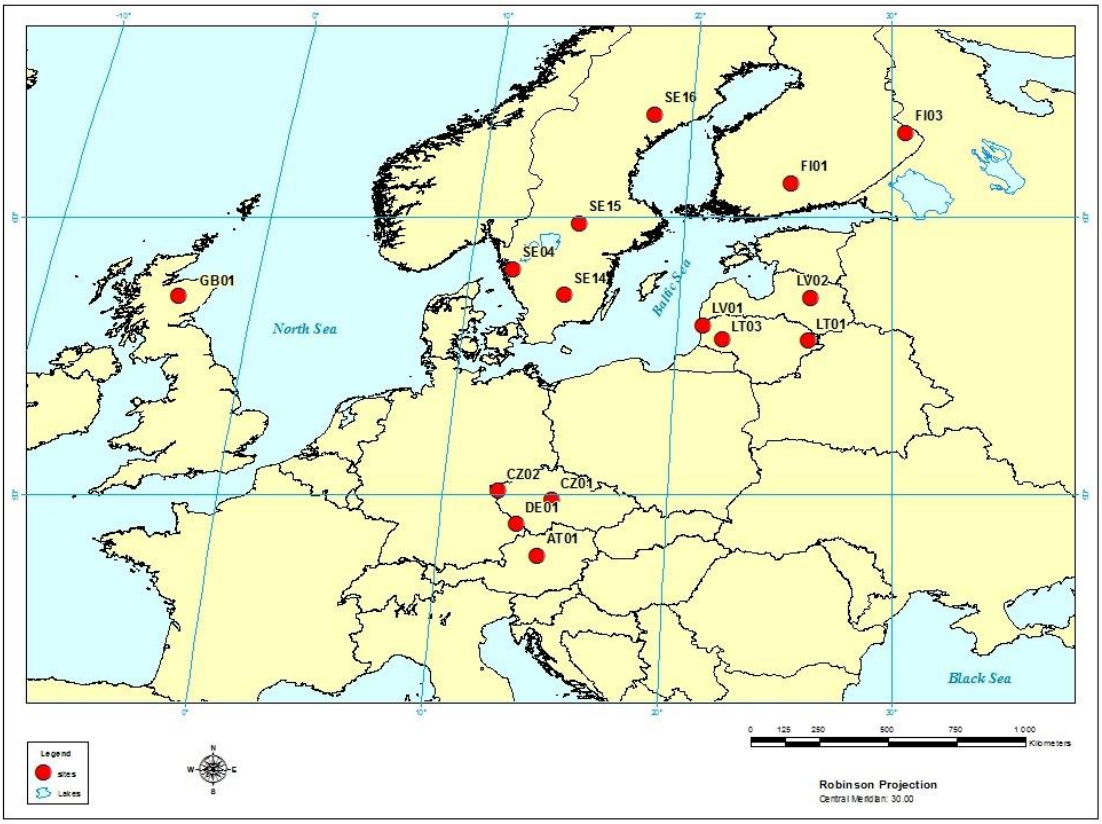


Fig. 2. Sites of the Integrated Monitoring (IM) network used for the assessment of trace metal budgets.

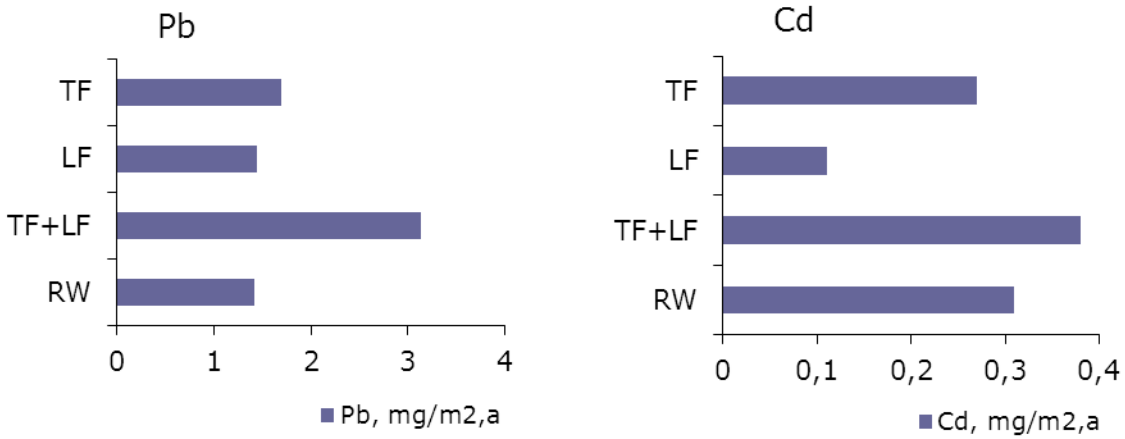
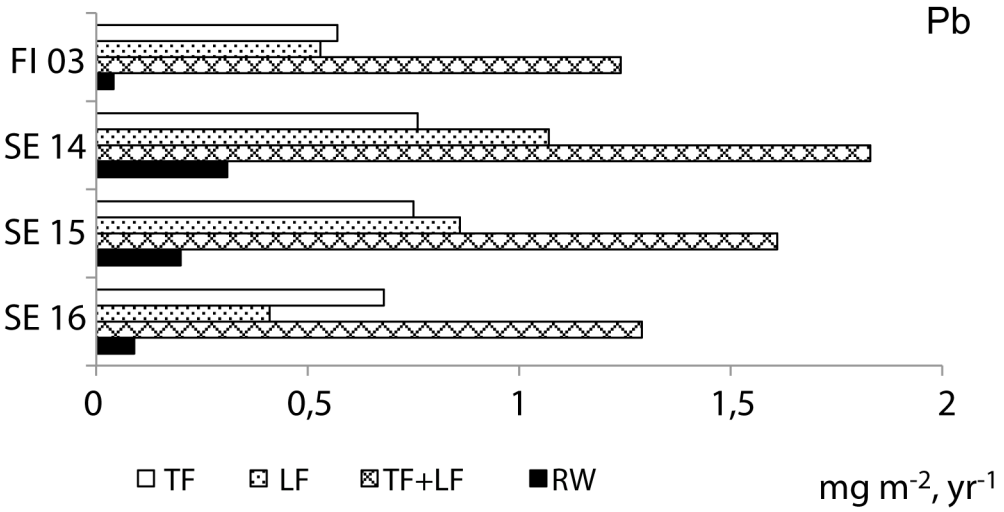


