PERSPEKTIVEN FÜR UMWELT & GESELLSCHAFT umweltbundesamt

Deposition of trace metals at IM Zöbelboden

LONG-TERM DEPOSITION OF TRACE METALS AT THE INTEGRATED MONITORING SITE ZÖBELBODEN

Element concentrations and loads between 1994 and 2008

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REPORT
REP-0246

Vienna, 2009

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Acknowledgment: This work was carried out within the framework of the International Cooperation Programme (ICP) on Integrated Monitoring as part of the UN-ECE Convention on Long-Range Transboundary Air Pollution (CLRTAP). We are extremely grateful for the manifold support from the "Kalkalpen" National Park and the Austrian Federal Forests (ÖBF).

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Imprint

Owner and Editor: Umweltbundesamt GmbH
Spittelauer Lände 5, 1090 Vienna/Austria

Printed on CO_2-neutral 100% recycled paper

ISBN 978-3-99004-046-1

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1 INTRODUCTION

Anthropogenic emissions of environmentally harmful metals are subject to long-range atmospheric transport across national borders. In Europe and Central Asia, 37 countries receive more than half of their anthropogenic lead deposition from cross-boundary atmospheric transport (MSC-E 2008). Consequently, the Aarhus Protocol on Heavy Metals (UNECE 1998) under the Convention on Long-Range Transboundary Air Pollution (CLRTAP) which entered into force in 2003 aims to reduce annual emissions of Hg, Cd and Pb in the participating countries below their levels of 1990[1].

The monitoring of the effectiveness of the Aarhus Protocol is based, amongst others, on the site network of previously established ICP Integrated Monitoring (IM)[2] which aims to determine and predict the state of ecosystems and their changes from a long-term perspective with respect to the regional variation and impact of air pollutants including their effects on biota (**http://www.unece.org/env/lrtap/WorkingGroups/wge/im.htm**). Integrated Monitoring of heavy metal fluxes is tightly interwoven with two other CLRTAP expert instruments: 1. ICP Modelling and Mapping (to assess critical pollutant loads and levels) and 2. ICP Forests (specifically surveying forest ecosystems).

At the ICP IM site *Zöbelboden*[3] the monitoring of trace metals started in the year 1993, hence before the Aarhus Convention was adopted. More than a decade's records of background ecosystem pollution have become available. The present study describes the deposition trends of various trace elements and compares their concentrations in different deposition pathways.

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[1] or any chosen year between 1985 and 1995

[2] International cooperative programme on integrated monitoring of air pollution effects on ecosystems

[3] EMEP-site AT0048R

2 SUMMARY

The present study provides a decade's records of trace metal deposition on the Austrian UNECE ICP Integrated Monitoring site *Zöbelboden*. Deposition concentrations and loads can be regarded as background levels due to their long distance to emission sources, i.e. that they are predominantly governed by long-range atmospheric transport. Accordingly, the observed deposition trends of heavy metals (except copper) corresponded to the large-scale emission history. Apart from aluminium and copper with oscillating trends, no trace metal concentration had increased over ten years, which indicates a successful reduction of emissions.

However, the long-term trends were transiently (2000–2003) masked by an episode of drastically increased deposition levels, which is likely to have been induced by the metalworking industry in the region. Those metals whose deposition levels were affected by regional emissions could be distinguished.

The above-mentioned trends determine the trends of litterfall chemistry at both Intensive Plots. However, as soil and tree species additionally affect the element concentrations in litter, the trends of aqueous and litterfall deposition differ regarding their direction and/or magnitude. Solely the cadmium concentration shows concurrent trends in bulk, wet, throughfall and litter deposition. What is most obvious is that the transient peaks of the zinc and copper concentrations mentioned above are not mirrored in the concentrations of litter.

The concentrations and loads of cadmium, lead and zinc remained well below regulatory thresholds, and concentrations were much lower than observed during the 1980s. Bulk loads of copper, zinc and nickel were high in comparison to (few available) other background data. Lead and cadmium loads were similar to results of EMEP deposition models for the corresponding area. Notably mercury and arsenic remained mostly below the analytical detection limits.

In terms of concentration, aluminium and zinc were the most abundant trace metals found in the deposition, regardless of the deposition pathway (bulk, wet or canopy throughfall). Both metals accounted, in about equal shares, for more than the half of the total metal content[4]. The most conspicuous difference in the metal composition of the various deposition pathways was the manganese enrichment of canopy throughfall on a coniferous stand. Quantitatively, the canopy throughfall on the dense coniferous plot was richer in trace metals than the throughfall from the broadleaved canopy as well as on the clearing area ("Wildwiese") (bulk deposition).

The contribution of different fluxes (bulk, wet, canopy throughfall) to the total deposition loads of a given metal varied between individual years, but the importance of a particular flux was not notably associated with overall loads. However, canopy throughfall added more to total aluminium than to lead flux, indicating the importance of forest canopy in capturing particles with lower deposition velocity.

[4] 11 metals considered

3 ZUSAMMENFASSUNG

Die vorliegende Studie zeichnet einen mehr als zehnjährigen Abschnitt der Depositionsgeschichte verschiedener Metalle an der österreichischen UNECE ICP Integrated Monitoring Messstelle *Zöbelboden* nach. Die Konzentrationen und die daraus entstehenden Frachten können als charakteristisch für Hintergrundstandorte, also vorrangig durch weiträumige Luftverfrachtung beeinflusst, betrachtet werden. Dementsprechend korrelieren die Depositionstrends der Schwermetalle (außer Kupfer) mit dem großräumigen Emissionsverlauf. Abgesehen von Aluminium und Kupfer mit ihrem oszillierenden Verhalten, nahm die Konzentration keines Metalles über den Beobachtungszeitraum hin zu, was auf erfolgreiche Emissionsminderungen hinweist.

Allerdings wurden die langjährigen Trends durch eine vorübergehende Periode (2000–2003) drastisch gesteigerter Depositionen, die wahrscheinlich auf regionale Metallverarbeitung zurückzuführen sind, überlagert. Mit Ausnahme von Kupfer waren die Konzentrationssprünge aber ausgeprägt genug, um den Einfluss regionaler Emissionen vom Hintergrundverlauf zu unterscheiden.

Die erwähnten Trends bilden die Grundlage für die Konzentrationen in den Streuproben, die auf beiden intensiv beprobten Flächen (Intensivplots) gesammelt wurden. Da jedoch die Konzentrationen im Streu auch vom Boden, dessen Eigenschaften und der Baumart beeinflusst werden, unterscheiden sich die Trends hinsichtlich ihres Verlaufs und/oder ihrer Stärke. Es zeigen nur die Kadmiumkonzentrationen gleichlaufende Trends in allen Proben. Am auffälligsten ist, dass sich die drastisch gesteigerten Depositionen (2000–2003) von Zink und Kupfer nicht in den Konzentrationen der Streuproben wiederspiegeln.

Die Konzentrationen und Frachten einschlägig bekannter Schwermetalle (Kadmium, Blei, Zink) blieben weit unter den anwendbaren Richt- und Grenzwerten und waren viel niedriger als in den 1980ern gemessene Werte. Die Gesamtfrachten von Kupfer, Zink und Nickel waren im Vergleich zu (den wenigen verfügbaren) anderen Hintergrunddaten hoch. Blei- und Kadmiumfrachten stimmten gut mit den vom EMEP für die Region modellierten Werten überein. Beachtenswert ist, dass die Quecksilber- und Arsengehalte hauptsächlich unter der analytischen Nachweisgrenze blieben.

Aluminium und Zink waren von der Konzentration her die wichtigsten Spurenmetalle, unabhängig vom Depositionstyp (Gesamt- und Nassdeposition, Kronendurchlass). Beide Metalle machten, zu ungefähr gleichen Anteilen, über die Hälfte der Gesamtmetallkonzentration[5] aus. Der auffälligste Unterschied zwischen den verschiedenen Depositionsformen war die Mangananreicherung im Niederschlag des Koniferenbestandes. Letzterer enthielt auch insgesamt mehr Spurenmetalle als die Deposition in weniger dichtem Laubholzbestand oder auf einer Freifläche.

Die relative Bedeutung verschiedener Depositionsformen (gesamt oder nass auf Freifläche, Kronendurchlass in Laub- und Nadelholzbestand) für die Depositionsfracht wechselte zwischen den Jahren, stand jedoch nicht in eindeutigem Zusammenhang mit dem absoluten Immissionsausmaß. Allerdings war der Beitrag des Bestandesniederschlags zu den Aluminiumfrachten höher als bei Blei, was auf die Bedeutung der Kronenschicht für die Filterung von Partikeln mit niedriger Sedimentationsgeschwindigkeit hinweist.

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[5] an 11 Metallen

Abbreviations

n.a.…not available: samples without valid measurement

n.d.…not detectable (value below analytical detection limit)

med…median

obs…sample size (observations)

out…outlier count

P_n…n^{th} percentile

sd…standard deviation

WADOS…wet-and-dry-only sampler

4 RESULTS AND DISCUSSION

4.1 Comparison with other sites

It has to be taken into account that a comparison of element concentrations in – and loads of – deposition between sites is confounded when temporal trends are strong and different measurement years are analysed. Therefore, the years of the measurements are given in the tables.

The bulk loads of environmentally notorious trace metals (Cd, Pb, Cu, Zn, Ni) on the studied site Zöbelboden remained below currently applicable regulatory standards. Cadmium loads were in the range of other background sites and only about one quarter of those recorded in western Austrian mountains. Lead loads were similar to those observed at western Austrian and other background sites and agreed with those calculated from EMEP models – however, they were a multiple of the values measured at two other sites in the province of Upper Austria (in which Zöbelboden is situated). In contrast to the former trace metals, copper, zinc and nickel loads were relatively high, compared to other European sites.

Starting around 2000, concentrations of iron, chromium, nickel, zinc, copper, aluminium, and manganese remained unusually high (for local conditions) over 4–5 years and levelled off again after 2003. The onset and decay of these peaks varied between particular metals. Fe, Cr and Ni bulk deposition reached a distinct plateau between 2000 and 2003. Accordingly, Fe, Cr and Ni concentrations were strongly correlated during 2000–03 (Figure 1). Zn and Cu deposition changed more gradually, starting to rise in 1999 with a peak in 2001 and decreasing afterwards. This pattern was, to a slighter extent, also observed for Al and Mn. A factor analysis based on the correlation between elements indicates that a single common factor (factor 1 in Figure 1 b) suffices to explain most of the variation of Fe, Cr, and Ni concentrations during 2000–03. Another conspicuous association, though less pronounced, was observed for zinc and aluminium concentrations (Figure 1 a, b).

The transient character and the elemental composition of the deposition peak suggest an influence of regional industrial emissions: some small scale metallurgical enterprises are found within a 12–37 km distance from the study site.

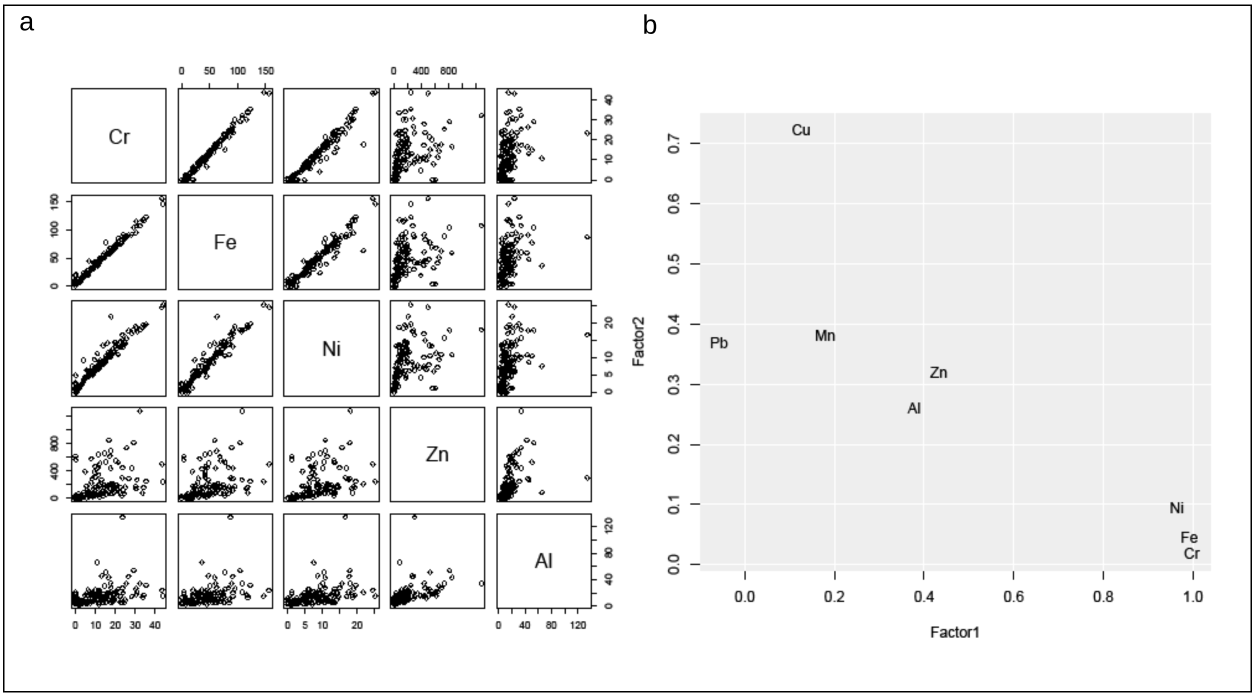


Figure 1: Association between metal concentrations in bulk deposition 2000–04, shown as (a) scatterplots and (b) factor loadings. Factors 1 and 2 explain 53% of total variation.

4.1.1 Bulk deposition

Concentrations of trace metals (except nickel) at *Zöbelboden* were roughly one order of magnitude lower than those observed three decades earlier at the peak time of forest decline. It is interesting to see how e.g. lead concentrations differ by a factor of nearly 50 (Table 1).

Table 1: Metal concentrations in bulk deposition at various sites.

Fe	Mn	Cd	Cr	Pb	Cu	Zn	Ni	Al	
3.75 *	**2.10**	**< 0.1**	**.75 ***	**0.62**	**2.92 ***	**9.2 ****	**2.5 ***	**11.7**	this study (median of 1995–2007)
191	44	1.5	1.4	27	23	142	2.6	117	broadleaf (beech) canopy, Sollingen (Germany), 1968–74, ca. 500 m a.s.l. (ULRICH et al. 1986)

*unit: µg l^{-1}; * without 2000–03 values; ** without 1999–03 values*

The loads of Cd, Pb, Cu, Zn, and Ni remained far below any applicable regulatory standards and current concentrations close to industrial sources. Observed lead loads corresponded to modelled EMEP loads for this region and were similar to the background values measured in western Austria. They were, however, at least twice as high as the lead loads calculated at two other sites of the same province (Upper Austria). Cadmium loads were inconspicuous. Copper and nickel loads at least doubled those recorded in western Austria or on Finnish background sites. Also zinc loads were clearly higher than observed at other background stations (Table 2).

Table 2: Metal loads from bulk deposition at various sites.

Cd	Pb	Cu	Zn	Ni	
0.21	**9.3**	**58.4**	**179.2 ***	**29.0 ***	this study (median of 1998–2008 annual deposition rates)
0.9	9	11.8	97	13.5	Achenkirch (Austria) 1997–98, wet + dry depo, 920 m a.s.l. (SMIDT & HERMAN 2007, BAUER et al. 2008)
0.9	10	18.6	148	15.5	Achenkirch (Austria) 1997–98, wet + dry depo, 1758 m a.s.l. (SMIDT & HERMAN 2007, BAUER et al. 2008)
	2				Upper Austria (Schöneben) 1994–2000, 920 m a.s.l. (SMIDT & HERMAN 2004)
	4				Upper Austria (Steyregg) 1994–2000, 335 m a.s.l., site near urban-industrial agglomeration (SMIDT & HERMAN 2004)
0.3	11				modelled immission 2006 for corresponding EMEP raster 74/47 (MSCE 2008)
1–17	70–375	10–80	100–2000		median values from five European regions with 4–17 investigations each region and element (RADEMACHER 2003)
0.2	8.75	5.7	20.3	1.8	mean of two remote Finnish IM plots, 1994–96 (UKONMAANAHO et al. 2001)
1.5–16.1	40–1405				range of current (2007) loads in the surroundings of selected Austrian metalworks (calculated from UMWELTBUNDESAMT 2008)
regulatory standards:					
7.4–15.8	20–53	–	–	–	Critical deposition loads for different forest ecosystem types: below these loads, 50 % of Austrian forest ecosystems can be expected to suffer no significant ecological consequences from deposition. (OBERSTEINER ET AL. 2005)
7.3	365	–	1460	–	calc. from Swiss regulatory immission limits (stated as µg m^{-2} d^{-1}; SCHWEIZ. BUNDESRAT 1985)
7.3	365	–	–	54.8	calc. from German regulatory immission limits (stated as µg m^{-2} d^{-1}; BUNDESMIN. F. UMWELT, NATURSCHUTZ U. REAKTORSICHERHEIT 2002)

*unit: g ha^{-1} a^{-1}; * without 2000–03 values; ** without 1999–03 values*

4.1.2 Wet deposition

Trace metal concentrations were about one order of magnitude lower than reported for a UK rural site (Table 3).

In contrast to the findings for bulk deposition, lead loads were only half of those observed at a height profile in western Austria. Loads of other trace metals (except aluminium) were also lower than reported for a French and a Czech site (Table 4) – even though the loads calculated for Zöbelboden site have *probably been overestimated,* as they were calculated from WADOS which were not designed for the assessment of loads.

Table 3: Metal concentrations in wet deposition at various sites.

	Fe	Mn	Cu	Zn	Al	
range	**n.d.–179 ***	**0.3–9.2**	**n.d.–100**	**1.5–668 ***	**1.5–342**	this study, 1996–2007
	n.d.–97	n.d.–50	0–44	0–990	0–900	S-England, rural surroundings, 1989–91, 100–150 m a.s.l. (NEAL et al. 1994)
median	**2.5 ***	**1.4**	**2.8**	**10.4 ***	**11.5**	this study
mean	18	14	1	188	100	(NEAL et al. 1994)

*unit: µg l^{-1}; * without 2000–03 values; ** without 1999–03 values*

Table 4: Approximate metal loads from wet deposition at various sites.

Fe	Mn	Cu	Zn	Cd	Pb	Al	
50 *	**24**	**53**	**125 ***	**0.8**	**4.8**	**191**	this study, 1996–2007
				0.9	9		Achenkirch (Austria) 1997–98, 920 m a.s.l. (SMIDT & HERMAN 2007)
				0.9	9		Achenkirch (Austria) 1997–98, 1758 m a.s.l. (SMIDT & HERMAN 2007)
77	105			0.9	12	107	Vosges mountains 1998–99, 1146 m a.s.l. (HERCKES et al. 2002)
219	68	419	187	1.9	14	296	Sumava mountains (Czech Republic) 1994–2003, 1123 m a.s.l. (TESAR et al. 2004)

*unit: g ha^{-1} a^{-1}; * without 2000–03 values; ** without 1999–2003 values*

4.1.3 Canopy throughfall

As expected from the higher trapping efficiency of dense coniferous canopies, throughfall from the coniferous plot IP1 was richer in various trace elements than that of the broadleaf stand IP2 (Table 5). Concentrations – except those of zinc – were much lower than observed on the German site Sollingen during the period of forest decline. The range of zinc concentrations, in contrast to those of the other trace metals, was also much higher than on a UK rural site (Table 5).

Table 5: Metal concentrations in canopy throughfall at various sites.

	Fe	Mn	Cu	Zn	Al	
range	**n.d.–359 ***	**1–284**	**1–54***	**2–7319 ***	**3–308 ***	this study (coniferous stand IP1), 1995–2008
	n.d.–126 *	**1–61**	**1–50 ***	**2–4148 ***	**3–358 ***	this study (deciduous stand IP2), 1997-2008
	n.d.–1840	3–1191	n.d.–40	n.d.–970	n.d.–400	broadleaf (beech) canopy, rural surroundings, 1989–91, S-England, 100-150 m a.s.l. (NEAL et al. 1994)
median	**12 ***	**22**	**6 ***	**21 ***	**24 ***	this study (coniferous stand IP1), 1995–2007
	8 *	**4**	**5 ***	**17 ***	**17 ***	this study (deciduous stand IP2), 1997–2007
mean	**18 ***	**32**	**9 ***	**211 ***	**34 ***	this study (coniferous stand IP1), 1995–2007
	10 *	**6**	**8 ***	**125 ***	**27 ***	this study (deciduous stand IP2), 1997–2007
	174	504	19	104	226	broadleaf (beech) canopy, Solling (Germany), 1968–74, ca. 500 m a.s.l. (ULRICH et al. 1986)

*unit: µg l^{-1}; * without 2000–03 values*

4.1.4 Litterfall

Within the limited number of available reference studies, element concentrations in litterfall were comparable to those observed in other regions (Table 6).

