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This is an author produced version of a paper published in
Water, Air and Soil Pollution.

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Citation for the published paper:

Lage Bringmark, Lars Lundin, Algirdas Augustaitis, Burkhard Beudert,
Helga Dieffenbach-Fries, Thomas Dirnböck, Maria-Theresia Grabner, Mike
Hutchins, Pavel Kram, Iraida Lyulko, Tuija Ruoho-Airola, Milan Vana.
(2013) Trace metal budgets for forested catchments in Europe – Pb, Cd, Hg,
Cu and Zn. *Water, Air and Soil Pollution*. Volume: 224, Number: 4, pp 1-14.
<http://dx.doi.org/10.1007/s11270-013-1502-8>.

Access to the published version may require journal subscription.

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Standard set statement from the publisher:

“The final publication is available at Springer via <http://dx.doi.org/10.1007/s11270-013-1502-8>”

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1 Trace metal budgets for forested catchments in Europe -Pb, Cd, 2 Hg, Cu, Zn

3

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20

21 Abstract

22

23 Input/output budgets for cadmium (Cd), lead (Pb) and mercury (Hg) in the years 1997-2011
24 were monitored and determined for 14 small forest covered catchments across Europe as part
25 of the Integrated Monitoring (IM) program on effects of long-range pollutants on ecosystems.
26 Metal inputs were considered to derive from bulk deposition, throughfall and litterfall.

27 Outputs were estimated from run-off values. Litterfall plus throughfall was taken as measure
28 of the total deposition of Pb and Hg (wet + dry), on the basis of evidence suggesting that for
29 these metals, internal circulation is negligible. The same is not true for Cd. Excluding a few
30 sites with high discharge, between 74 and 94% of the input Pb was retained within the
31 catchments; significant Cd retention was also observed. High losses of Pb ($> 1.4 \text{ mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$)
32 and Cd ($> 0.15 \text{ mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$) were observed in two mountainous Central European sites with
33 high water discharge. All other sites had outputs below or equal to 0.36 and $0.06 \text{ mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$,

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

37

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

39

40

41 **Introduction**

42

43 Metals have accumulated in soils and catchments over long time periods; this accumulation is
44 partly responsible for the unnaturally high metal levels encountered at many sites. Such high
45 metal concentrations can have negative influences on biota in soils and on downstream
46 systems along hydrologic pathways in the catchments and beyond (Johansson et al 2001). It
47 should be noted that the current metal contents of soils are in a great extent reflective of the
48 higher pollution loads of previous decades. Moss surveys conducted in Sweden have shown
49 that the lead (Pb) content of the carpets of forest mosses fell by 85% between 1970 and 1995;
50 similarly, between 1970 and 1990, that of cadmium (Cd) and mercury (Hg) declined by 75%
51 and 70%, respectively (Rühling and Tyler 2001). The changes in the carpets' metal contents
52 were associated with significant reductions of the pollution loads. A long-term study of bulk
53 deposition at rural sites in Denmark demonstrated that Pb levels decreased from about 12
54 $\text{mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ in 1973 to about $1.0\text{ mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ in 1999, while Cd levels fell from $0.23\text{ mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$
55 to $0.04\text{ mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ over the same period (Hovmand and Kemp 2007); these changes are
56 comparable in magnitude to those observed in the aforementioned moss surveys. The moss
57 studies showed that the deposition of Pb and of Cd in less polluted areas such as northern
58 Scandinavia fell more or less in tandem with the falling trends in highly polluted areas
59 (Rühling and Tyler 2001). However, no reduction in the Hg load was observed in the northern
60 region in contrast to trends in more polluted areas. Europe-wide data on metals in mosses are
61 available covering the period between 1990 and 2000; they show that with few exceptions,
62 levels of Pb and Cd have fallen throughout Europe, irrespective of their initial absolute levels
63 (Harmens et al 2008).