Fig. 3. Lead and cadmium balances for the DE 01 catchment including throughfall, TF, litterfall, LF and runoff, RW. The sum of TF+LF also presented. Note different x-axis scales.



Fig, 4. Lead balances for the Finnish FI 03 catchment (note; BD instead of TF) and the three Swedish catchments SE 14, SE15 and SE 16 with throughfall- TF, litterfall- LF, throughfall+ litterfall-TF+LF (FI 03 BD+LF) and runoff- RW included.

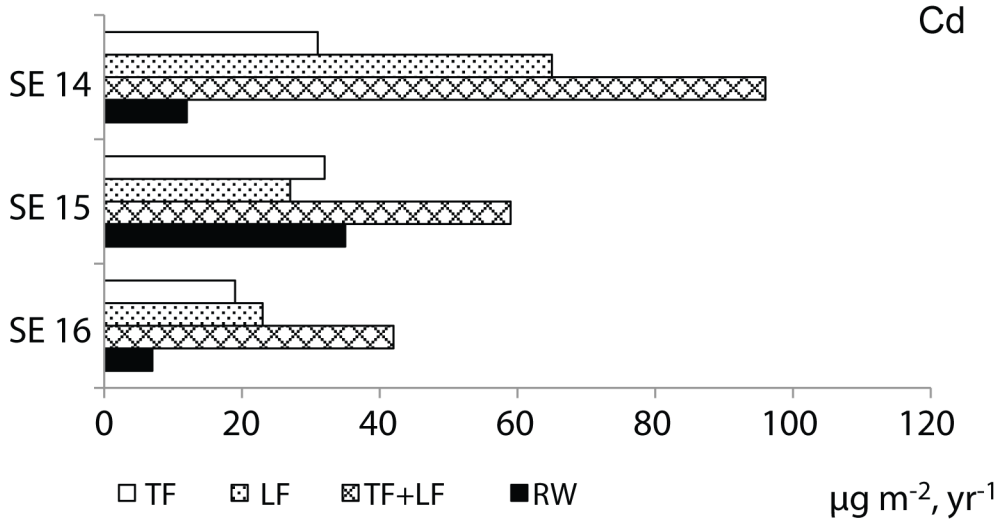


Fig. 5. Cadmium balances for the three Swedish catchments SE 14, SE 15 and SE 16 including throughfall- TF, litterfall- LF, throughfall+ litterfall-TF+LF and runoff- RW.

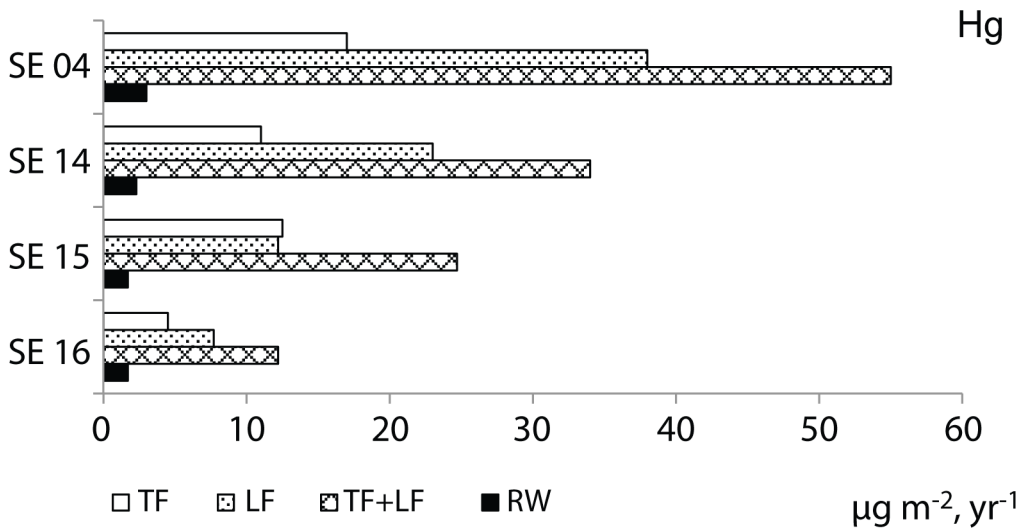


Fig. 6. Mercury balances for the four Swedish catchments SE 04, SE 14, SE15 and SE 16 showing throughfall- TF, litterfall- LF, throughfall+ litterfall-TF+LF and runoff- RW.