Table 6: Metal concentrations in litterfall at various sites.

	Cd	Pb	Cu	Zn	
median	**0.1–1**	**3.18–9.16**	**3.8–6.9**	**43.2–153.7**	this study (coniferous stand IP1), annual medians 1997–2007
	0.1–0.4	**4.81–9.75**	**5.0–8.6**	**35.1–123**	this study (deciduous stand IP2), annual medians 1997–2007
	0.3	3.4–6.5	3.7–5.1	52.5–77.1	four background integrated monitoring sites, mixed species (conif., deciduous), Finland, 1989–96 (UKONMAANAHO et al. 1998)
range	**0.04–2.6**	**1.1–19.0**			this study (deciduous stand IP2), annual data 1997–2007
	ca. 0.02–0.25	ca. 0.5–2			19 beech stands in Swiss province Basel, 1999 (INSTITUT F. ANGEWANDTE PFLANZENBIOLOGIE 2003)

unit: mg kg^{-1} d.m.

4.2 Comparison of deposition fluxes

Throughfall deposition on the coniferous stand (IP1) showed the highest loads per unit ground surface, usually followed by throughfall in the deciduous stand, bulk deposition and, obviously, wet deposition. Therefore, throughfall in the coniferous stand (IP1) was more enriched in trace elements than in the deciduous stand (IP2) illustrating the efficiency of dense coniferous canopies in capturing airborne pollutants.

The elemental composition was very similar along different deposition pathways, except that the throughfall from the coniferous stand was about four times as rich in manganese as the other deposition types.

An investigation of the quantitatively most abundant trace metals (Al, Zn) and of lead showed that the loads of the studied deposition pathways were quite variable between years and were unrelated to overall deposition loads (Figure 2–Figure 4). However, bulk deposition was relatively stronger for lead than for aluminium while canopy throughfall was more important for aluminium which suggests that horizontal canopy filtering was more relevant for the trace metal with lower deposition velocity (Table 7).

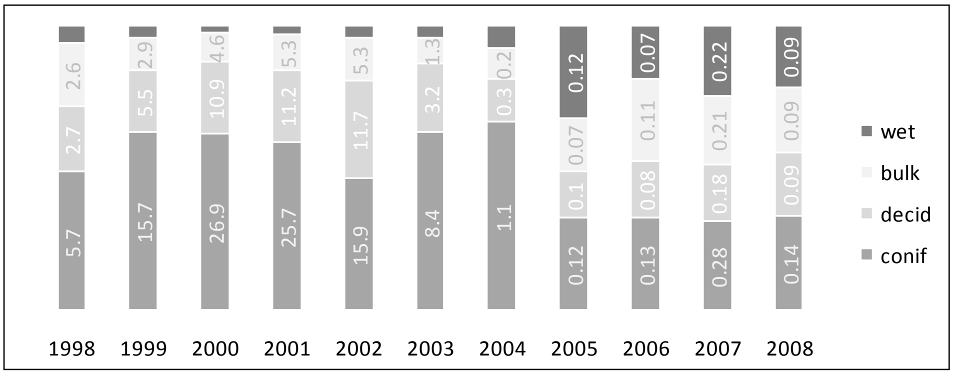


Figure 2: Contribution of various deposition paths to zinc loads. Absolute values (kg ha^{-1} a^{-1}) indicated on bars. wet/bulk…wet/bulk deposition, decid/conif…canopy throughfall on deciduous/coniferous stand.

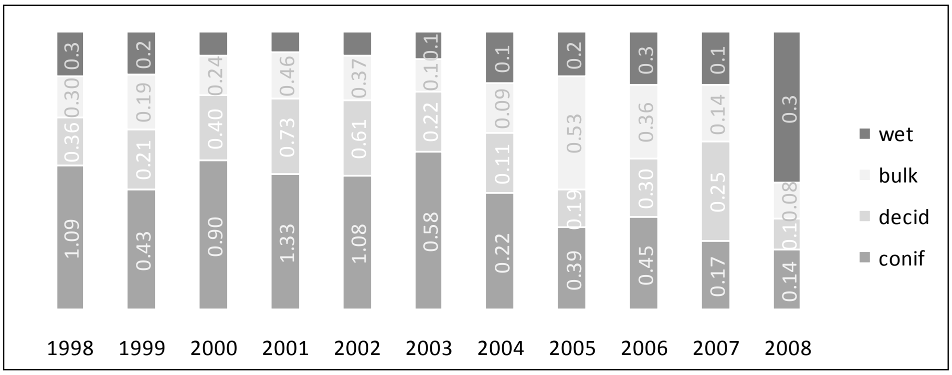


Figure 3: Contribution of various deposition paths to aluminium loads. Absolute values (kg ha^{-1} a^{-1}) indicated on bars. wet/bulk…wet/bulk deposition, decid/conif…canopy throughfall on deciduous/coniferous stand.

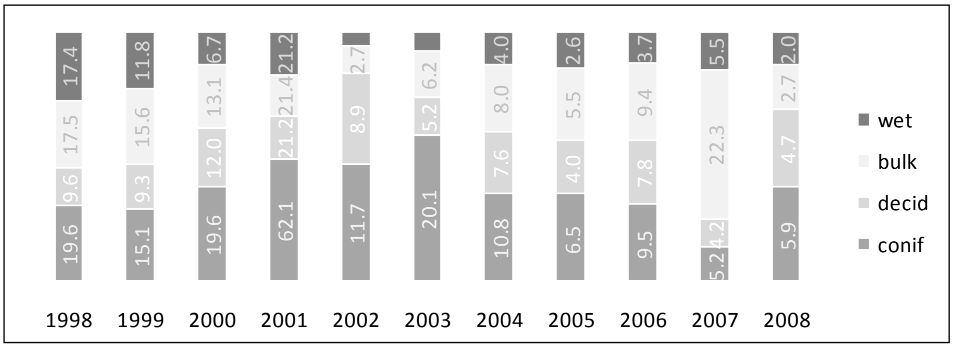


Figure 4: Contribution of various deposition paths to lead loads. Absolute values ($g\ ha^{-1}\ a^{-1}$) indicated on bars. wet/bulk…wet/bulk deposition, decid/conif…canopy throughfall on deciduous/coniferous stand.

Table 7: Relative importance of different pathways for deposition loads.

	bulk	wet	conif	decid
Zn	0,15	0,06	0,49	0,22
Al	0,17	0,16	0,44	0,22
Pb	0,26	0,13	0,35	0,21

shown are the median fractions of cumulated (bulk + wet + canopy throughfall on coniferous and deciduous plot) annual deposition loads for the period 1998–2008

4.3 Deposition trends

Temporal trends of concentrations in canopy throughfall were similar to those in bulk and wet deposition. Moreover, the observed deposition trends agreed with large scale emission trends of neighbouring or/and quantitatively important European source countries (taken from Annex D to EEA 2008), except copper, whose deposition concentration did not follow the steadily increasing emissions (see below).

As described earlier, a number of trace metals showed a transient deposition peak during the years 2000–03. Apart from this peak which is likely to have been caused by regional industrial activities, element concentrations in deposition exhibited the following temporal trends:

- manganese decreased almost steadily from 1995 to 2007
- cadmium concentrations decreased also, most notably between 1995 and 2000, in agreement with emission trends (Figure 5).

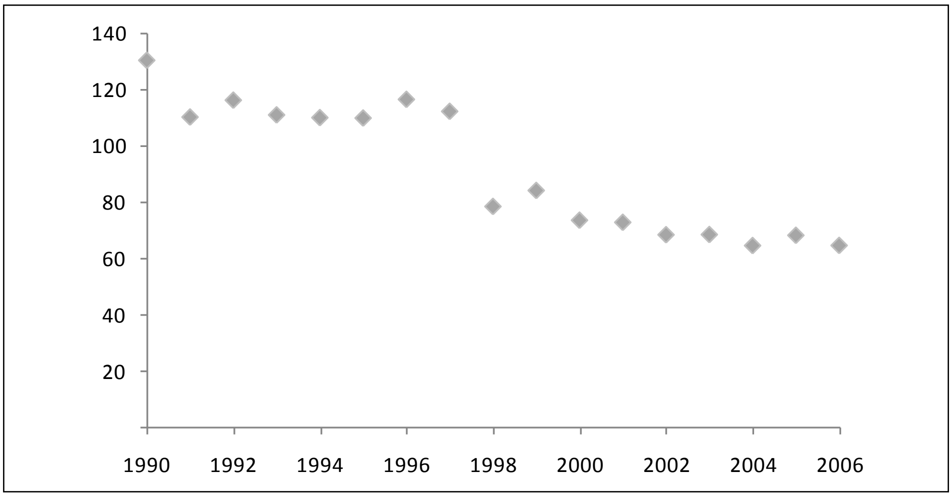


Figure 5: Total annual cadmium emissions (tons) for Austria, Czech Republic, Germany, Italy, Poland, Slovakia and Slovenia (calculated from data in EEA 2008).

- lead concentrations decreased during most of the observation period; this trend was more apparent in canopy throughfall than in bulk deposition on a clearing area and is in line with the considerable decrease of lead emissions in Europe (Figure 6).

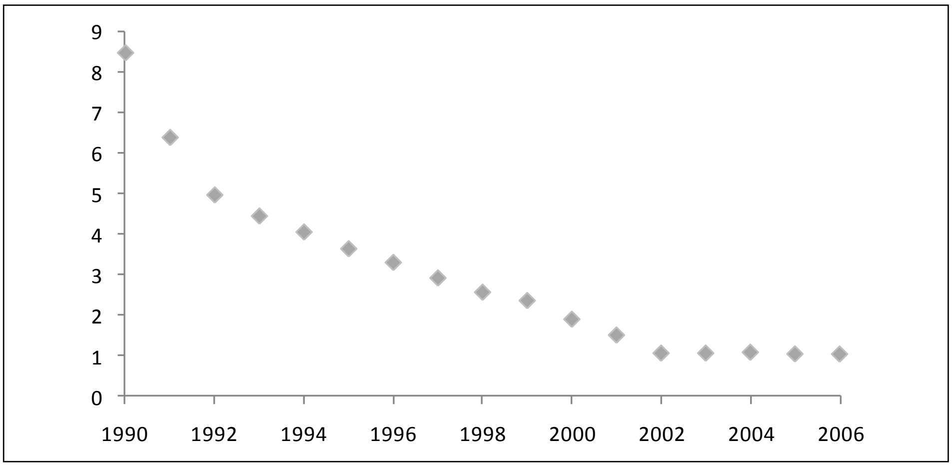


Figure 6: Total annual lead emissions (kilotons) for Austria, Czech Republic, Germany, Italy, Poland, Slovakia and Slovenia (calculated from data in EEA 2008).

- copper levels oscillated, cycles lasting approximately eight years; however, with the limited observation period given, there is no safe distinction between the time of the apparent oscillation and the deposition peak observed for several other metals (see above). In neither case did deposition reflect the continuously increasing emissions during this period (Figure 7).

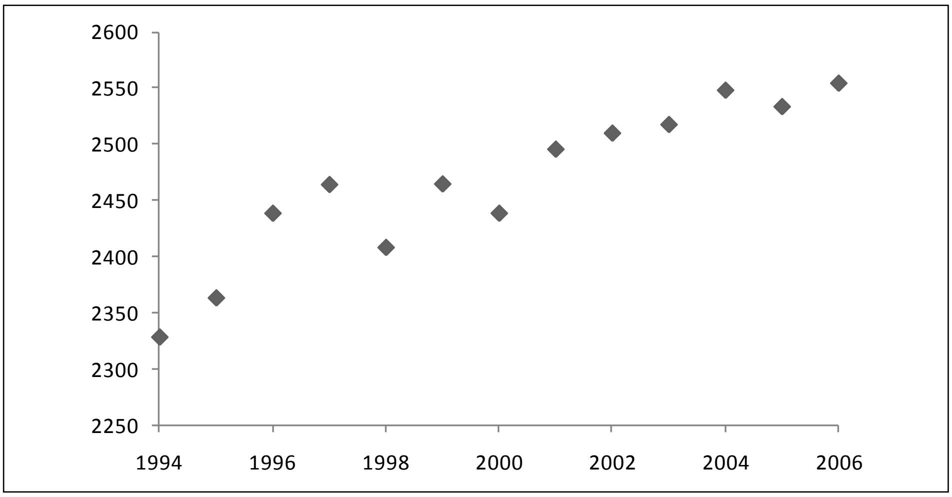


Figure 7: Total annual copper emissions (tons) for Germany, Italy, Poland and Slovakia (calculated from data in EEA 2008).

- aluminium deposition varied in a similar way to that of copper; again, the apparent oscillation cannot sufficiently be distinguished from the general deposition peak 2000–03
- zinc deposition, like that of other metals, was stronger during 2000–03 but levels started to rise in 1998 already

The above mentioned trends determine the trends of litterfall chemistry at both Intensive Plots. However, as soil with its characteristics and tree species additionally affect the concentrations of litter, the trends differ regarding direction and/or magnitude. Solely the cadmium concentration shows concurrent trends in bulk, wet, throughfall and litter deposition. What is most obvious is that the transient peaks of zinc and copper concentrations are not mirrored in the concentrations of litter.

4.4 Detailed results

4.4.1 Bulk deposition on the clearing area "Wildwiese"

Among the trace elements measured in bulk deposition, zinc and aluminium were the most abundant elements. Figure 8 shows that these two elements accounted for more than 60% of the total deposition loads of the nine elements examined. The wet deposition and throughfall deposition on the coniferous stand (IP1) does not differ substantially from the bulk deposition. By contrast, throughfall deposition from the deciduous stand (IP2) deviates by its strongly enriched manganese content.

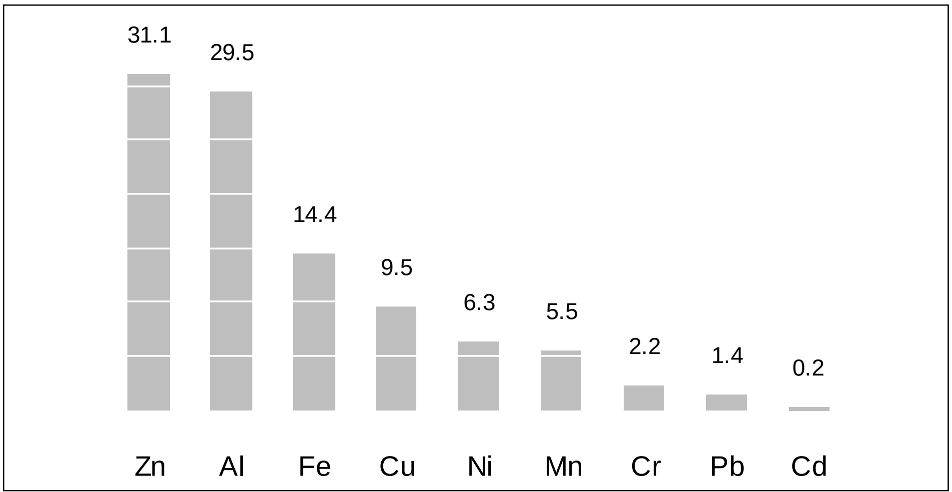


Figure 8: Element composition (%) of bulk deposition on a "Wildwiese" meadow.

4.4.1.1 Iron (Fe)

Table 8: Iron concentration in bulk deposition on "Wildwiese" meadow.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1995	37	3	1	8.0	5.8	1.3	3.1	4.0	6.0	10	17	23.6
1996	38	3	3	5.7	4.2	2.5	2.5	2.5	2.5	7	14	14.8
1997	42	1	1	4.9	2.7	2.3	2.3	2.3	4.0	7	9.0	13.0
1998	38	1	1	6.9	2.8	3.8	3.8	3.8	6.7	9	11.0	13.4
1999	20	4	3	4.4	1.1	3.8	3.8	3.8	3.8	5.4	6.1	6.8
2000	23	2	0	52.7	32.5	3.8	4.6	31.6	49.4	73.9	82.2	117.5
2001	25	0	2	52.9	31.6	11.0	19.4	30.2	46.0	68.1	100.6	123.1
2002	26	0	0	59.7	24.4	22.0	29.5	40.3	60.5	74.0	91.5	108.0
2003	25	1	0	42.8	27.8	8.0	8.0	19.0	42.0	60.0	85.0	92.0
2004	26	0	0	11.8	14.3	n.d.	n.d.	n.d.	7.5	18.1	35.9	44.7
2005	23	2	2	n.d.	–	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2006	23	2	1	n.d.	–	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2007	20	6	0	n.d.	–	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1995–2007	**340**	**51**	**14**	**9.9**	**12.7**	**n.d.**	**n.d.**	**2.3**	**5.3**	**11**	**31**	**50.8**

unit: µg l^{-1}

Note: the drop in iron concentrations after 2004 (Figure 5) is in fact caused by a less sensitive analysis (detection limit raised from 3 to 10 µg l^{-1}).

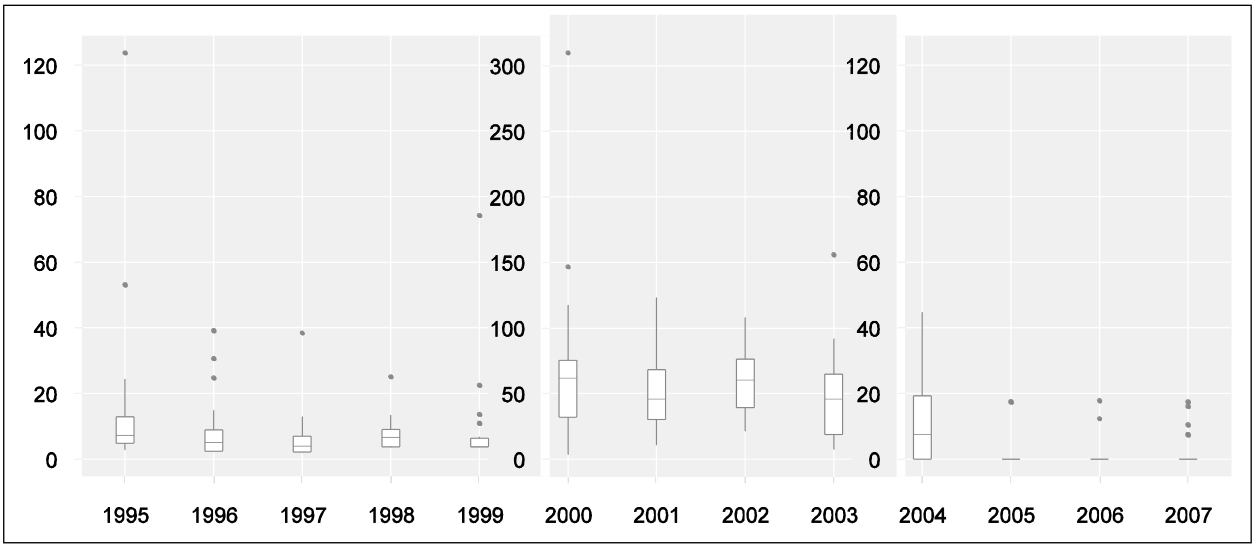


Figure 5: Iron concentration [µg l^{-1}] in bulk deposition on "Wildwiese" meadow (note reduced scale for years 2000–03).