64

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

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

73
74 Catchment monitoring with well defined inputs and outputs can provide a lot of useful data on
75 pollution loads in ecosystems. Such investigations are costly, but the international cooperative
76 program on Integrated Monitoring of Air Pollution Effects on Ecosystems (ICP-IM) in
77 Europe makes it possible to perform Europe-wide comparisons of sites with different climates
78 that have been subjected to different pollution loads. The program is one of six environmental
79 monitoring and modelling programs initiated to support the work of the UN ECE Convention
80 on Long-range Transboundary Air Pollution, CLRTAP (Sliggers and Kakeebeke 2004). The
81 aim of ICP-IM is to quantify the effects of regional air pollutants on forest ecosystems. It is a
82 multidisciplinary project based on the monitoring and modelling of well-defined small
83 catchments in natural/semi-natural forest areas; natural/semi-natural areas were chosen to
84 avoid distortion of the results by the local effects of land use such as forestry (Manual for
85 Integrated Monitoring 1998). The study reported herein focused on levels of lead (Pb),
86 cadmium (Cd) and mercury (Hg), all of which are atmospheric long-range pollutants that are
87 readily transported across national borders and were identified as being particularly harmful
88 in the 1998 Aarhus Protocol on Heavy Metals, one of the international agreements on
89 pollution control under the convention. Although copper (Cu) and zinc (Zn) were not
90 identified as being particularly harmful in CLRTAP, their concentrations also exhibit regional
91 patterns (Rühling and Tyler 2001).

92

93 **Methods**

94

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

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

116

117 Individual national institutions were free to use analytical methods of their own choosing,
118 although the IM manual recommends the use of ICP-MS for measuring the Cd, Pb, Cu and Zn
119 contents of water samples. Generally, GFAAS (atomic absorption spectrophotometer using
120 graphite furnace), ICP-OES (inductively coupled plasma - optical emission spectrometry) and
121 ICP-MS (MS: mass spectrometry); both PerkinElmer, were used (ISO 11885, ISO 8288, ISO
122 15586). Clean sampling procedures were observed. Litter material was analysed by acid
123 digestion of dried samples with HNO₃ followed by AAS and ICP-OES or ICP-MS methods
124 (DIN 38406-6, ISO 5961, ISO 11885). A graphite furnace was used for the AAS
125 determination of Cd levels. Hg in litter samples was determined by acid digestion and cold-
126 vapor-AAS.

127

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

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

137

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

145

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

154

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

158

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

165

166

167

168

169 **Site descriptions**

170

171 Data from 14 sites in eight countries was examined (Figure 2). However, the available data on
172 heavy metals in different compartments varies from site to site. Country specific site codes
173 are shown in Table 1 and Figure 2. The sites are all small hydrological catchments, which
174 usually have well-defined water divides. Forests dominate the land cover to various extents,
175 although one site (GB01) is primarily covered with shrubs and grass (Table 1). The monitored
176 sites are generally in protected areas with unmanaged forests that have been allowed to
177 develop naturally. The sites' altitudes range from near sea level to mountain locations of up to
178 1292 meters above sea level. The sites' annual precipitation ranged from 590 to 1650 mm,
179 decreasing moving eastwards and increasing with altitude.

180

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

194

195 **Results**

196

197 ***Deposition and litterfall***

198

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

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

216

217 The mean annual bulk deposition of Cd for different sites was found to range from 0.015
218 $\text{mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ to $0.24\text{ mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$. The quantity of Cd deposited by TF was mostly higher than
219 that deposited via BD; in some cases similar or even lower. The beech stand at AT01 had low
220 cadmium TF. Comparatively high levels of Cd deposition via both BD and TF were observed
221 at the high-altitude DE01 site (Table 2). At the site also LF showed high values. Cd fluxes in
222 the LF were in some cases of similar magnitudes as those of the TF sometimes less, but the
223 resulting TF+LF values were exceeding BD except for the beech stand.