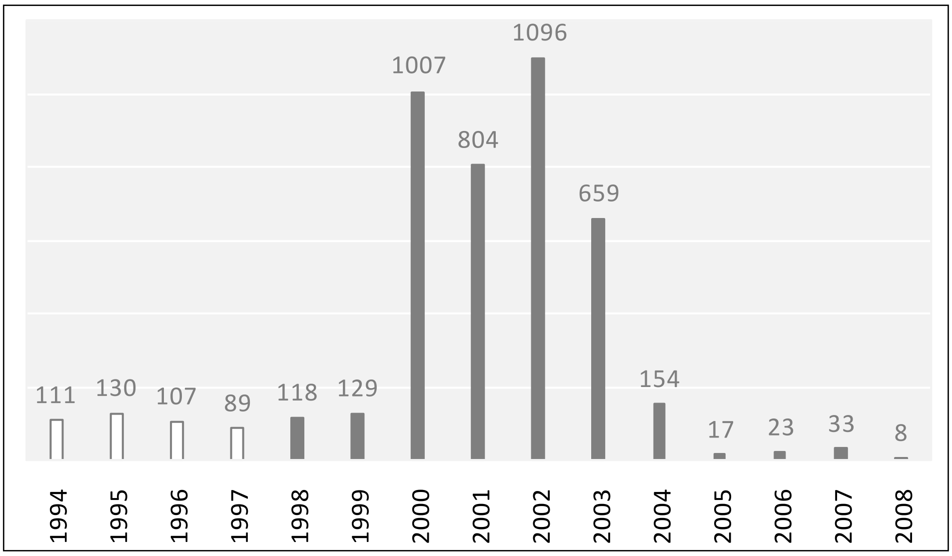


Figure 6: Annual iron loads (g ha^{-1} a^{-1}) by bulk deposition on "Wildwiese" meadow. White bars: more than 30 days of interpolated data.

4.4.1.2 Manganese (Mn)

Table 9: Manganese concentration in bulk deposition on "Wildwiese" meadow.

year	obs	out	na	mean	sd	min	P10	P25	med	P75	P90	max
1995	38	2	1	3.97	2.88	1.30	1.30	1.30	3.25	4.63	8.40	12.10
1996	38	3	3	1.81	0.98	1.30	1.30	1.30	1.30	1.30	3.50	4.60
1997	36	7	1	2.25	0.78	1.90	1.90	1.90	1.90	1.90	3.40	4.70
1998	35	4	1	2.43	1.40	0.75	0.75	1.60	2.10	3.20	3.96	6.00
1999	22	3	2	2.05	0.91	0.75	0.78	1.50	2.10	2.40	3.34	4.00
2000	24	1	0	3.72	2.08	0.75	0.75	2.36	3.99	4.72	5.58	8.38
2001	23	2	2	3.14	1.47	0.75	1.74	2.11	2.87	3.89	4.96	6.39
2002	24	2	0	2.98	1.26	0.80	1.69	2.20	2.75	3.60	4.44	6.30
2003	25	1	0	3.13	1.99	0.30	1.18	1.50	2.80	4.50	5.48	9.00
2004	25	1	0	1.92	0.88	0.61	0.85	1.09	2.10	2.60	3.00	3.60
2005	24	1	2	2.04	1.20	0.30	0.87	1.30	1.75	3.03	3.38	5.70
2006	23	2	1	1.59	0.87	0.30	0.56	0.89	1.50	2.40	2.66	3.10
2007	24	2	0	1.84	1.11	0.30	0.64	1.00	1.60	2.50	3.71	4.00
1995–2007	**361**	**31**	**13**	**2.47**	**1.44**	**0.30**	**1.00**	**1.30**	**2.10**	**3.20**	**4.50**	**7.10**

unit: µg l^{-1}

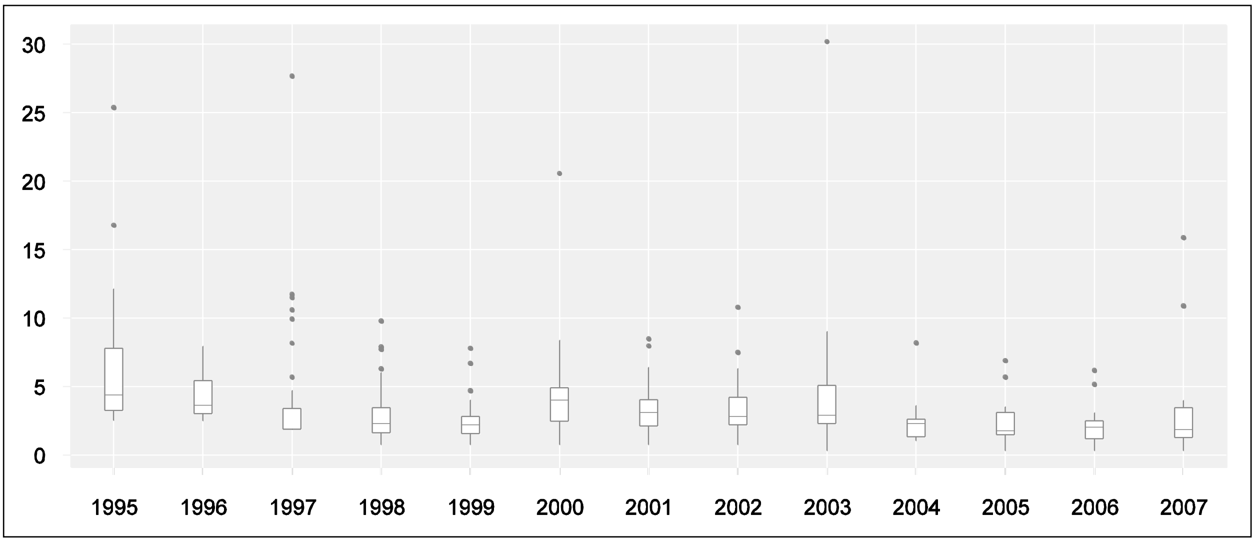


Figure 7: Manganese concentration [µg l^{-1}] in bulk deposition on "Wildwiese" meadow.

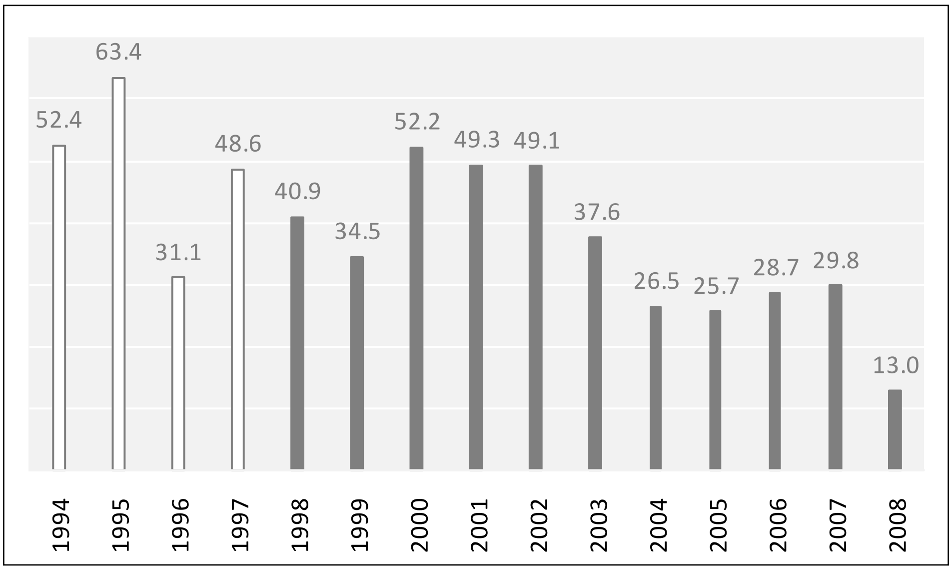


Figure 8: Annual manganese loads (g ha^{-1} a^{-1}) by bulk deposition on "Wildwiese" meadow. White bars: more than 30 days of interpolated data.

4.4.1.3 Cadmium (Cd)

Table 10: Cadmium concentration in bulk deposition on "Wildwiese" meadow.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1995	36	4	1	0.11	0.07	n.d.	n.d.	0.10	0.10	0.13	0.20	0.30
1996	34	7	3	0.06	0.07	n.d.	n.d.	n.d.	0.10	0.10	0.10	0.20
1997	39	4	1	0.10	0.09	n.d.	n.d.	n.d.	0.10	0.10	0.20	0.40
1998	33	6	1	0.09	0.01	0.08	0.08	0.08	0.08	0.08	0.11	0.13
1999	21	4	2	0.08	n.d.	0.08	0.08	0.08	0.08	0.08	0.08	0.08
2000	25	0	0	0.03	0.04	n.d.	n.d.	n.d.	n.d.	0.08	0.08	0.08
2001	24	1	2	0.02	0.04	n.d.	n.d.	n.d.	n.d.	0.08	0.08	0.08
2002	24	2	0	n.d.	–	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2003	24	2	0	n.d.	–	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2004	23	3	0	n.d.	–	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2005	20	5	2	n.d.	–	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2006	23	2	1	n.d.	–	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2007	26	0	0	0.03	0.05	n.d.	n.d.	n.d.	n.d.	0.06	0.10	0.13
1995–2007	**368**	**24**	**13**	**0.05**	**0.06**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**0.10**	**0.10**	**0.23**

unit: µg l^{-1}

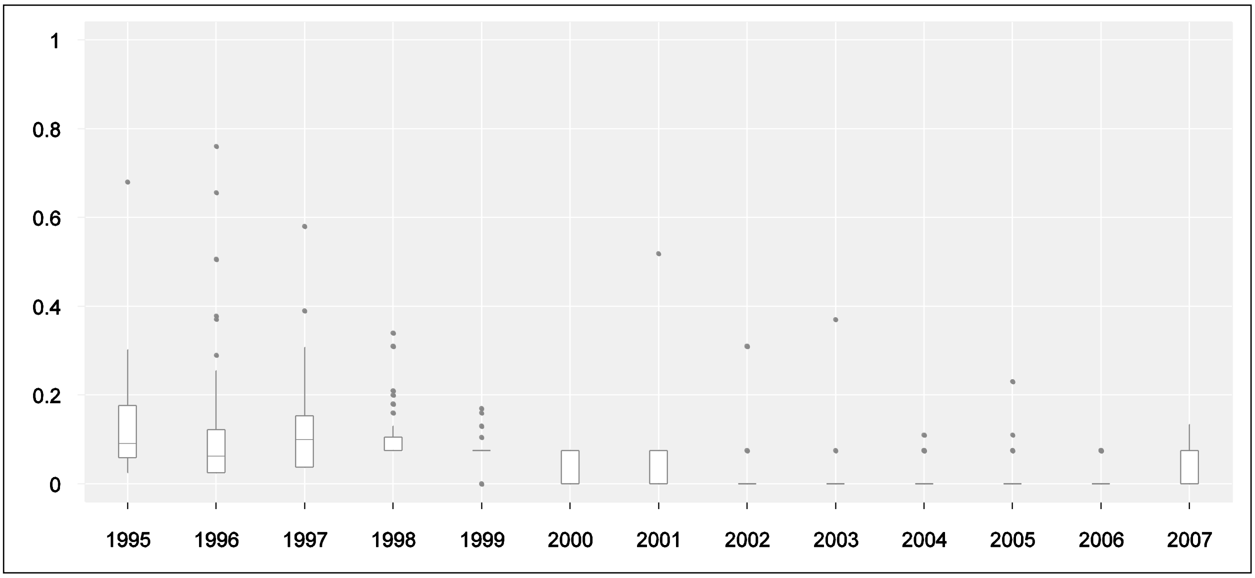


Figure 9: Cadmium concentration [µg l⁻¹] in bulk deposition on "Wildwiese"meadow. Five values > 1 (1995: 3.01, 3.28, 1.35, 1997: 2.81, 2.25) not shown.

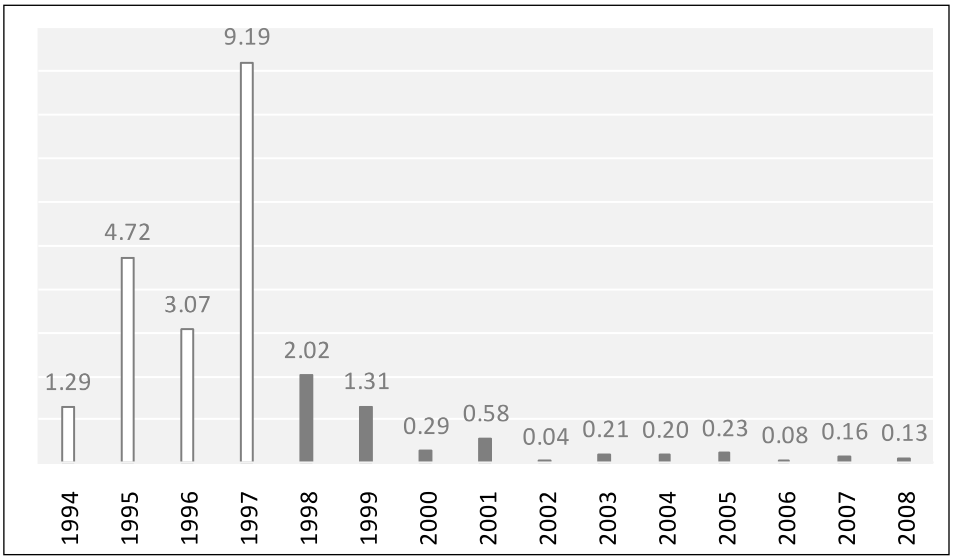


Figure 10: Annual cadmium loads (g ha^{-1} a^{-1}) by bulk deposition on "Wildwiese" meadow. White bars: more than 30 days of interpolated data.

4.4.1.4 Chromium (Cr)

Table 11: Chromium concentration in bulk deposition on "Wildwiese" meadow.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1995	39	1	1	1.3	n.d.	1.3	1.3	1.3	1.3	1.3	1.3	1.3
1996	40	1	3	1.3	n.d.	1.3	1.3	1.3	1.3	1.3	1.3	1.3
1997	43	0	1	1.9	n.d.	1.9	1.9	1.9	1.9	1.9	1.9	1.9
1998	39	0	1	0.8	n.d.	0.8	0.8	0.8	0.8	0.8	0.8	0.8
1999	24	1	2	0.8	n.d.	0.8	0.8	0.8	0.8	0.8	0.8	0.8
2000	23	2	0	14.1	9.8	n.d.	n.d.	8.2	13.8	20.7	23.4	34.3
2001	21	4	2	10.9	5.3	1.4	4.8	8.0	11.5	14.0	16.7	23.5
2002	26	0	0	17.1	7.4	5.6	8.5	11.1	17.2	21.7	27.4	32.3
2003	25	1	0	11.8	7.7	1.6	2.3	4.0	12.0	18.0	22.8	25.0
2004	20	6	0	0.1	0.3	n.d.	n.d.	n.d.	n.d.	n.d.	0.1	1.2
2005	23	2	2	n.d.	–	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2006	25	0	1	n.d.	–	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2007	25	1	0	n.d.	–	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1995–2007	**312**	**80**	**13**	**1.2**	**1.4**	**n.d.**	**n.d.**	**n.d.**	**0.8**	**1.3**	**1.9**	**8.0**

unit: µg l^{-1}

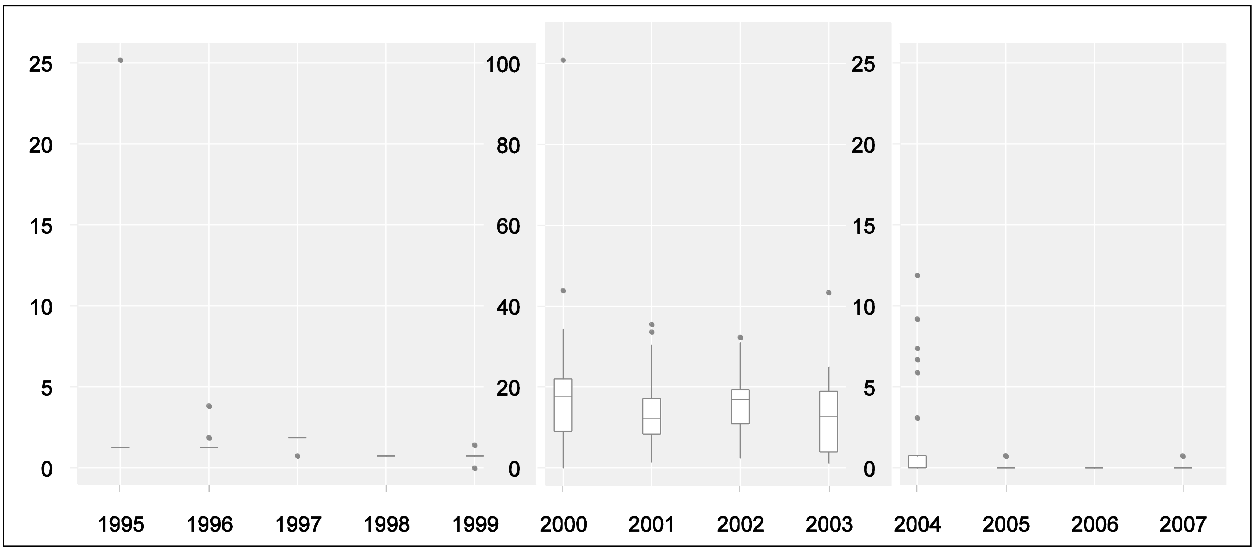


Figure 11: Chromium concentration [µg l^{-1}] in bulk deposition on "Wildwiese"meadow (note reduced scale for years 2000–03).

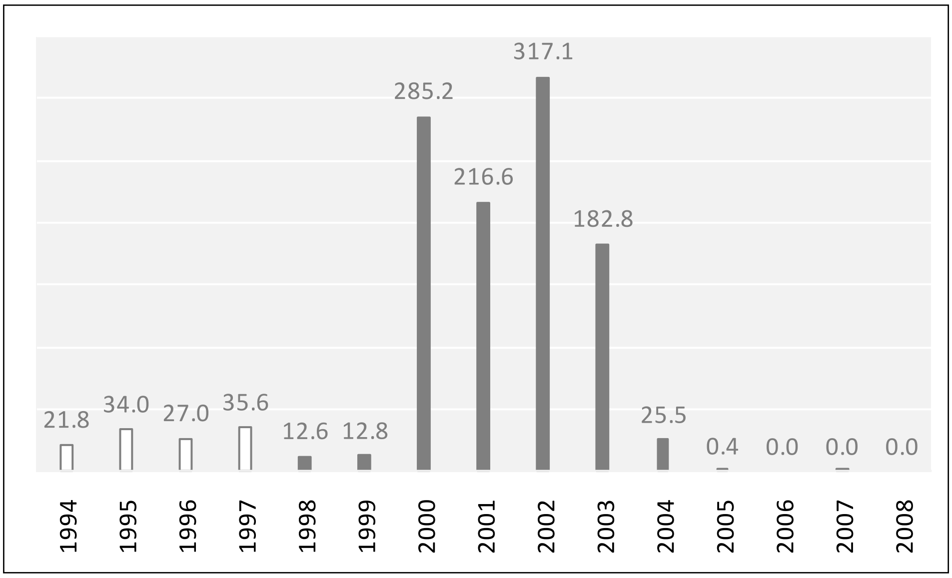


Figure 12: Annual chromium loads (g ha^{-1} a^{-1}) by bulk deposition on "Wildwiese" meadow. White bars: more than 30 days of interpolated data.

4.4.1.5 Lead (Pb)

Table 12: Lead concentration in bulk deposition on "Wildwiese" meadow.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1995	35	5	1	0.91	0.63	0.50	0.50	0.50	0.50	1.25	1.56	2.80
1996	38	3	3	1.22	1.05	0.50	0.50	0.50	0.50	1.85	3.10	3.70
1997	38	5	1	1.41	0.53	0.80	0.80	1.03	1.30	1.70	1.99	2.80
1998	33	6	1	0.92	0.22	0.80	0.80	0.80	0.80	1.00	1.20	1.70
1999	21	4	2	0.80	0.14	0.75	0.75	0.75	0.75	0.75	1.05	1.18
2000	17	8	0	1.00	0.33	0.75	0.75	0.75	0.75	1.24	1.46	1.73
2001	22	3	2	0.58	0.60	n.d.	n.d.	n.d.	0.75	0.98	1.39	1.74
2002	26	0	0	0.28	0.44	n.d.	n.d.	n.d.	n.d.	0.80	0.80	1.30
2003	22	4	0	0.35	0.12	0.30	0.30	0.30	0.30	0.30	0.53	0.72
2004	24	2	0	0.44	0.23	0.30	0.30	0.30	0.30	0.52	0.86	0.95
2005	18	7	2	0.30	–	0.30	0.30	0.30	0.30	0.30	0.30	0.30
2006	23	2	1	0.43	0.30	n.d.	0.30	0.30	0.30	0.57	0.87	1.10
2007	21	5	0	0.30	–	0.30	0.30	0.30	0.30	0.30	0.30	0.30
1995–2007	**358**	**34**	**13**	**0.71**	**0.53**	**n.d.**	**n.d.**	**0.30**	**0.60**	**1.00**	**1.50**	**2.40**

unit: µg l^{-1}

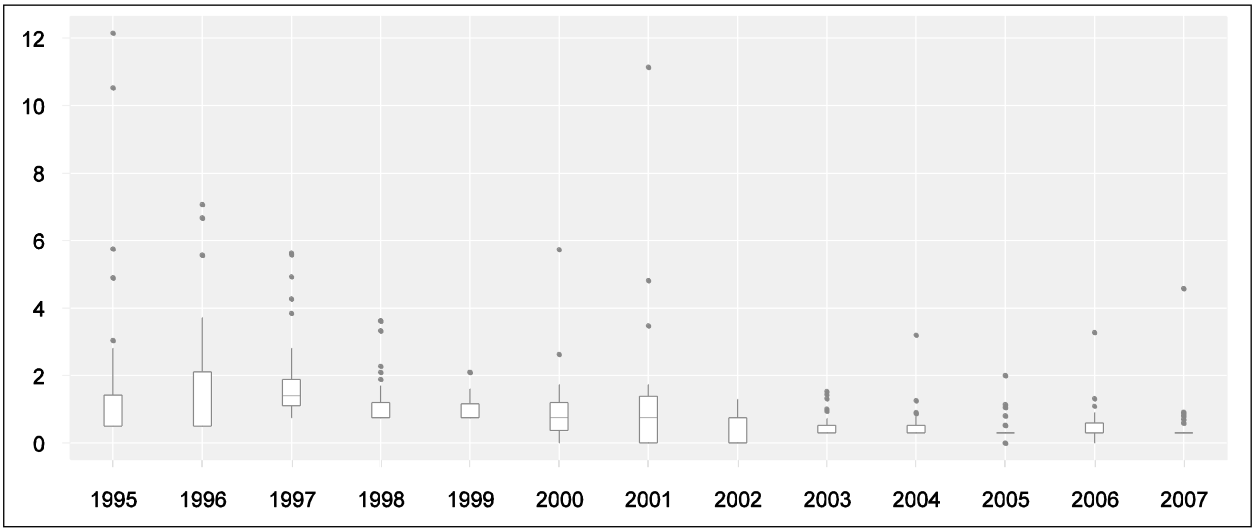


Figure 13: Lead concentration [µg l^{-1}] in bulk deposition on "Wildwiese" meadow.

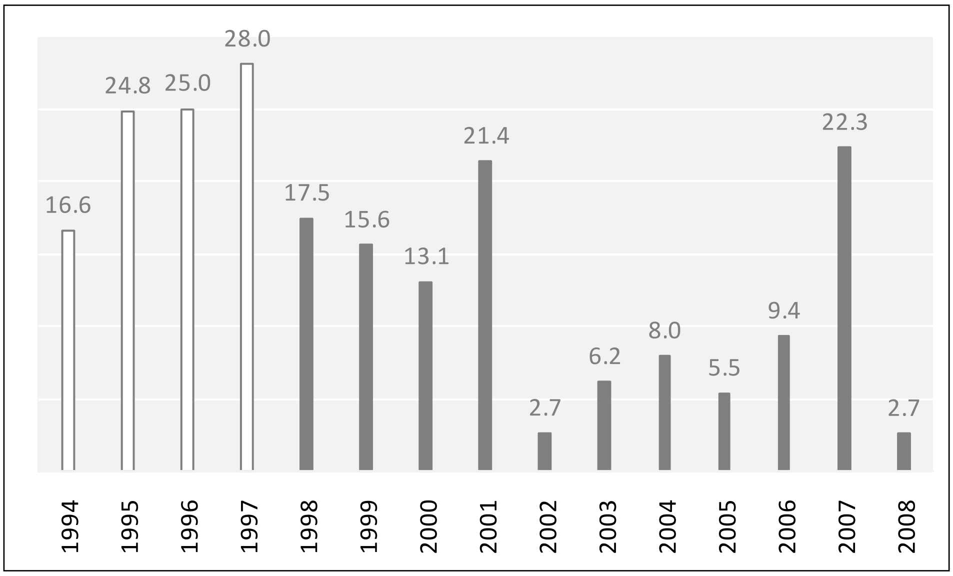


Figure 14: Annual lead loads (g ha^{-1} a^{-1}) by bulk deposition on "Wildwiese" meadow. White bars: more than 30 days of interpolated data.

4.4.1.6 Copper (Cu)

Table 13: Copper concentration in bulk deposition on "Wildwiese" meadow.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1995	39	1	1	5.1	3.4	1.3	1.3	2.8	3.9	6.8	10.1	12.7
1996	37	4	3	2.8	2.4	1.3	1.3	1.3	1.3	3.5	6.5	11.1
1997	39	4	1	2.9	1.4	1.9	1.9	1.9	1.9	3.6	4.9	6.6
1998	36	3	1	3.8	1.8	0.8	1.4	2.4	3.9	4.8	6.0	8.8
1999	20	5	2	4.5	2.0	1.8	2.7	3.2	3.9	5.5	6.6	10.0
2000	23	2	0	9.0	5.5	1.1	3.7	5.3	6.4	13.2	17.7	20.5
2001	25	0	2	11.9	9.2	1.5	3.1	4.9	7.4	20.2	23.7	33.7
2002	24	2	0	5.5	3.5	1.9	2.4	2.7	4.2	7.9	11.2	13.9
2003	25	1	0	4.8	3.6	0.8	1.3	2.0	3.0	7.4	9.4	13.0
2004	24	2	0	2.8	2.3	n.d.	0.8	0.8	1.9	4.5	6.0	8.1
2005	21	4	2	1.2	0.6	n.d.	0.8	0.8	1.2	1.5	1.7	2.5
2006	25	0	1	3.2	1.7	0.8	1.1	1.8	3.3	4.1	5.6	6.5
2007	26	0	0	7.1	5.4	n.d.	0.8	2.3	6.7	10.5	15.0	18.0
1995–2007	**352**	**40**	**13**	**4.1**	**2.9**	**n.d.**	**1.3**	**1.8**	**3.3**	**5.8**	**8.4**	**13.0**

unit: µg l⁻¹

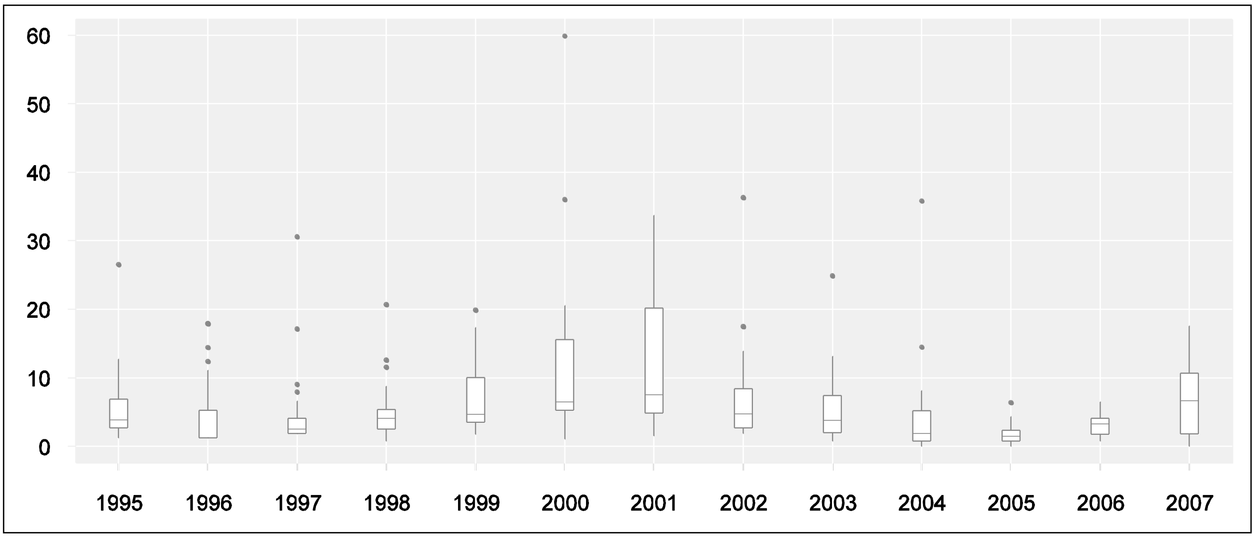


Figure 15: Copper concentration [µg l⁻¹] in bulk deposition on "Wildwiese" meadow.

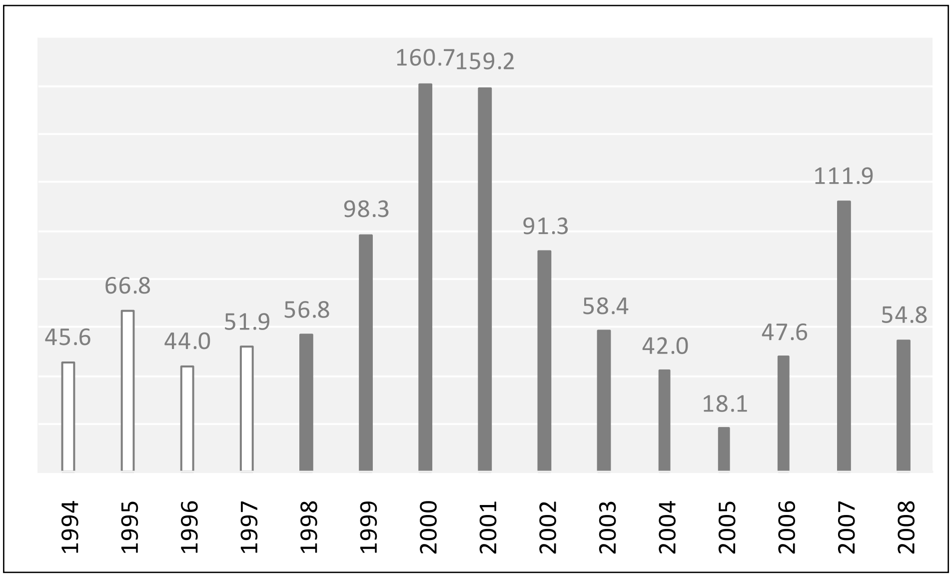


Figure 16: Annual copper loads (g ha^{-1} a^{-1}) by bulk deposition on "Wildwiese" meadow. White bars: more than 30 days of interpolated data.

4.4.1.7 Zinc (Zn)

Table 14: Zinc concentration in bulk deposition on "Wildwiese" meadow.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1995	38	2	1	12.5	6.7	2.0	5.8	7.4	10.8	15.7	21.6	30.2
1996	41	0	3	13.7	11.9	2.0	2.0	4.7	9.1	21.7	27.5	45.8
1997	39	4	1	14.0	7.2	5.1	6.2	8.7	12.1	18.9	22.6	35.7
1998	32	7	1	30.7	30.0	3.7	6.9	10.8	18.8	44.4	67.4	145.0
1999	23	2	2	141.8	135.6	21.7	25.9	43.1	86.2	190.0	301.0	512.0
2000	25	0	0	276.9	198.1	26.4	56.7	139.4	191.9	471.4	561.0	611.8
2001	25	0	2	327.9	239.3	43.8	84.6	114.4	266.9	452.6	652.3	849.5
2002	23	3	0	173.0	109.0	40.0	64.6	83.0	158.0	207.0	285.2	441.0
2003	25	1	0	78.2	56.3	8.4	17.0	22.0	69.0	116.0	161.2	200.0
2004	26	0	0	12.5	14.3	1.5	2.4	3.3	5.1	19.3	34.4	48.8
2005	24	1	2	4.6	2.0	2.1	2.3	3.4	4.1	5.3	7.6	8.8
2006	25	0	1	7.3	3.7	1.5	2.4	4.8	7.4	9.8	11.6	16.5
2007	24	2	0	12.5	6.8	2.2	4.4	6.4	12.7	16.3	22.8	25.0
1995–2007	**333**	**59**	**13**	**32.1**	**42.4**	**1.5**	**3.8**	**6.8**	**13.7**	**36.0**	**94.0**	**187.0**

unit: µg l^{-1}

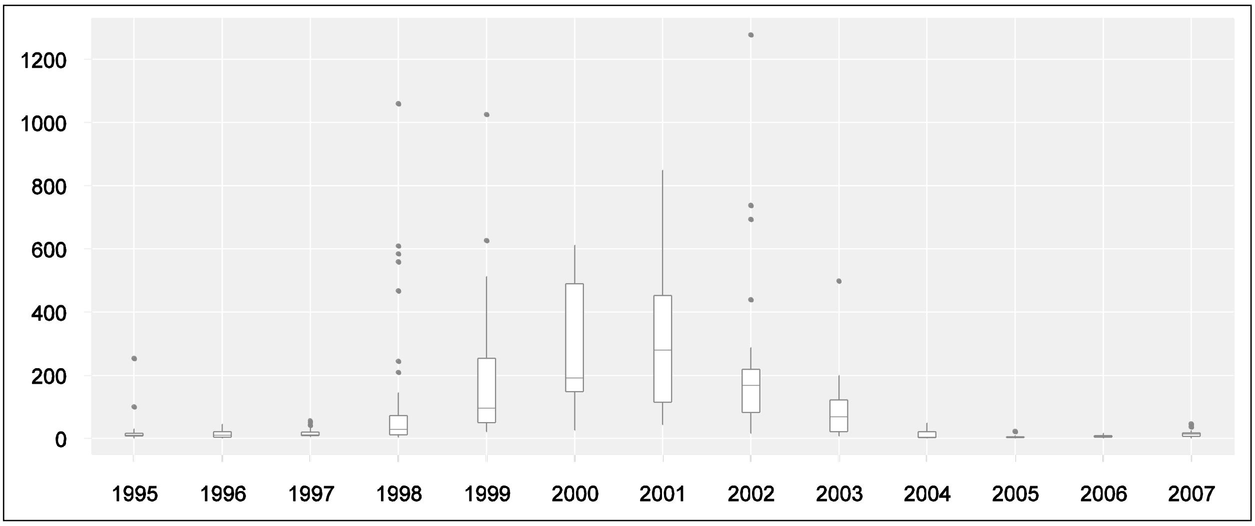


Figure 17: Zinc concentration [µg l^{-1}] in bulk deposition on "Wildwiese"meadow.

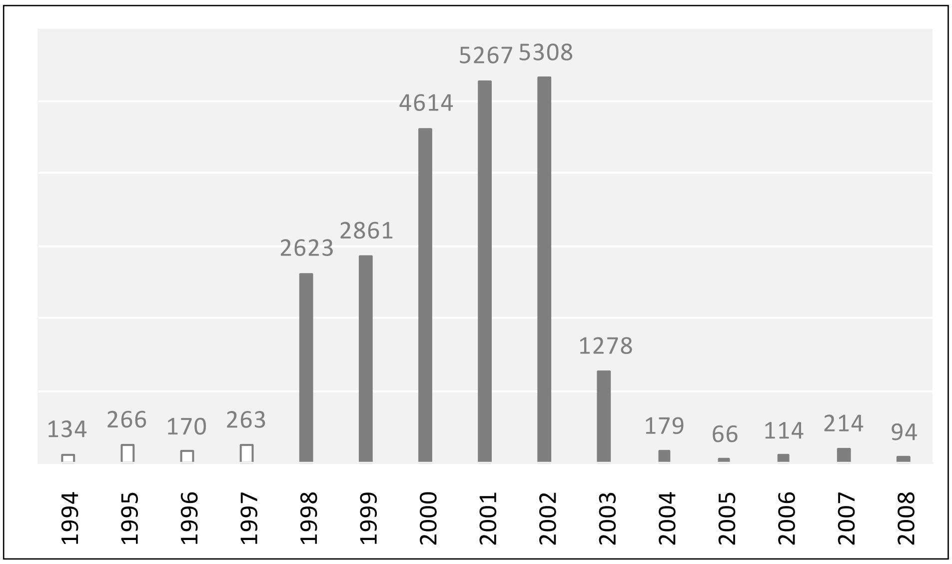


Figure 18: Annual zinc loads (g ha^{-1} a^{-1}) by bulk deposition on "Wildwiese" meadow. White bars: more than 30 days of interpolated data.

4.4.1.8 Nickel (Ni)

Table 15: Nickel concentration in bulk deposition on "Wildwiese" meadow.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1995	35	5	1	3.7	2.1	2.5	2.5	2.5	2.5	4.9	6.5	10.7
1996	36	5	3	3.6	2.3	1.3	1.3	1.3	3.6	5.2	7.1	8.6
1997	38	5	1	4.2	2.3	1.9	1.9	2.7	3.9	4.7	7.3	11.5
1998	38	1	1	4.1	2.4	0.8	1.5	2.1	3.8	5.7	6.9	10.7
1999	23	2	2	2.2	0.9	0.8	1.1	1.4	2.2	2.8	3.5	4.0
2000	24	1	0	10.3	6.2	1.1	1.9	6.2	10.3	14.2	17.4	25.2
2001	23	2	2	8.8	4.5	1.6	4.1	6.3	7.7	10.6	16.0	18.6
2002	26	0	0	11.4	4.5	4.6	5.4	8.6	10.8	13.9	17.6	21.8
2003	25	1	0	7.3	4.1	1.4	1.8	3.7	6.9	11.0	12.6	14.0
2004	25	1	0	1.6	1.9	0.0	0.0	0.0	0.8	2.3	4.7	5.9
2005	24	1	2	1.0	1.1	0.0	0.0	0.0	0.8	1.6	2.1	4.2
2006	22	3	1	1.1	0.5	0.0	0.8	0.8	1.1	1.4	1.7	2.5
2007	23	3	0	1.6	1.2	0.0	0.2	0.8	1.1	2.3	3.6	4.0
1995–2007	**365**	**27**	**13**	**4.4**	**3.9**	**0.0**	**0.8**	**1.5**	**2.9**	**6.5**	**10.7**	**16.4**

unit: µg l^{-1}

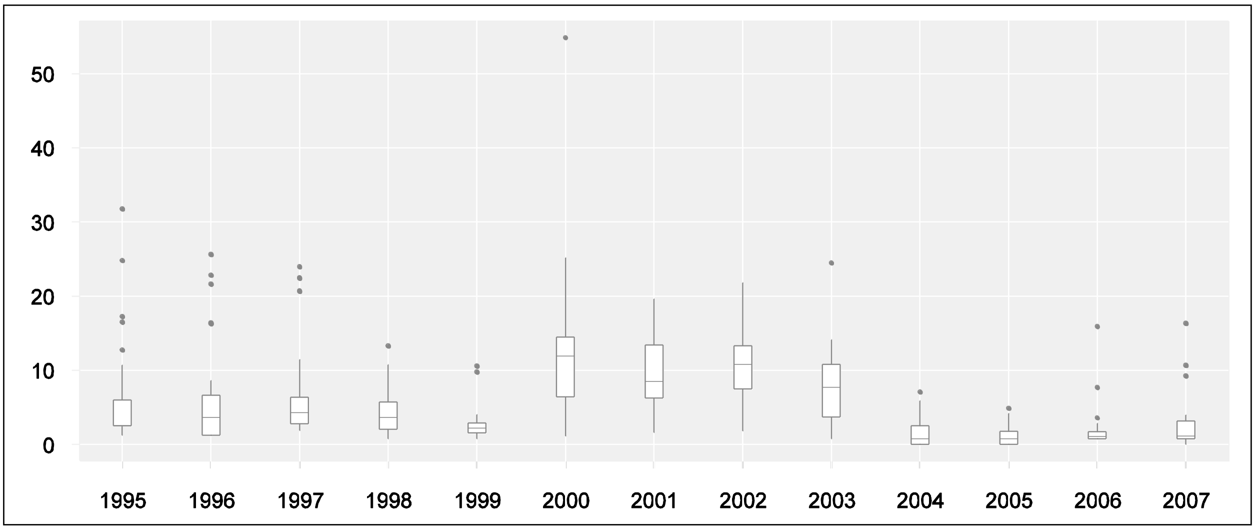


Figure 19: Nickel concentration [µg l^{-1}] in bulk deposition on "Wildwiese" meadow (one extreme value = 366 µg l^{-1} from 2005 not shown).