224

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

232

233 *Metals in stream flows*

234

235 Annual water discharges varied greatly between the sites; this in turn affected the metal
236 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 $0.36 \text{ mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$. 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 $1.8 \text{ mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ and $1.4 \text{ mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$
252 ¹, 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. $1 \text{ mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$. 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 $0.003\text{-}0.06 \text{ mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ and
270 was not sensitive to differences in the water discharge (Table 2). Effluxes were low at FI01,

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

276

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

281

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

288

289 *Mercury at Swedish sites*

290

291 Hg levels were monitored at Swedish sites during special one year campaigns that moved
292 from site to site with one repetition. Additionally, in some years, Hg levels in the litterfall and
293 stream water were measured. The mean annual BD values for sites SE04, SE14, SE15 and
294 SE16 were 7, 6, 5 and $2.4 \text{ }\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, respectively (Figure 6). This corresponds with the
295 gradient for several pollutants throughout Scandinavia with the highest levels in the south-
296 west, represented by SE04, and the lowest in the north (SE16). The Hg flows in TF and LF
297 followed this pattern (Figure 6). The four sites had average annual Hg deposition by TF of 17,
298 14, 12 and $4 \text{ }\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, respectively, corresponding values by LF at 39, 23, 12 and $8 \text{ }\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$.
299 Determinations of Hg in TF were made 2 to 6 years at the different sites and for Hg in
300 LF 8 to 12 years. Correlation analysis of annual values showed that Hg flows in TF and LF
301 were correlated ($p = 0,024$, $n = 11$). There was a very pronounced enrichment of both TF and
302 LF compared to BD, which indicates very large dry deposition (Steinnes and Andersson,
303 1991). There were north-south gradients for deposition and litterfall but no such gradient for

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

309

310 **Discussion**

311

312 *Metal deposition in forest ecosystems*

313

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

329

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

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

346

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

356

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

369

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

380

381 The EMEP estimated of the total deposition of Cd in Scandinavia and Germany in 2008 to be
382 between 0.01 mg·m⁻² and 0.1 mg·m⁻², with higher values in some Eastern European areas
383 (EMEP 2010). This is lower input as compared to estimations with TF+LF and the possible
384 internal component of its circulation makes Cd less suitable for the comparison. The
385 deposition of Hg in Scandinavia and Germany was estimated to range from 0.007 mg·m⁻² to
386 0.02 mg·m⁻² along a north-south gradient, with even higher levels in other parts of Europe.
387 Our assessments of TF+LF of Hg in Swedish forest sites were clearly larger than the EMEP
388 deposition estimates for Hg (Figure 6).

389

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

399

400 ***Catchment balances***

401

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

404 deposited metals, with a few remarkable exceptions. Disregarding DE01 and CZ02, the
405 average outflow of Pb was 16% of the input by throughfall (TF) for the coniferous sites; it
406 should be noted here that TF is only a part of the total deposition. For Cd corresponding
407 output was 26% of TF, but SE15 with high output of Cd was also excluded from the average.
408 Cd is considered to be more mobile than Pb in soils (Bergkvist, 2001); it is more soluble and
409 is subject to cation exchange, whereas Pb is tightly bound to the soil organic material (SOM)
410 and its mobility dependent on that of the SOM. High retention of Pb and Cd has been
411 observed in numerous catchment studies, often with the addition that Pb is retained to a larger
412 degree than Cd (Lindberg and Turner 1988, Johnson et al 1995, Aastrup et al 1995,
413 Ukonmaanaho et al 2001, Minarik et al 2003, Watmough and Dillon 2007). The period
414 examined in this study was one of dramatically lowered pollution loads, but this did not affect
415 the general pronounced retention of these elements. Consequently, on the catchment level, the
416 stores of Pb and Cd in soils continue to accumulate. Huang et al (2011) recently reported that
417 the deposition and outflow of Cd in a Bavarian forest catchment were almost in balance,
418 which is a first case that was attributed to a reduction in the load. Model calculations
419 involving soil processes in catchments in semi-natural moorlands have demonstrated that the
420 changes in the abundance of loosely sorbed Cd and Zn may occur over timescales of decades
421 to centuries, while for Pb, the changes will occur over centuries or millennia (Tipping et al
422 2006). This does not mean that no improvement is possible. The relocation of Pb, Cd and
423 other elements in soils have been reported in many cases (Friedland et al 1992, Bergkvist
424 2001, Eriksson 2002, Watmough et al 2004, Johnson and Richter 2010, Kobler et al 2010). In
425 combination with reduced deposition, this lowers the metal burden on the biologically
426 important top-soils. The reduction of these more available stores may also cause decreases in
427 the outflow to aquatic recipients (Watmough and Dillon 2007).