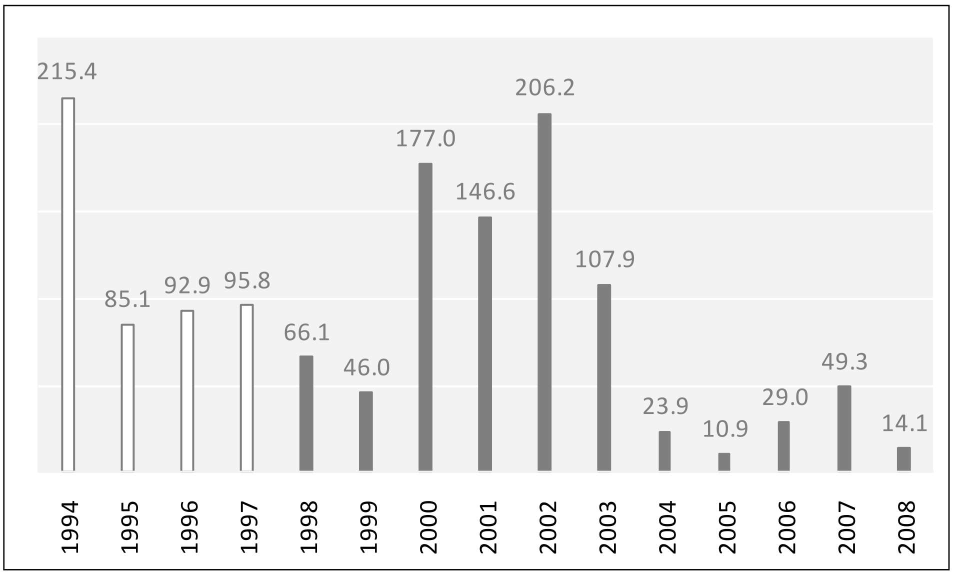


Figure 20: Annual nickel loads (g ha^{-1} a^{-1}) by bulk deposition on "Wildwiese" meadow. White bars: more than 30 days of interpolated data.

4.4.1.9 Arsenic (As)

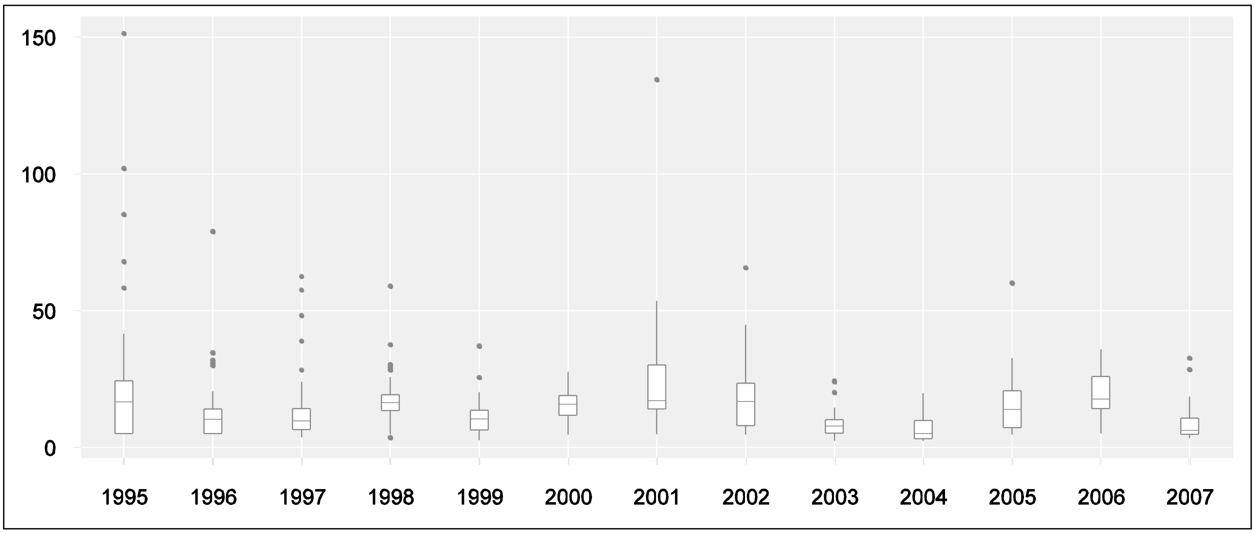
Only three 1995 samples contained quantifiable arsenic concentrations (of up to 0.5 µg l^{-1}) in bulk deposition on "Wildwiese" meadow.

4.4.1.10 Aluminium (Al)

Table 16: Aluminium concentration in bulk deposition on "Wildwiese" meadow.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1995	35	5	1	14.8	9.0	5.0	5.0	5.0	14.5	19.5	27.2	41.5
1996	40	1	3	11.6	8.5	5.0	5.0	5.0	10.3	14.9	21.4	34.6
1997	38	5	1	9.2	4.3	3.8	3.8	6.1	8.9	11.4	15.2	20.6
1998	36	3	1	15.8	6.3	3.6	7.3	13.1	15.9	18.3	24.7	29.3
1999	23	2	2	10.5	4.8	2.7	5.3	6.2	10.4	13.5	16.6	20.1
2000	25	0	0	15.2	5.7	4.7	7.6	11.7	15.6	19.0	21.0	27.6
2001	24	1	2	22.4	13.6	4.9	10.4	13.9	17.1	27.3	45.0	53.5
2002	25	1	0	17.2	11.1	4.7	5.9	7.9	14.1	21.2	34.2	44.7
2003	23	3	0	7.6	3.1	2.5	4.3	5.3	7.3	9.7	11.6	14.0
2004	26	0	0	7.0	4.5	2.4	2.8	3.1	5.1	9.8	12.2	19.7
2005	23	2	2	13.0	7.8	4.4	5.1	6.5	9.6	17.0	23.4	33.0
2006	25	0	1	20.2	8.0	5.0	12.4	14.0	19.0	26.0	31.4	36.0
2007	24	2	0	7.3	3.7	3.4	4.3	4.7	6.2	9.1	12.0	18.0
1995–2007	**371**	**21**	**13**	**13.0**	**8.0**	**2.4**	**4.9**	**5.9**	**11.7**	**17.7**	**25.0**	**37.6**

unit: µg l^{-1}



one value (366 from 2005) not shown

Figure 21: Aluminium concentration [µg l^{-1}] in bulk deposition on "Wildwiese"meadow.

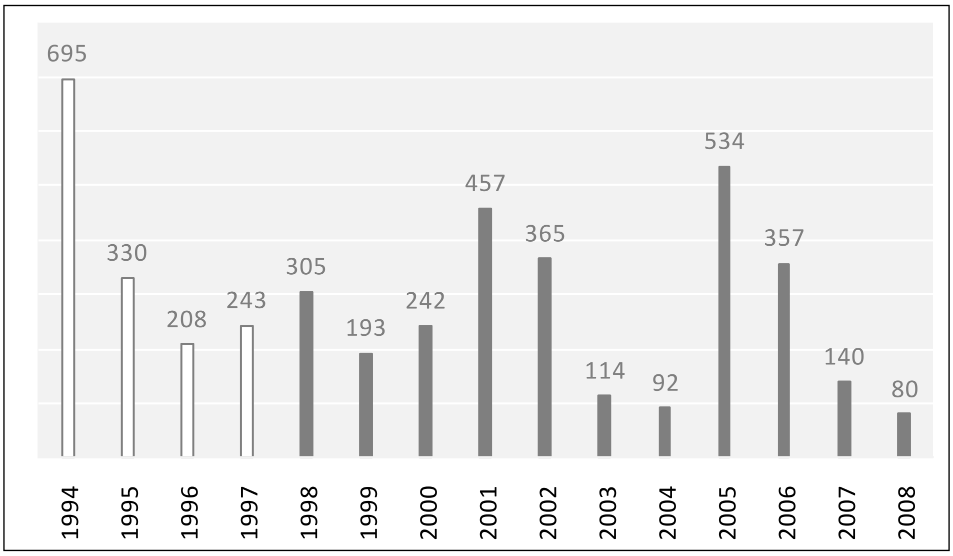


Figure 22: Annual aluminium loads (g ha^{-1} a^{-1}) by bulk deposition on "Wildwiese" meadow. White bars: more than 30 days of interpolated data.

4.4.1.11 Mercury (Hg)

Mercury was not detectable in bulk deposition during the first half of 1995, and afterwards the measurements were discontinued.

4.4.2 Wet deposition on "Wildwiese" meadow

Please note that this section also reports pollutant loads calculated from concentrations of wet-only samplers (WADOS). However, the samplers employed were not designed to accurately collect a defined cross section. Area specific loads should therefore be interpreted with caution.

The trace metal pattern in wet deposition (Figure 5) was almost identical to that found in bulk deposition (Figure 8), except that aluminium replaced zinc as the most abundant element. (Compared were the nine elements' median concentrations of the years 1995–99 plus 2004–07, thus omitting the period of probable short-range pollutant inputs 2000–03).

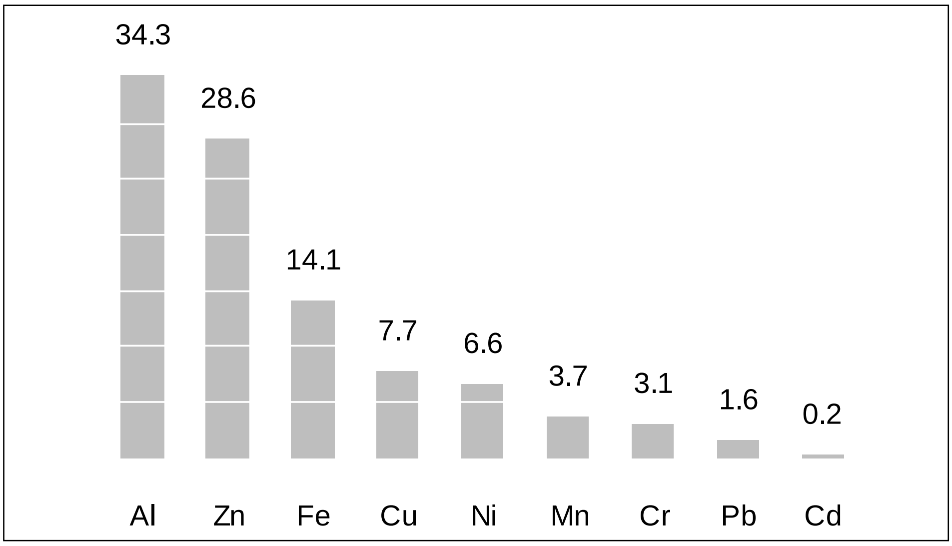


Figure 23: Element composition (%) of wet deposition on "Wildwiese" meadow.

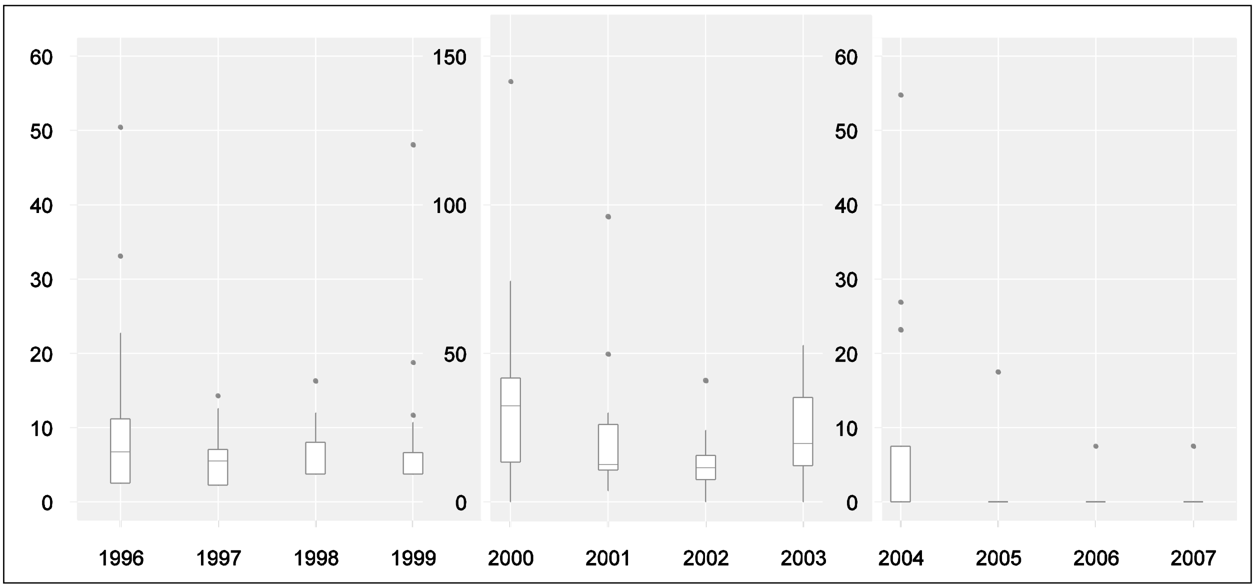
4.4.2.1 Iron (Fe)

Wet deposition of iron followed the trend observed for bulk deposition. The massive decrease of loads after 2004 was even more pronounced than in bulk deposition (cf. Figure 5).

Table 17: Iron concentration in wet deposition on "Wildwiese" meadow.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1996	33	3	9	7.10	5.22	2.50	2.50	2.50	6.29	8.57	13.17	22.71
1997	34	1	9	5.36	3.01	2.25	2.25	2.25	5.45	6.77	9.80	12.58
1998	31	1	9	5.84	2.81	3.75	3.75	3.75	3.75	7.83	10.00	11.95
1999	21	3	3	4.66	1.89	3.75	3.75	3.75	3.75	3.75	7.10	10.70
2000	22	1	2	28.35	19.07	n.d.	4.07	13.03	32.22	41.50	47.76	74.28
2001	23	2	2	15.47	7.68	3.75	8.64	10.45	12.18	19.81	28.11	29.98
2002	21	1	4	12.29	6.18	n.d.	7.50	7.50	11.50	14.40	22.40	24.10
2003	25	1	1	21.76	14.09	n.d.	7.50	12.20	18.70	27.20	42.58	52.70
2004	21	4	1	1.43	3.02	n.d.	n.d.	n.d.	n.d.	n.d.	7.50	7.50
2005	22	3	2	–	–	–	–	–	–	–	–	n.d.
2006	20	1	5	–	–	–	–	–	–	–	–	n.d.
2007	26	2	0	–	–	–	–	–	–	–	–	n.d.
1996–2007	**293**	**29**	**47**	**6.57**	**7.09**	**n.d.**	**n.d.**	**n.d.**	**3.75**	**10.24**	**17.40**	**29.98**

unit: µg l^{-1}



two values (2003: 251, 2004: 179) not shown

Figure 24: Iron concentration [µg l^{-1}] in wet deposition on "Wildwiese" meadow (note reduced scale for years 2000–03).

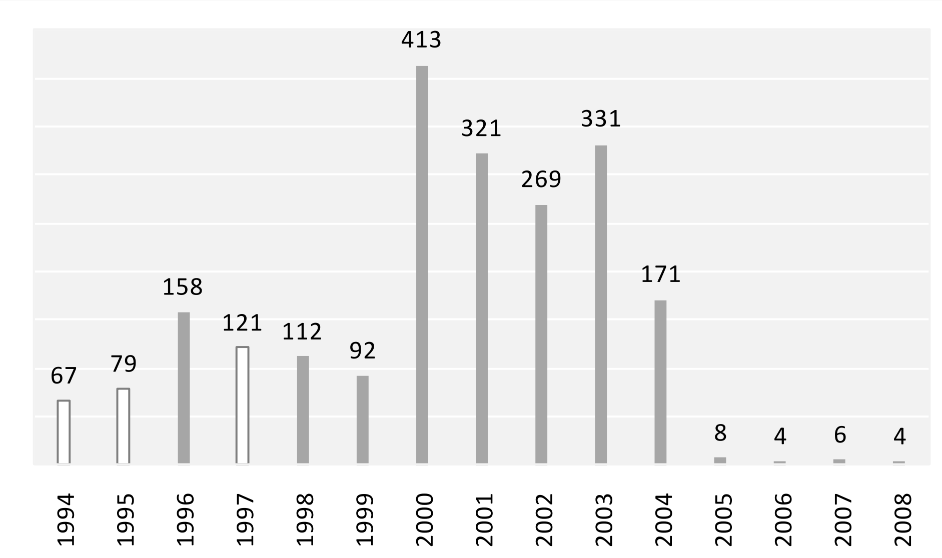


Figure 25: Approximate annual iron loads (g ha^{-1} a^{-1}) by wet deposition on "Wildwiese" meadow. White bars: more than 30 days of interpolated data.

4.4.2.2 Manganese (Mn)

Manganese concentrations in wet deposition did not reach a distinct plateau between 2000 and 2003, in contrast to what was found for bulk deposition and canopy throughfall (albeit far less pronounced than for other trace metals like iron or chromium). Instead, there was a rather steady decline from 1997 onwards (Figure 26–Figure 27).

Table 18: Manganese concentration in wet deposition on "Wildwiese" meadow.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1996	31	5	9	1.25	n.d.	1.25	1.25	1.25	1.25	1.25	1.25	1.25
1997	33	2	9	2.64	1.04	1.88	1.88	1.88	1.88	3.08	4.35	5.33
1998	29	3	9	2.13	0.96	0.75	1.00	1.42	2.20	2.60	3.62	4.10
1999	24	1	2	1.88	0.80	0.75	0.75	1.38	1.83	2.43	2.97	3.50
2000	23	0	2	2.16	1.09	0.75	0.75	1.51	2.19	2.84	3.24	4.42
2001	22	3	2	1.53	0.74	0.75	0.75	1.07	1.31	1.78	2.52	3.48
2002	21	1	4	1.27	0.66	n.d.	0.75	0.75	1.25	1.51	2.40	2.60
2003	22	4	1	1.74	0.92	0.30	0.93	1.24	1.42	2.30	2.59	4.40
2004	21	4	1	1.06	0.31	0.56	0.65	0.82	1.05	1.24	1.34	1.69
2005	25	0	2	1.26	0.71	0.30	0.63	0.70	0.97	1.71	1.97	3.00
2006	20	1	5	1.14	0.67	0.30	0.51	0.66	0.99	1.50	2.37	2.56
2007	26	2	0	1.27	0.67	0.30	0.53	0.79	1.18	1.68	2.02	3.12
1996–2007	**301**	**22**	**46**	**1.64**	**0.84**	**n.d.**	**0.75**	**1.01**	**1.41**	**2.11**	**2.90**	**4.16**

unit: µg l^{-1}

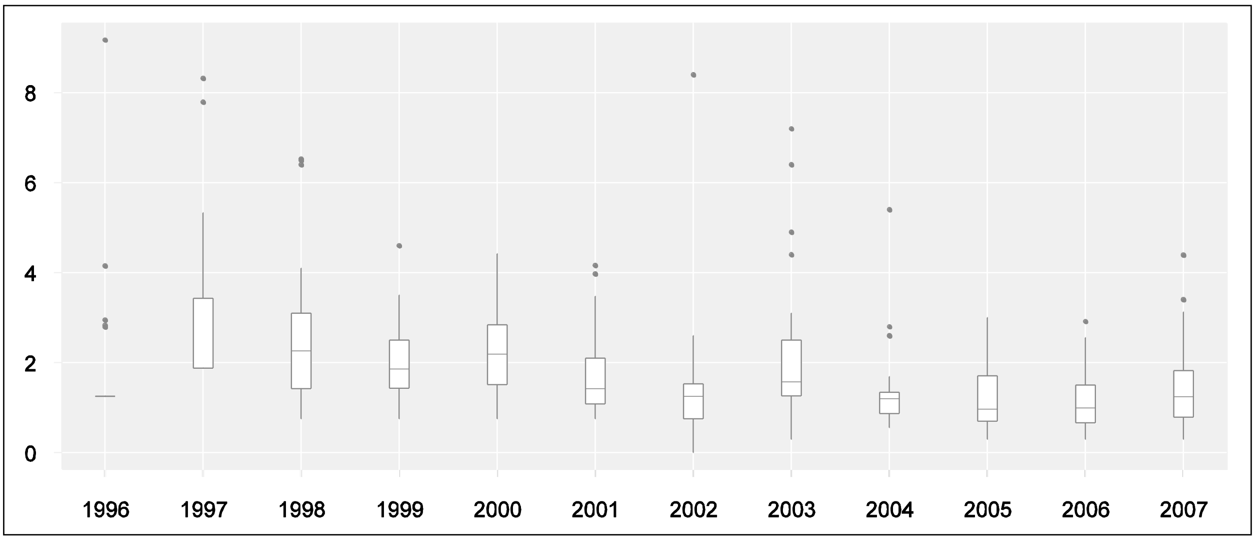


Figure 26: Manganese concentration [µg l^{-1}] in wet deposition on "Wildwiese" meadow (two values > 10 [2001: 14.4, 2003: 16.0] not shown).