428
429 The retention of Cd and Pb at the Scandinavian sites was less extensive than the extreme
430 values observed in some eastern European sites such as LV01, LV02 and CZ01. The
431 differences in retention between groups of sites were highly significant (ANOVA). For the
432 eastern European group the strong retention is partly due to the very small water discharge.
433 Two of the mountainous sites, AT01 and DE01 had very large water discharge volumes
434 (Table 1); notably, the losses of Pb and Cd from the German DE01 site were almost equal to
435 the input from throughfall (Table 2, Figure 3). However, the total deposition (here defined as
436 TF+LF) would exceed the outflow even at DE01. The situation at AT01 is more complex
437 because of its unusual soil conditions and the irregular hydrological flow paths within its

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

442

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

446

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

458

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

466

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

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

478

479 **Conclusions**

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

486

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

494

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634 Table 1. Descriptions of the IM sites examined in this work and compiled into regions based
635 on similar P and R. P – average annual precipitation during the period over which metal
636 concentrations were measured; RW- annual runoff during the period over which metal
637 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

639 Note: The nation codes are: AT-Austria, CZ-Czech republic, DE-Germany, FI-Finland, GB-United kingdom,

640 LT-Lithuania, LV-Latvia and SE-Sweden.

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644 Table 2a. Flows of lead (Pb) in bulk deposition (BD), throughfall (TF), litterfall (LF) and
645 stream water (runoff-RW) at ICP IM sites for parts of the period 1996-2011 (mg m⁻²·yr⁻¹).

646 Coefficient of variation – CV and number of values (years) – N.

647

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

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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

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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.m⁻².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

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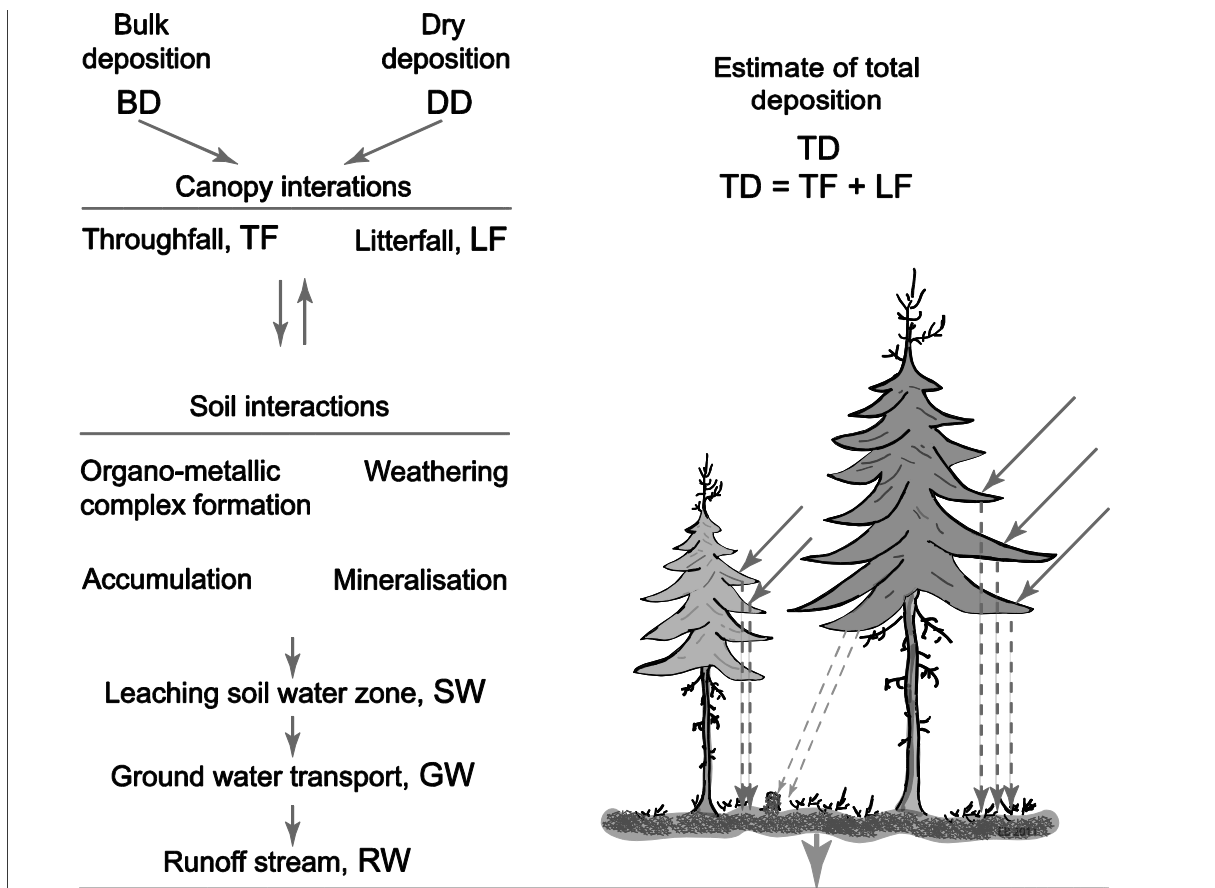
664 Table 3b. Flows of zinc (Zn) in bulk deposition (BD), throughfall (TF), litterfall (LF) and
665 stream water (runoff-RW) at ICP IM sites for parts of the period 1996-2011 (mg.m⁻².yr⁻¹).
666 Coefficient of variation – CV and number of values (years) – N.

667

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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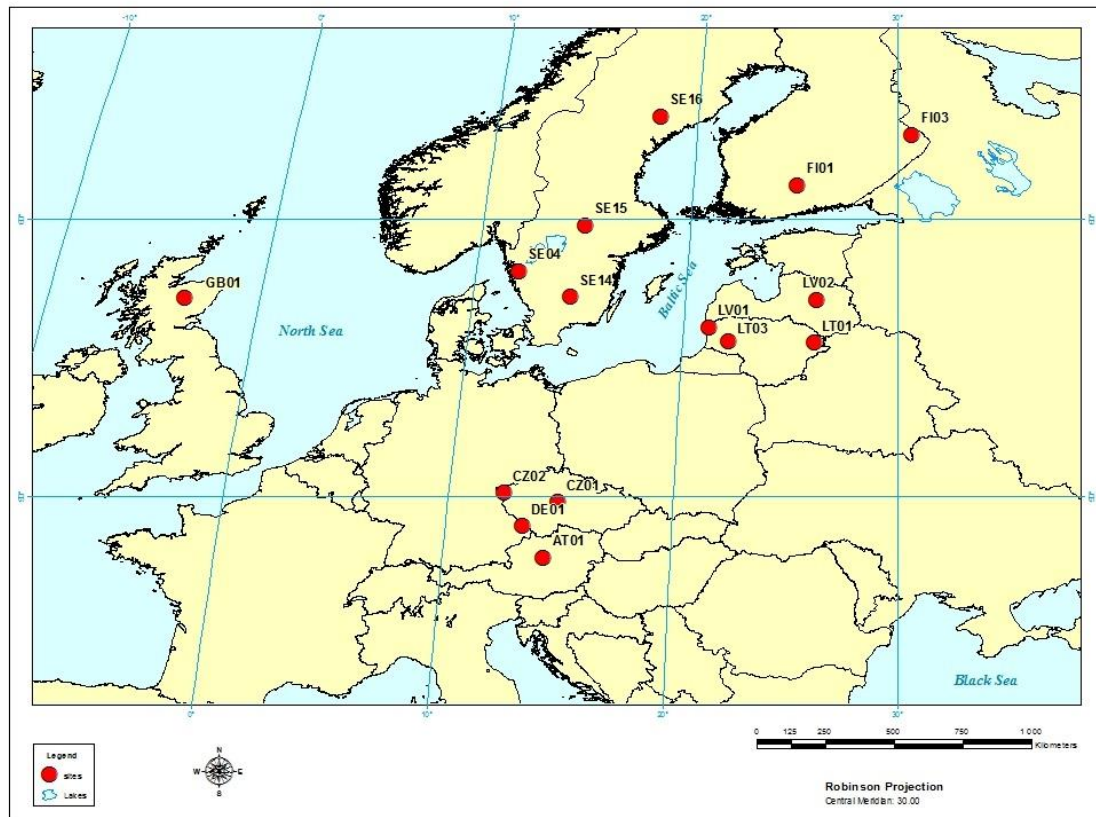


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Fig. 1. Processes involving metals in forest catchment. Uptake from the soil to the vegetation via the roots is not shown, and is not significant for Pb and Hg.