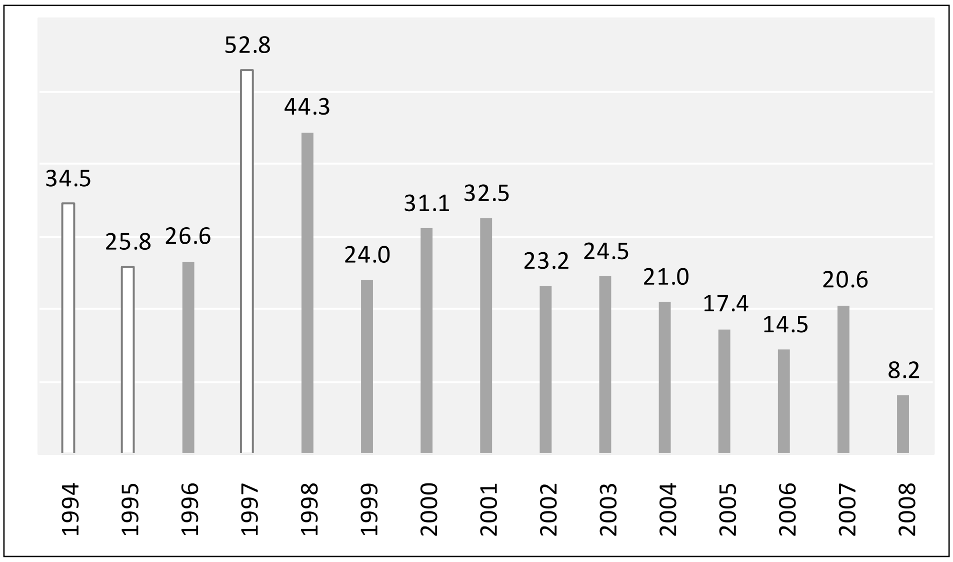


Figure 27: Approximate annual manganese loads (g ha^{-1} a^{-1}) by wet deposition on "Wildwiese" meadow. White bars: more than 30 days of interpolated data.

4.4.2.3 Cadmium (Cd)

Table 19: Cadmium concentration in wet deposition on "Wildwiese" meadow.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1996	33	2	10	0.097	0.071	0.025	0.025	0.049	0.071	0.136	0.208	0.273
1997	35	0	9	0.175	0.104	0.038	0.060	0.085	0.180	0.255	0.310	0.420
1998	30	2	9	0.158	0.123	0.075	0.075	0.075	0.075	0.248	0.333	0.500
1999	21	4	2	0.075	n.d.	0.075	0.075	0.075	0.075	0.075	0.075	0.075
2000	22	1	2	0.094	0.070	n.d.	n.d.	0.075	0.088	0.135	0.190	0.243
2001	22	3	2	0.030	0.049	n.d.	n.d.	n.d.	n.d.	0.075	0.075	0.154
2002	21	1	4	0.080	0.091	n.d.	n.d.	n.d.	0.075	0.130	0.180	0.290
2003	21	5	1	n.d.	–	–	–	–	–	–	–	n.d.
2004	22	3	1	n.d.	–	–	–	–	–	–	–	n.d.
2005	19	6	2	n.d.	–	–	–	–	–	–	–	n.d.
2006	20	1	5	n.d.	–	–	–	–	–	–	–	n.d.
2007	23	5	0	n.d.	–	–	–	–	–	–	–	n.d.
1996–2007	**297**	**25**	**47**	**0.058**	**0.067**	**n.d.**	**n.d.**	**n.d.**	**0.058**	**0.075**	**0.155**	**0.263**

unit: µg l^{-1}

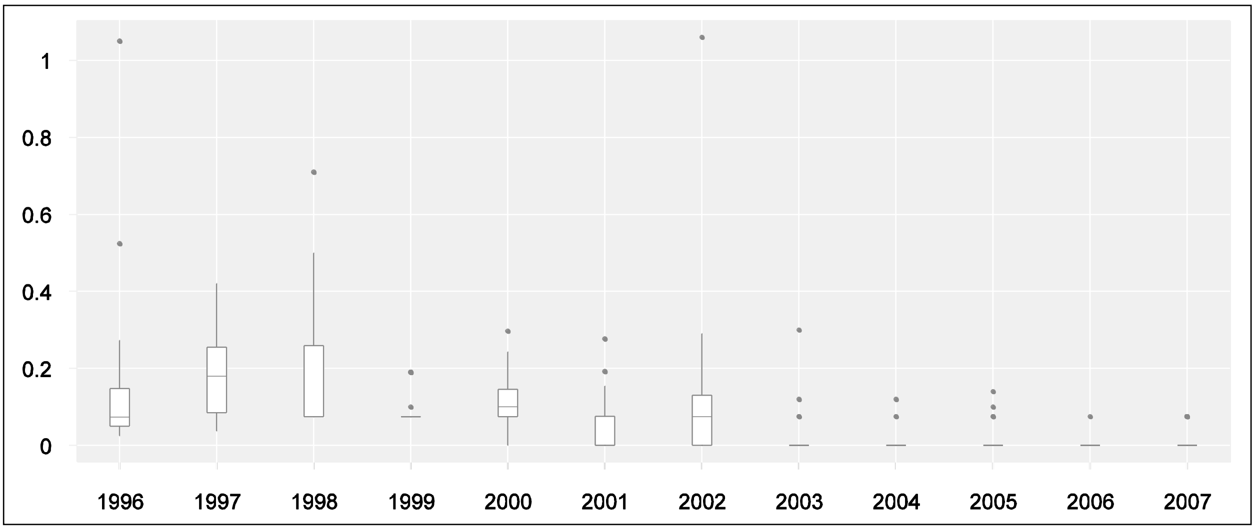


Figure 28: Cadmium concentration [µg l^{-1}] in wet deposition on "Wildwiese" meadow (two values > 1.2 [1998: 2.09, 2001: 4.41] not shown).

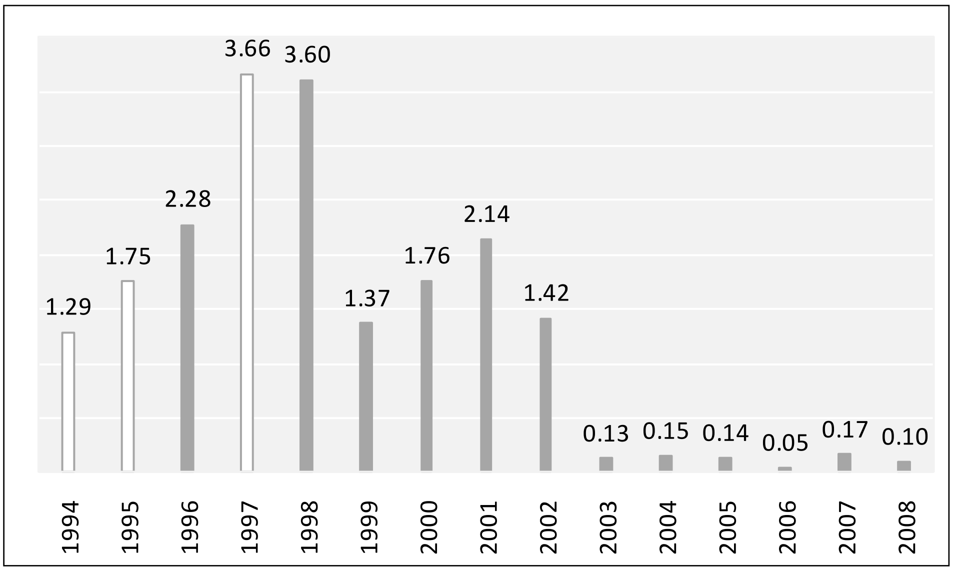


Figure 29: Approximate annual cadmium loads (g ha^{-1} a^{-1}) by wet deposition on "Wildwiese" meadow. White bars: more than 30 days of interpolated data.

4.4.2.4 Chromium (Cr)

Table 20: Chromium concentration in wet deposition on a "Wildwiese" meadow.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1996	36	1	8	1.25	n.d.	1.25	1.25	1.25	1.25	1.25	1.25	1.25
1997	35	0	9	1.88	n.d.	1.88	1.88	1.88	1.88	1.88	1.88	1.88
1998	31	1	9	0.75	n.d.	0.75	0.75	0.75	0.75	0.75	0.75	0.75
1999	24	1	2	0.75	n.d.	0.75	0.75	0.75	0.75	0.75	0.75	0.75
2000	22	1	2	6.61	5.69	n.d.	n.d.	2.95	4.03	11.34	12.35	21.53
2001	23	2	2	3.06	1.54	n.d.	1.57	1.96	2.89	3.97	5.49	5.84
2002	21	1	4	3.33	1.71	0.75	1.65	2.20	3.00	3.90	6.40	6.60
2003	25	1	1	5.02	3.89	0.75	0.86	2.10	3.80	7.20	9.86	14.70
2004	22	3	1	0.25	0.50	n.d.	n.d.	n.d.	n.d.	n.d.	1.18	1.50
2005	25	0	2	–	–	–	–	–	–	–	–	n.d.
2006	21	0	5	–	–	–	–	–	–	–	–	n.d.
2007	28	0	0	–	–	–	–	–	–	–	–	n.d.
1996–2007	**288**	**36**	**45**	**1.11**	**1.11**	**n.d.**	**n.d.**	**n.d.**	**0.75**	**1.88**	**2.89**	**4.64**

unit: µg l^{-1}

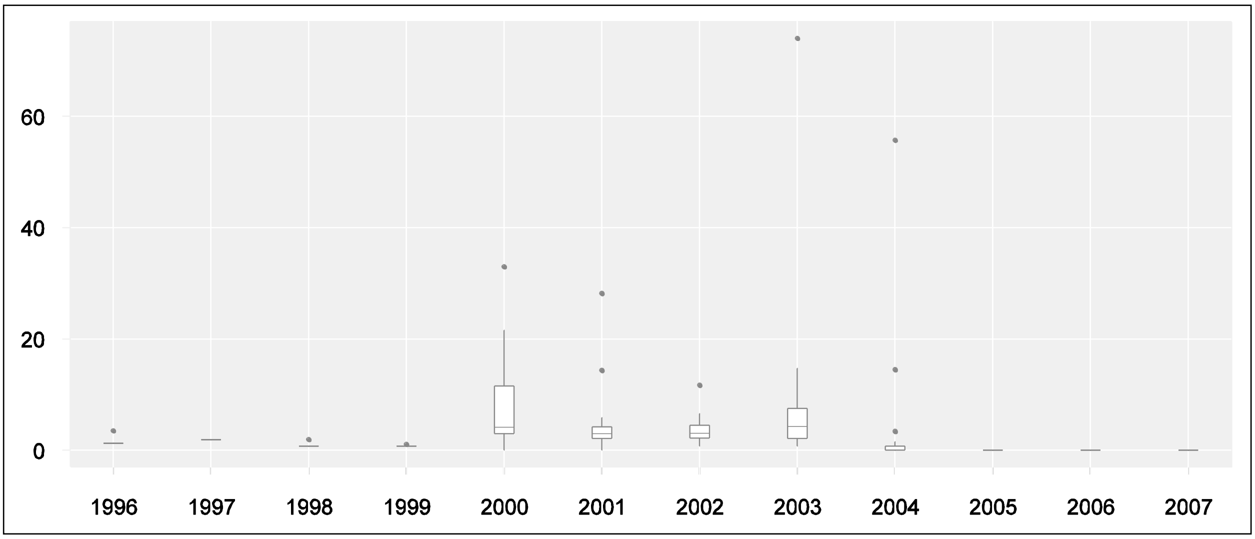


Figure 30: Chromium concentration [µg l^{-1}] in wet deposition on a "Wildwiese" meadow.

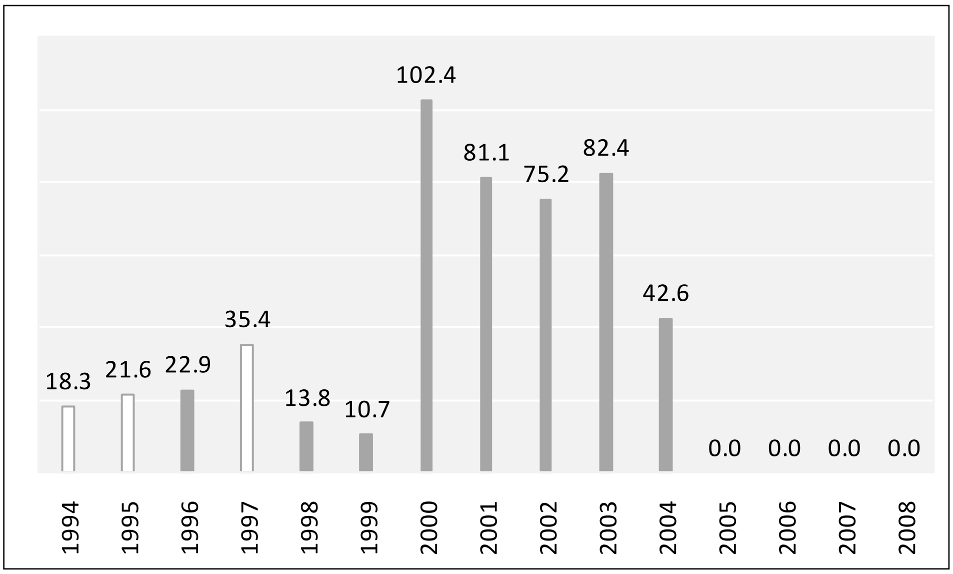


Figure 31: Approximate annual chromium loads (g ha^{-1} a^{-1}) by wet deposition on "Wildwiese" meadow. White bars: more than 30 days of interpolated data.

4.4.2.5 Lead (Pb)

Table 21: Lead concentration in wet deposition on "Wildwiese" meadow.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1996	32	3	10	1.27	0.75	0.50	0.50	0.50	1.15	1.85	2.26	3.18
1997	33	2	9	1.44	0.92	0.75	0.75	0.75	1.04	1.89	3.06	3.87
1998	31	1	9	1.06	0.46	0.75	0.75	0.75	0.75	1.30	1.73	2.18
1999	22	3	2	0.75	0.00	0.75	0.75	0.75	0.75	0.75	0.75	0.75
2000	23	0	2	0.47	0.50	–	–	n.d.	0.75	0.75	0.96	1.68
2001	23	2	2	0.32	0.49	–	–	–	n.d.	0.75	0.75	1.55
2002	19	3	4	n.d.	–	–	–	–	–	–	–	n.d.
2003	18	8	1	0.30	0.00	0.30	0.30	0.30	0.30	0.30	0.30	0.30
2004	23	2	1	0.18	0.19	–	–	–	0.30	0.30	0.30	0.59
2005	23	2	2	0.09	0.14	–	–	–	n.d.	0.30	0.30	0.30
2006	13	8	5	0.30	0.00	0.30	0.30	0.30	0.30	0.30	0.30	0.30
2007	26	2	0	0.27	0.25	–	–	n.d.	0.30	0.30	0.58	0.88
1996–2007	**289**	**33**	**47**	**0.49**	**0.46**	**–**	**–**	**n.d.**	**0.30**	**0.75**	**1.13**	**1.81**

unit: µg l^{-1}

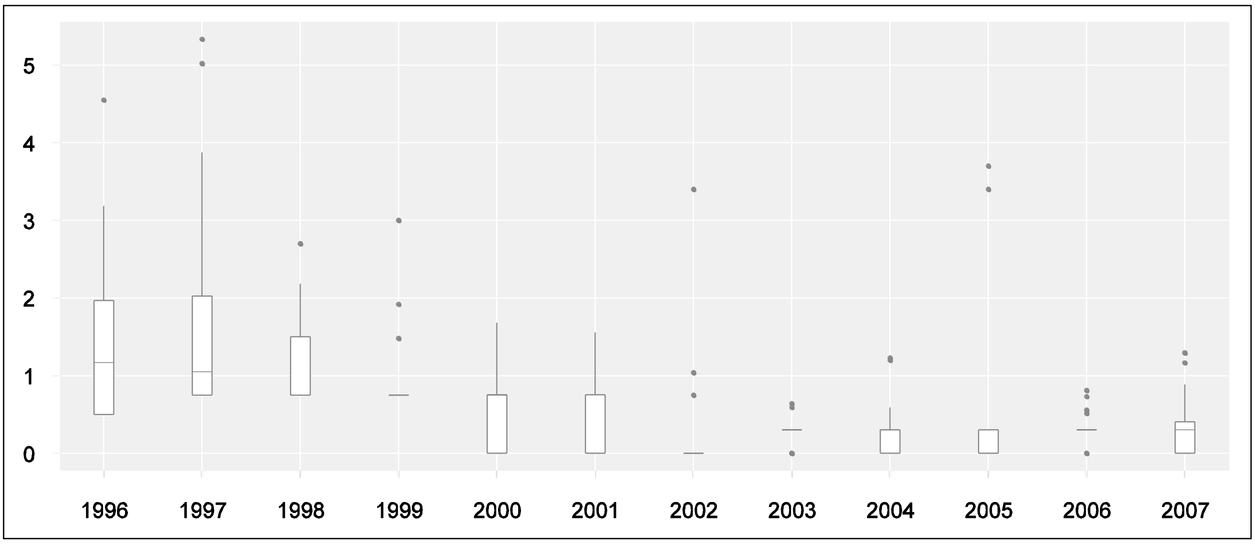


Figure 32: Lead concentration [µg l^{-1}] in wet deposition on "Wildwiese"meadow.

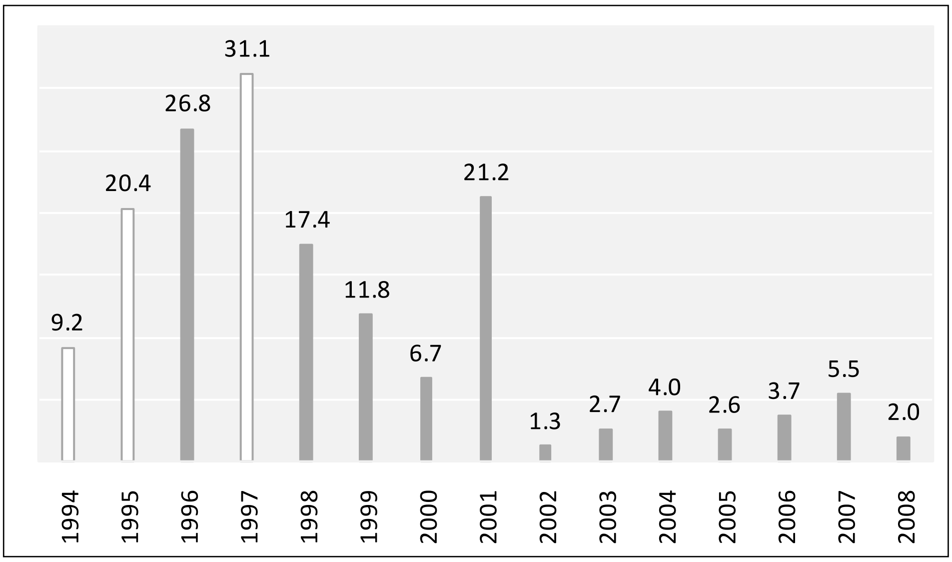


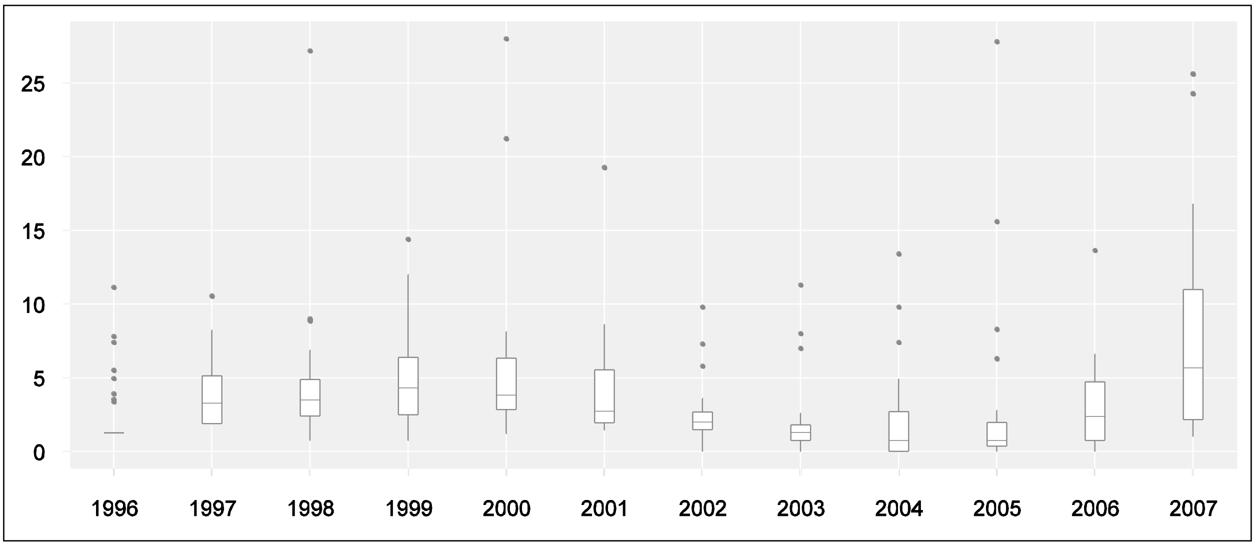
Figure 33: Approximate annual lead loads (g ha^{-1} a^{-1}) by wet deposition on "Wildwiese" meadow. White bars: more than 30 days of interpolated data.