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

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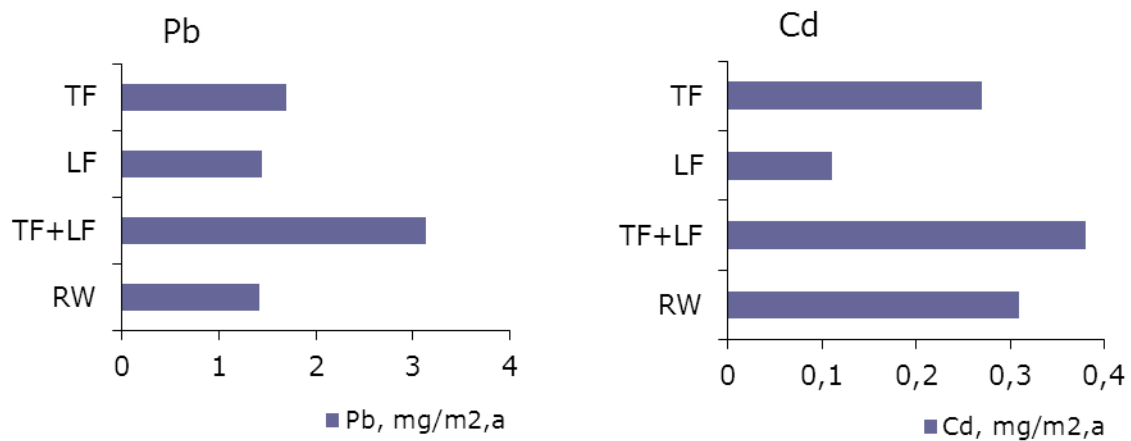
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708 **Fig. 3.** Lead and cadmium balances for the DE 01 catchment including throughfall, TF,

709 litterfall, LF and runoff, RW. The sum of TF+LF also presented. Note different x-axis scales.