4.4.2.6 Copper (Cu)

Table 22: Copper concentration in wet deposition on "Wildwiese" meadow.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1996	28	8	9	1.25	0.00	1.25	1.25	1.25	1.25	1.25	1.25	1.25
1997	34	1	9	3.69	1.83	1.88	1.88	1.88	3.18	4.91	6.26	8.24
1998	29	3	9	3.34	1.57	0.75	1.50	2.36	3.00	4.33	5.22	6.88
1999	24	1	2	4.83	3.36	0.75	1.75	2.40	4.05	5.73	11.23	12.00
2000	20	3	2	4.08	1.98	1.19	1.76	2.80	3.68	4.99	6.62	8.13
2001	22	3	2	3.53	2.17	1.45	1.62	1.90	2.66	5.04	6.50	8.63
2002	18	4	4	1.90	0.83	0.00	1.09	1.32	1.98	2.45	2.78	3.60
2003	23	3	1	1.25	0.72	0.00	0.75	0.75	1.13	1.64	2.36	2.60
2004	22	3	1	1.26	1.45	n.d.	n.d.	n.d.	0.75	2.33	2.72	4.90
2005	19	6	2	0.75	0.77	n.d.	n.d.	n.d.	0.75	0.75	1.79	2.80
2006	20	1	5	2.41	2.01	n.d.	0.68	0.75	2.00	3.74	5.13	6.59
2007	26	2	0	7.71	6.88	1.03	1.50	2.21	5.69	10.85	15.72	25.61
1996–2007	**294**	**29**	**46**	**2.95**	**2.37**	**0.00**	**0.75**	**1.25**	**2.31**	**4.15**	**6.50**	**10.55**

unit: µg l^{-1}



eight values > 30 (2000: 33.4, 2001: 35.6, 31.3, 2002: 33.2, 2005: 99.7, 41.0, 2007: 33.6, 58.8) not shown

Figure 34: Copper concentration [µg l^{-1}] in wet deposition on "Wildwiese"meadow.

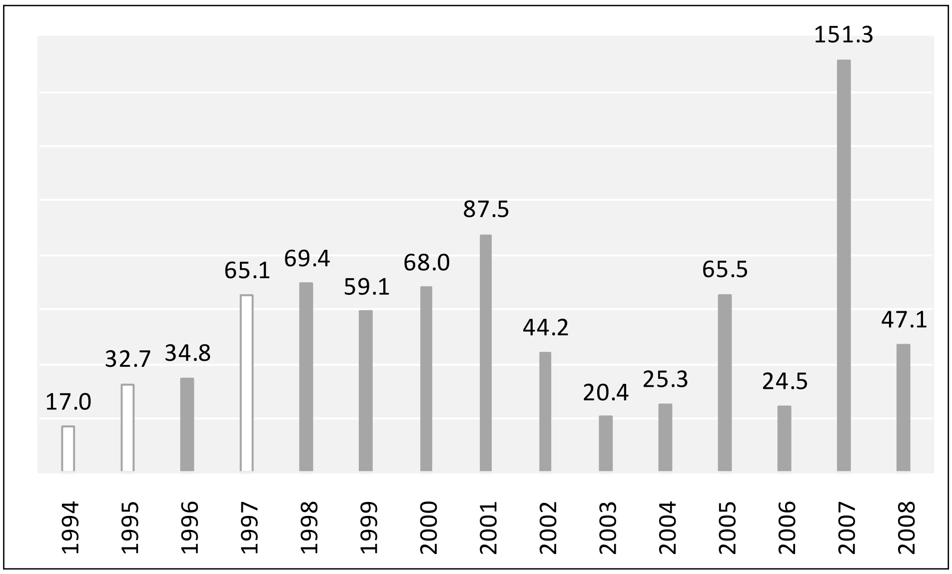


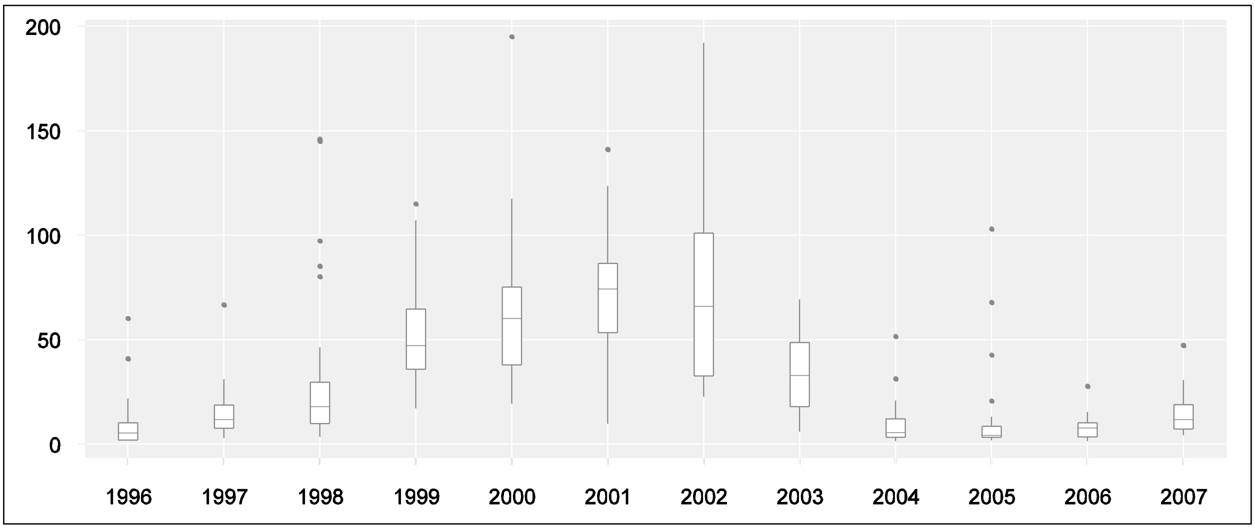
Figure 35: Approximate annual copper loads (g ha^{-1} a^{-1}) by wet deposition on ”Wildwiese“ meadow. White bars: more than 30 days of interpolated data.

4.4.2.7 Zinc (Zn)

Table 23: Zinc concentration in wet deposition on “Wildwiese” meadow.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1996	34	2	9	6.4	4.9	2.0	2.0	2.0	5.2	8.7	11.1	21.8
1997	34	1	9	13.2	7.4	3.0	5.4	7.6	11.4	17.5	22.1	31.0
1998	26	6	9	17.0	10.6	3.7	7.3	9.8	11.7	23.6	29.7	46.2
1999	23	2	2	54.3	26.2	17.1	29.4	35.8	47.1	64.7	88.2	115.0
2000	22	1	2	57.8	26.6	19.4	23.5	37.9	57.9	71.7	96.8	117.4
2001	23	2	2	70.2	26.9	9.8	39.8	53.4	74.2	83.3	105.7	123.3
2002	22	0	4	74.0	45.6	22.8	25.5	33.4	65.9	100.8	130.1	192.0
2003	25	1	1	33.2	17.9	6.1	11.7	18.0	32.9	48.6	55.7	69.1
2004	23	2	1	7.7	6.2	1.5	2.2	3.0	4.6	9.9	18.2	20.7
2005	21	4	2	4.8	2.8	2.0	2.6	3.2	4.0	4.8	8.5	13.0
2006	20	1	5	6.9	4.3	1.5	2.0	3.3	7.2	9.6	12.4	15.3
2007	27	1	0	13.4	7.5	4.4	4.5	7.2	11.6	17.7	24.1	30.5
1996–2007	**306**	**17**	**46**	**27.0**	**27.0**	**1.5**	**3.4**	**6.2**	**15.5**	**38.6**	**69.6**	**107.0**

unit: µg l^{-1}



five values > 200 (1998: 655, 1999: 514, 668, 2001: 316, 2003: 571) not shown

Figure 36: Zinc concentration [µg l^{-1}] in wet deposition on "Wildwiese"meadow.

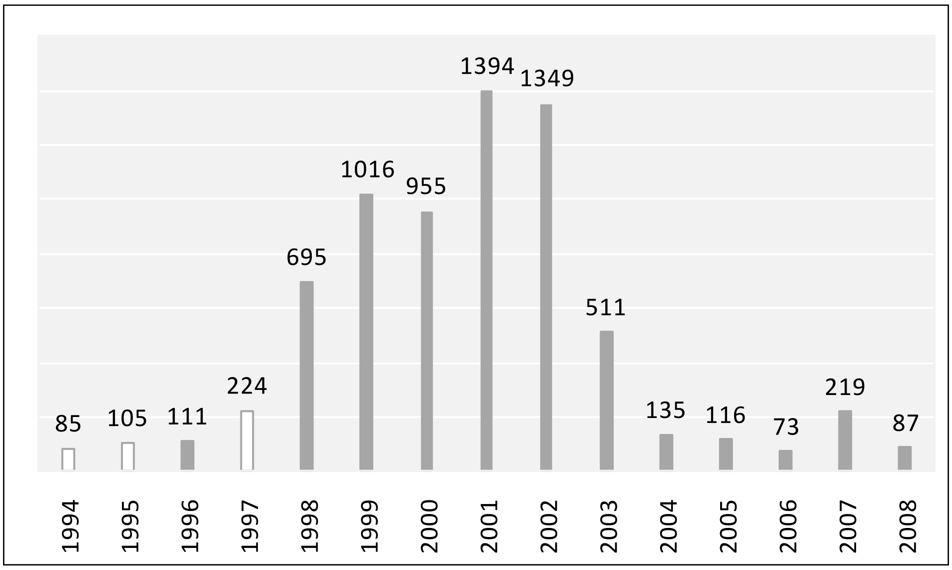


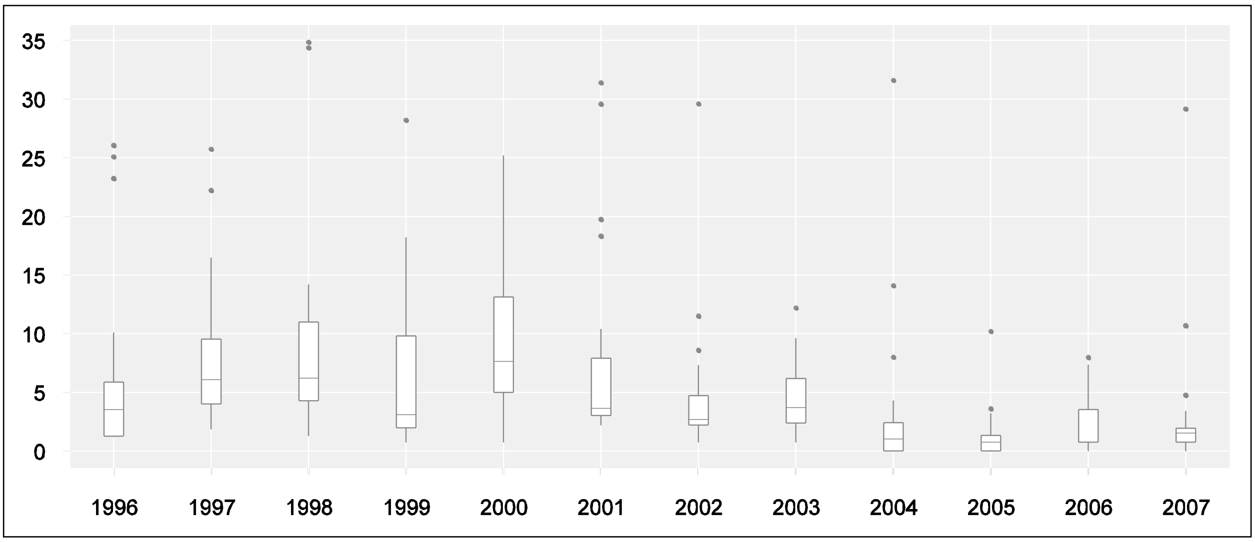
Figure 37: Approximate annual zinc loads (g ha^{-1} a^{-1}) by wet deposition on "Wildwiese" meadow. White bars: more than 30 days of interpolated data.

4.4.2.8 Nickel (Ni)

Table 24: Nickel concentration in wet deposition on "Wildwiese" meadow.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1996	32	4	9	3.54	2.67	1.25	1.25	1.25	3.07	4.90	8.17	10.09
1997	32	3	9	6.60	3.56	1.88	2.81	3.94	6.03	8.76	10.65	16.45
1998	29	3	9	6.99	3.77	1.30	2.82	4.06	5.90	10.20	12.34	14.20
1999	24	1	2	5.93	5.53	0.75	1.11	1.91	3.05	8.60	15.36	18.20
2000	23	0	2	9.76	6.70	0.75	3.02	5.00	7.63	13.15	19.30	25.19
2001	21	4	2	4.32	2.45	2.21	2.36	2.77	3.46	4.44	7.90	10.40
2002	19	3	4	3.04	1.57	0.75	1.63	2.20	2.60	3.85	4.88	7.30
2003	24	2	1	3.97	2.45	0.75	1.18	2.26	3.65	5.45	7.44	9.60
2004	22	3	1	0.98	1.26	n.d.	n.d.	n.d.	0.38	1.45	2.85	4.30
2005	23	2	2	0.70	0.89	n.d.	n.d.	n.d.	0.75	0.99	1.83	3.20
2006	20	1	5	1.99	2.28	n.d.	n.d.	0.56	0.75	3.06	5.04	7.34
2007	25	3	0	1.34	0.80	n.d.	0.75	0.75	1.24	1.81	1.96	3.40
1996–2007	**299**	**24**	**46**	**4.14**	**3.74**	**n.d.**	**0.75**	**1.25**	**3.07**	**6.05**	**9.86**	**16.45**

unit: µg l^{-1}



three values > 35 (1997: 74.23, 1998: 53.63, 2003: 45.00) not shown

Figure 38: Nickel concentration [µg l^{-1}] in wet deposition on "Wildwiese" meadow.

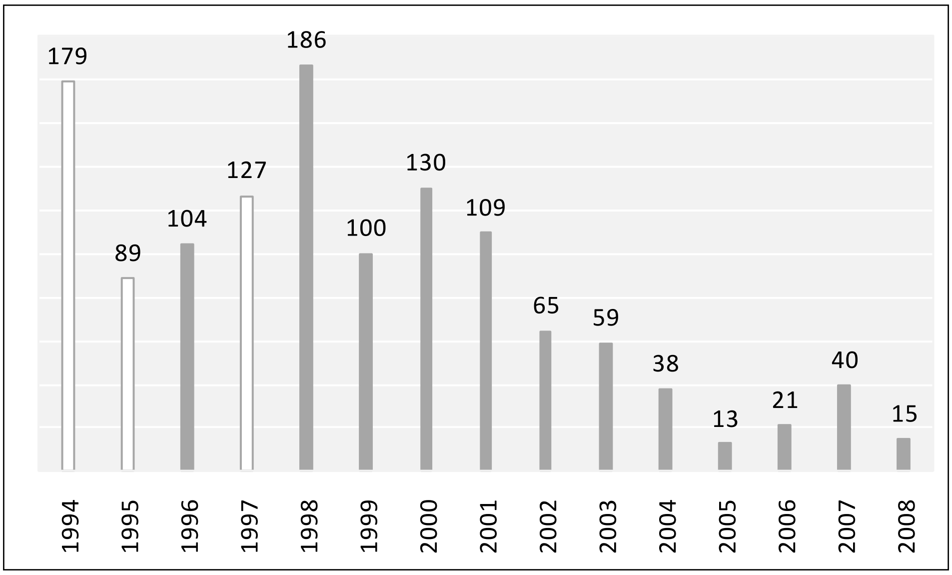


Figure 39: Approximate annual nickel loads (g ha^{-1} a^{-1}) by wet deposition on "Wildwiese" meadow. White bars: more than 30 days of interpolated data.

4.4.2.9 Arsenic (As)

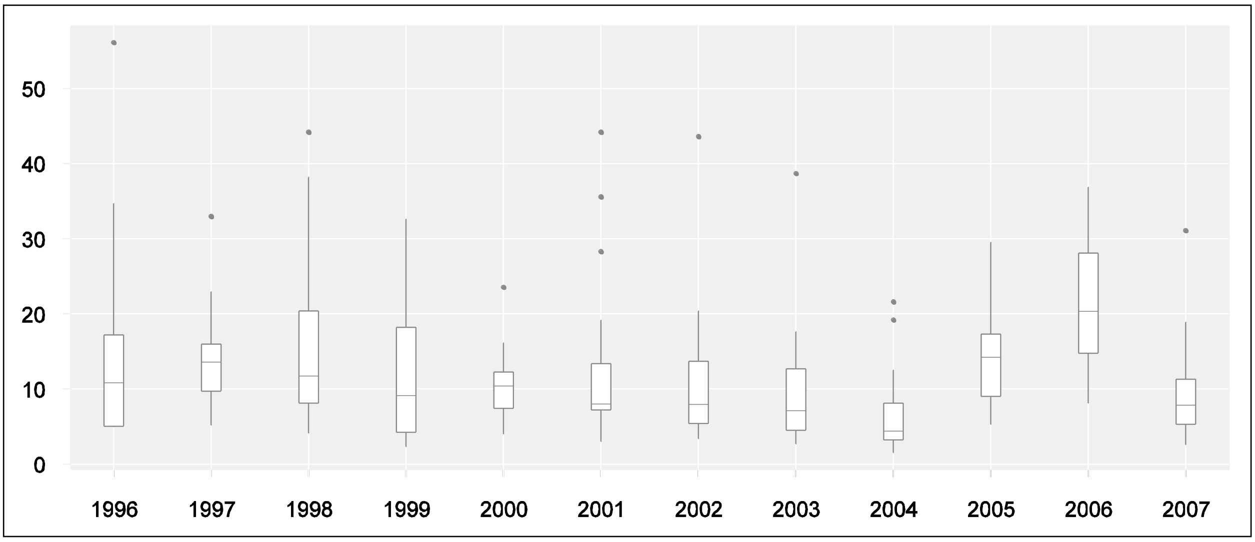
No arsenic was detected in wet deposition.

4.4.2.10 Aluminium (As)

Table 25: Aluminium concentration in wet deposition on "Wildwiese" meadow.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1996	34	2	9	11.84	7.89	5.00	5.00	5.00	10.65	16.45	22.47	34.70
1997	33	2	9	12.99	4.99	5.16	6.33	9.70	13.23	15.93	20.81	22.96
1998	29	3	9	16.68	11.27	4.10	5.96	8.10	11.70	20.40	36.74	44.20
1999	25	0	2	12.22	8.85	2.30	3.48	4.20	9.10	18.20	22.32	32.60
2000	22	1	2	9.89	3.27	4.01	6.18	7.27	10.14	12.04	13.82	16.15
2001	22	3	2	8.83	3.99	3.02	3.54	6.83	7.74	11.02	14.23	19.18
2002	21	1	4	8.98	4.68	3.40	4.40	5.40	7.70	13.00	14.80	20.40
2003	25	1	1	8.06	4.55	2.70	3.64	4.50	7.10	11.40	14.44	17.60
2004	23	2	1	4.96	2.96	1.50	1.60	3.05	4.18	5.85	8.44	12.50
2005	25	0	2	14.66	6.90	5.30	6.26	9.00	14.20	17.30	25.32	29.50
2006	21	0	5	20.73	8.26	8.08	10.12	14.75	20.33	28.09	30.01	36.87
2007	27	1	0	8.45	4.11	2.60	4.67	5.31	7.28	11.04	14.07	18.92
1996–2007	**302**	**21**	**46**	**11.03**	**6.46**	**1.50**	**4.21**	**5.60**	**9.98**	**14.47**	**21.19**	**30.01**

unit: µg l^{-1}



five values > 60 (1996: 90.5, 1997: 92.2, 1998: 134.0, 300.0, 109.7) not shown

Figure 40: Aluminium concentration [µg l^{-1}] in wet deposition on "Wildwiese" meadow.