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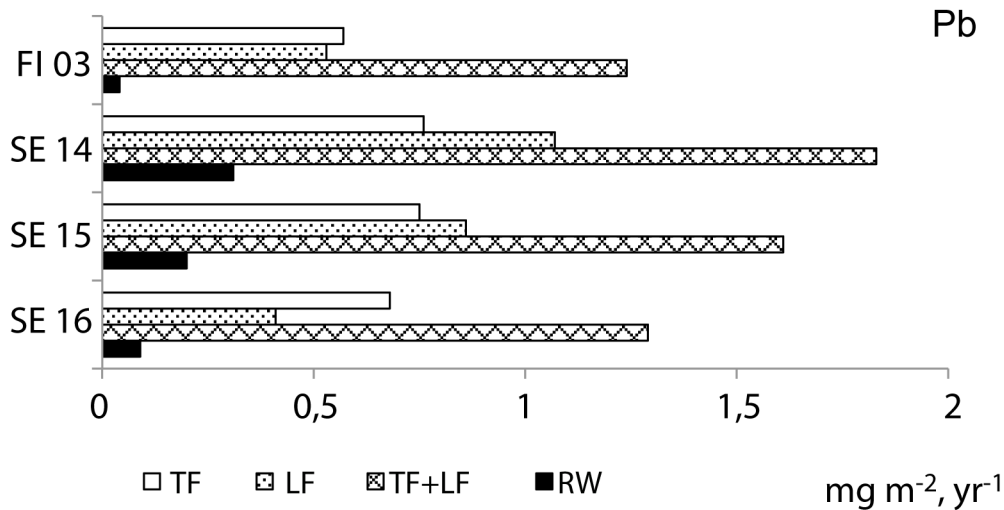
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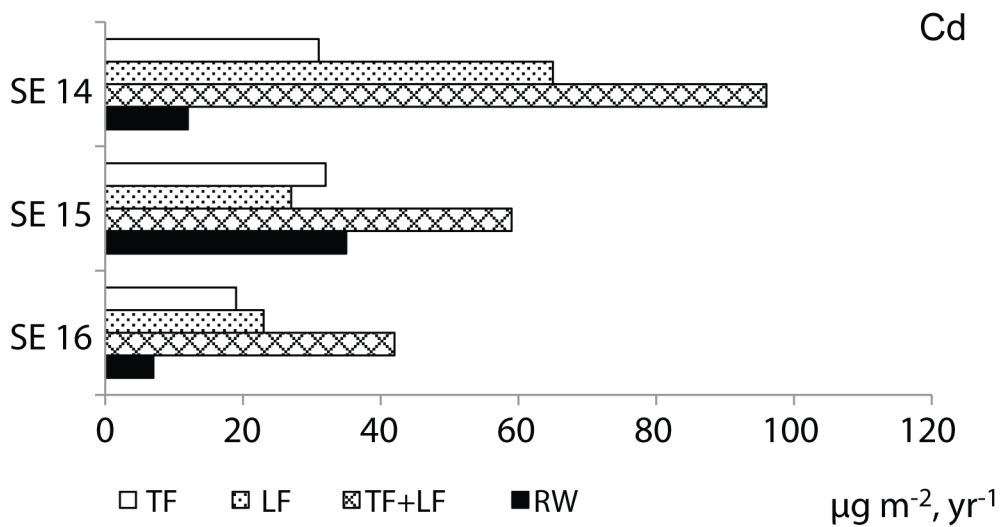
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737 **Fig. 4.** Lead balances for the Finnish FI 03 catchment (note; BD instead of TF) and the three
738 Swedish catchments SE 14, SE15 and SE 16 with throughfall- TF, litterfall- LF, throughfall+
739 litterfall-TF+LF (FI 03 BD+LF) and runoff- RW included.

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

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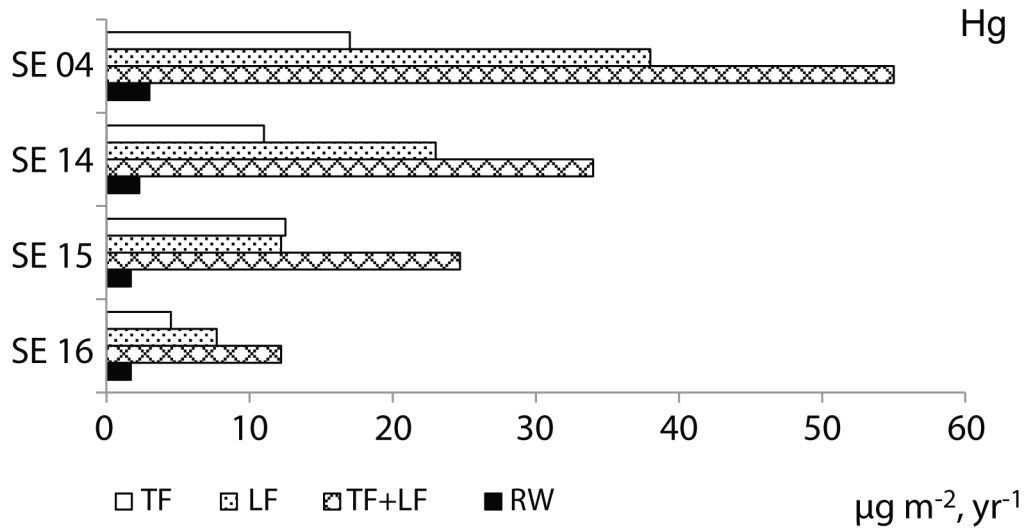
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757 **Fig. 6.** Mercury balances for the four Swedish catchments SE 04, SE 14, SE15 and SE 16

758 showing throughfall- TF, litterfall- LF, throughfall+ litterfall-TF+LF and runoff- RW.

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