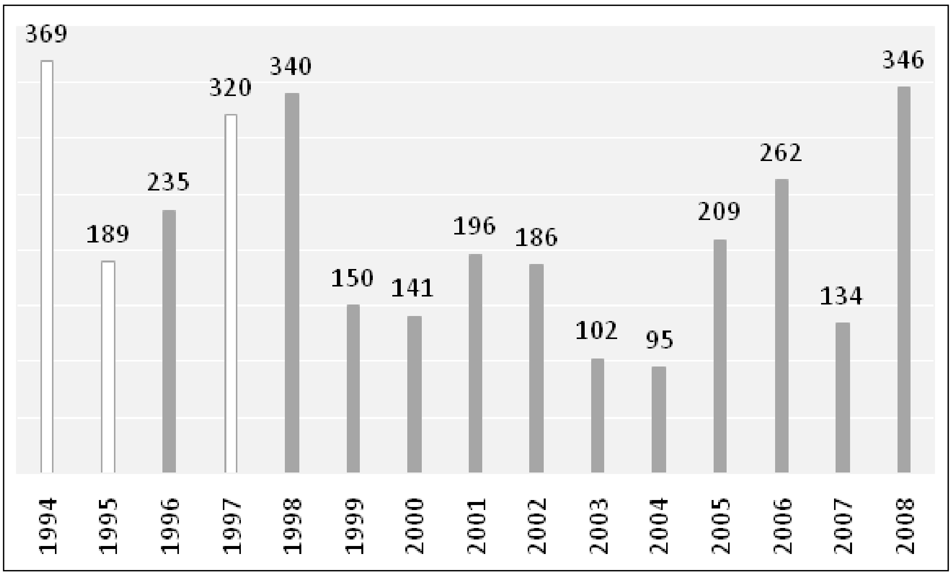


Figure 41: Approximate annual aluminium loads (g ha^{-1} a^{-1}) by wet deposition on "Wildwiese" meadow. White bars: more than 30 days of interpolated data.

4.4.2.11 Mercury (Hg)

No mercury was detected in wet deposition.

4.4.3 Canopy throughfall

Not surprisingly, trace element concentrations were higher in canopy throughfall in the coniferous stand (IP1) than on the deciduous plot (IP2), except for the nickel concentrations outside the 2000–2003 period of increased deposition. During this period, a number of metals showed peak concentrations and loads. The transient pollutant plateaus were most prominent for iron, chromium and zinc, raising the deposition of these elements by one order of magnitude. The changed pollutant regime is thought to stem from an industrial source in the region, although the earlier onset (1999) of copper and zinc enrichment suggests that there might have been more than one plant and/or process involved.

The composition of canopy throughfall on the deciduous stand (Figure 42, left) was very similar to that of wet deposition, except the negligible chromium content and an inverse order of Mn and Ni. Canopy throughfall from the coniferous plot, by contrast, differed from bulk and wet deposition and throughfall in the deciduous stand by its high manganese contents (Figure 42, right). Similarly, litterfall from the deciduous canopy contained about one order of magnitude less manganese than on the coniferous plot. The other investigated elements (Cd, Pb, Cu, and Zn) showed much smaller differences between coniferous and broadleaf litter (65 ff).

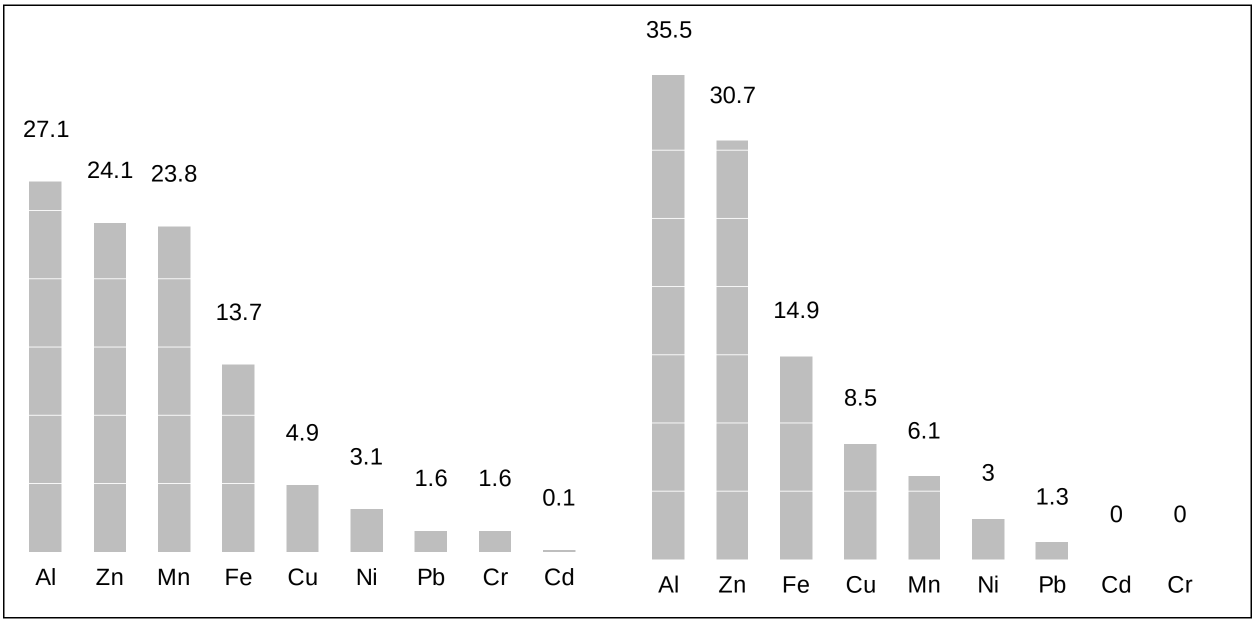


Figure 42: Element composition (%) of canopy throughfall on the deciduous plot IP2 (left) and on the coniferous plot IP1 (right).

4.4.3.1 Iron (Fe)

Iron concentrations in canopy throughfall were 1.3 to 1.8 times higher on the coniferous plot than on the deciduous site (Table 26–Table 27). During the years 2000–03 there was a transient increase of concentrations by one order of magnitude, probably caused by industrial emissions in the region.

Table 26: Iron concentration in canopy throughfall on the coniferous plot IP1.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1995	45	2	12	11.0	5.0	1.3	5.4	7.5	10.2	14.2	17.3	23.3
1996	40	2	2	15.1	8.2	2.5	6.8	8.6	12.5	21.1	28.4	34.0
1997	37	3	2	11.0	3.6	4.4	6.5	8.5	10.2	13.4	16.0	18.1
1998	36	3	2	14.5	5.1	5.5	7.9	11.3	14.0	18.5	20.2	25.7
1999	21	3	3	11.7	4.8	3.8	5.4	8.4	11.6	15.8	16.7	20.3
2000	24	1	0	402.2	294.2	3.8	8.4	155.0	382.1	599.3	779.5	984.1
2001	25	0	2	243.4	179.0	18.0	50.1	123.9	186.3	373.4	498.1	635.0
2002	24	2	0	259.1	123.3	10.9	106.5	200.3	271.5	330.8	362.8	542.0
2003	26	0	0	346.3	258.5	71.3	81.4	151.0	233.5	578.5	686.0	969.0
2004	20	5	1	14.3	6.7	7.5	7.5	7.5	13.6	17.0	24.7	29.3
2005	25	0	2	8.0	10.6	n.d.	n.d.	n.d.	n.d.	17.5	17.5	34.8
2006	13	12	1	7.5	n.d.	7.5	7.5	7.5	7.5	7.5	7.5	7.5
2007	24	2	1	8.4	6.1	n.d.	n.d.	5.6	7.5	12.5	15.1	20.0
1995–2007	**310**	**85**	**28**	**16.5**	**19.8**	**n.d.**	**3.6**	**7.5**	**12.1**	**17.5**	**29.3**	**133.0**

unit: µg l^{-1}

Table 27: Iron concentration in canopy throughfall on the deciduous plot IP2.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1997	38	4	0	8.7	3.3	3.3	4.6	6.9	7.9	10.6	13.3	18.1
1998	39	0	1	11.2	5.7	3.8	4.9	6.7	10.5	14.7	18.5	25.0
1999	20	3	5	8.0	4.1	3.8	3.8	5.2	6.6	10.6	13.3	18.8
2000	24	1	0	188.4	136.4	3.8	7.5	95.2	179.2	272.2	353.1	501.0
2001	24	2	1	124.3	74.7	18.3	30.1	75.3	128.8	160.9	213.6	299.2
2002	25	1	0	174.9	85.3	17.6	78.9	114.0	163.0	234.0	288.2	343.0
2003	25	1	0	135.0	80.2	21.8	35.8	53.0	139.0	204.0	232.2	259.0
2004	15	10	1	8.7	1.9	7.5	7.5	7.5	7.5	10.5	11.5	12.2
2005	20	5	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2006	24	1	1	3.5	4.4	n.d.	n.d.	n.d.	n.d.	7.5	7.5	12.8
2007	24	2	0	5.0	4.5	n.d.	n.d.	n.d.	7.5	7.5	11.1	11.7
1997–2007	**282**	**26**	**11**	**39.7**	**60.5**	**n.d.**	**n.d.**	**5.6**	**10.4**	**35.5**	**145.1**	**221.0**

unit: µg l^{-1}

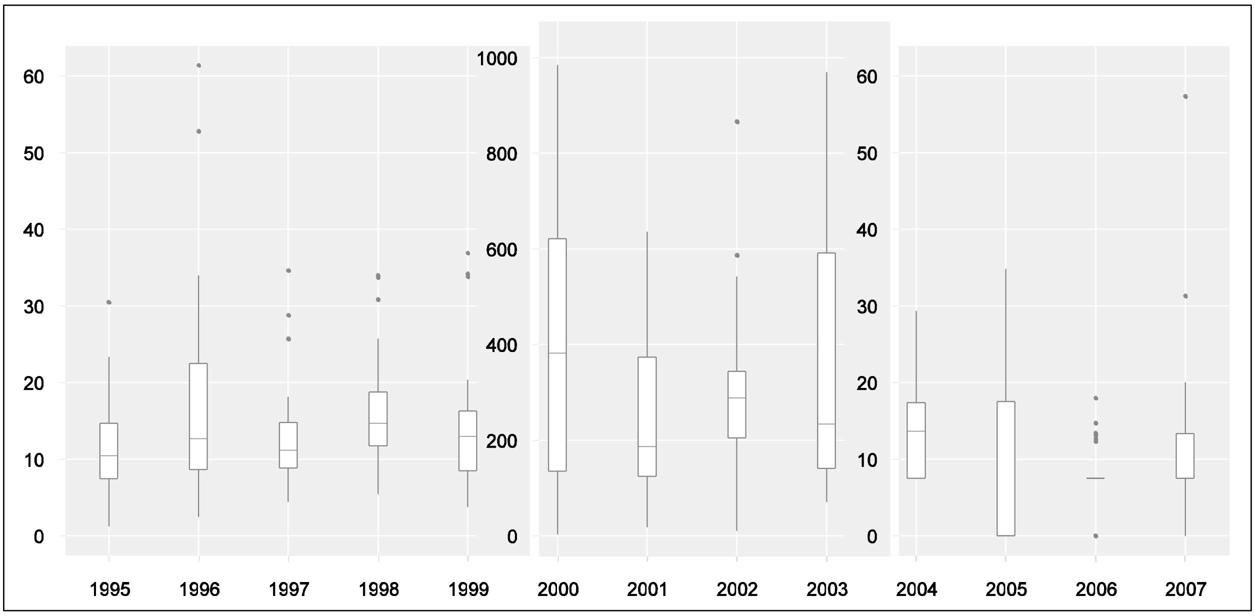


Figure 43: Iron concentration [µg l^{-1}] in canopy throughfall on the coniferous plot IP1 (note reduced scale for years 2000–03). Five values > 100 (1995: 102, 2004: 264, 304, 359, 230, 171) and one value (6206) from 2000 not shown.

While concentrations differed between stands already by a factor of 1.3–1.8, the corresponding load differences sometimes exceeded a factor of four (Table 28).

Table 28: Annual iron loads from canopy troughfall.

	coniferous	deciduous
1994	188.4	
1995	196.8	
1996	188.6	90.32
1997	159.2	97.03
1998	164.9	81.36
1999	135.0	90.58
2000	6799	1985
2001	2943	1490
2002	3882	2423
2003	3865	1411
2004	878.8	209.4
2005	63.69	18.38
2006	69.83	45.24
2007	91.63	36.46
2008	63.19	28.62

unit: g ha^{-1} a^{-1}; grey font: annual values including more than 35 days of interpolated data.

4.4.3.2 Manganese (Mn)

Canopy throughfall contained roughlyfive times as much manganese on the coniferous as on the deciduous plot (Table 29–Table 30). As observed with iron, but less pronounced, a period of increased throughfall deposition occurred between 2000 and 2003 (Figure 44).

Table 29: Manganese concentration in canopy throughfall on the coniferous plot IP1.

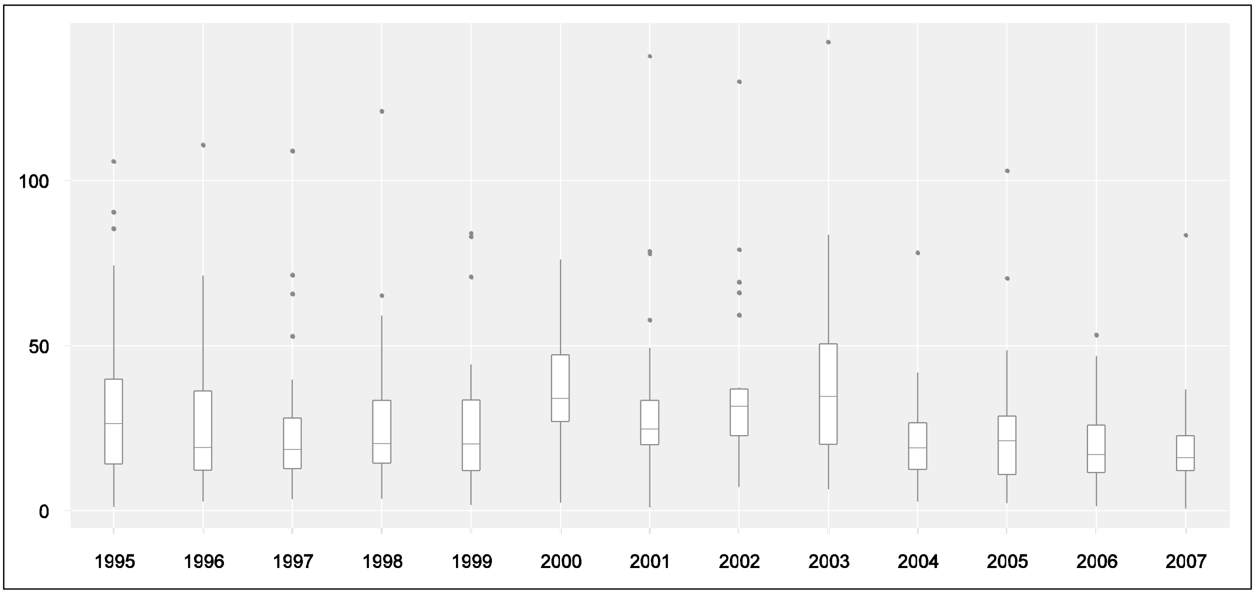
year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1995	44	3	12	26.4	18.1	1.3	5.8	13.0	23.7	35.7	55.5	74.2
1996	40	1	3	24.1	17.6	2.9	6.7	12.2	18.9	32.9	49.1	71.2
1997	35	6	1	19.7	10.3	3.6	10.3	12.7	17.5	24.0	32.7	52.9
1998	37	2	2	24.1	14.8	3.7	8.9	14.2	20.0	32.6	43.7	59.0
1999	22	3	2	20.1	11.2	1.8	9.8	11.9	19.3	27.6	34.9	44.2
2000	23	2	0	36.3	18.3	2.5	13.3	27.0	34.0	47.2	57.4	76.0
2001	21	4	2	23.3	10.2	1.1	13.1	18.1	22.4	27.1	33.4	49.3
2002	21	5	0	26.4	9.3	7.3	13.5	17.5	29.6	33.7	36.1	37.2
2003	24	2	0	36.9	20.9	6.6	14.6	20.1	33.6	49.9	65.6	83.5
2004	24	1	1	20.4	10.9	2.9	8.4	11.9	19.0	26.4	35.6	41.8
2005	23	2	2	20.8	14.0	2.4	5.0	10.4	19.5	24.7	44.9	48.5
2006	24	1	1	19.0	11.4	1.4	8.8	11.5	16.5	25.8	35.5	46.8
2007	24	2	1	17.5	8.6	0.7	7.8	12.1	15.9	21.6	28.2	36.7
1995–2007	**363**	**33**	**27**	**24.1**	**14.8**	**0.7**	**8.2**	**13.4**	**20.4**	**32.6**	**46.2**	**68.1**

unit: µg l^{-1}

Table 30: Manganese concentration in canopy throughfall on the deciduous plot IP2.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1997	38	4	0	3.65	1.87	1.88	1.88	1.88	2.99	4.53	6.45	8.67
1998	35	4	1	4.13	2.24	1.43	1.92	2.60	3.30	5.18	7.31	10.70
1999	24	0	4	3.86	2.21	1.17	1.50	2.30	3.45	4.88	7.27	8.80
2000	23	2	0	8.69	4.65	1.60	2.73	5.16	8.90	11.31	14.02	18.90
2001	26	0	1	6.98	3.82	0.75	3.44	4.54	5.65	10.09	12.52	14.73
2002	24	2	0	6.83	2.22	1.62	3.90	5.83	7.30	7.98	9.27	10.60
2003	26	0	0	9.50	6.43	1.78	2.35	5.28	7.85	12.75	19.15	24.10
2004	24	1	1	3.45	1.33	1.43	1.70	2.55	3.25	4.50	5.41	5.80
2005	24	1	2	3.35	1.68	1.09	1.46	2.10	3.05	4.40	5.47	7.00
2006	25	0	1	3.35	1.71	0.73	1.56	2.12	2.85	4.79	5.82	6.54
2007	24	2	0	3.15	1.91	0.59	1.35	1.91	2.54	4.57	5.62	8.12
1997–2007	**291**	**18**	**10**	**4.85**	**3.07**	**0.59**	**1.82**	**2.48**	**4.19**	**6.40**	**9.10**	**14.50**

unit: µg l^{-1}



seven values > 150 (1997: 228, 284, 275, 2000: 155, 208.7, 2003: 211, 2007: 154) not shown

Figure 44: Manganese concentration [µg l^{-1}] in canopy throughfall on the coniferous plot IP1.

Table 31: Annual manganese loads from canopy throughfall.

	coniferous	deciduous
1994	350.8	
1995	278.8	
1996	279.9	47.96
1997	356.0	44.34
1998	310.3	33.95
1999	220.2	26.88
2000	384.6	80.14
2001	305.9	64.00
2002	334.9	80.77
2003	296.9	63.76
2004	229.6	33.68
2005	221.1	27.17
2006	221.5	31.97
2007	206.9	29.16
2008	94.39	20.69

unit: g ha^{-1} a^{-1}; grey font: annual values including more than 35 days of interpolated data.

4.4.3.3 Cadmium (Cd)

No transient deposition peak between 2000 and 2003 (as observed for e.g., iron and manganese) became apparent for cadmium. By contrast, cadmium concentrations in canopy throughfall were conspicuously high during 1997. *Concentrations decreased from 1996 on* and, even on the coniferous plot, remained mainly below the detection limit (50 ng l^{-1}) after 2002 (Table 32, Table 33).

Table 32: Cadmium concentration in canopy throughfall on the coniferous plot IP1.

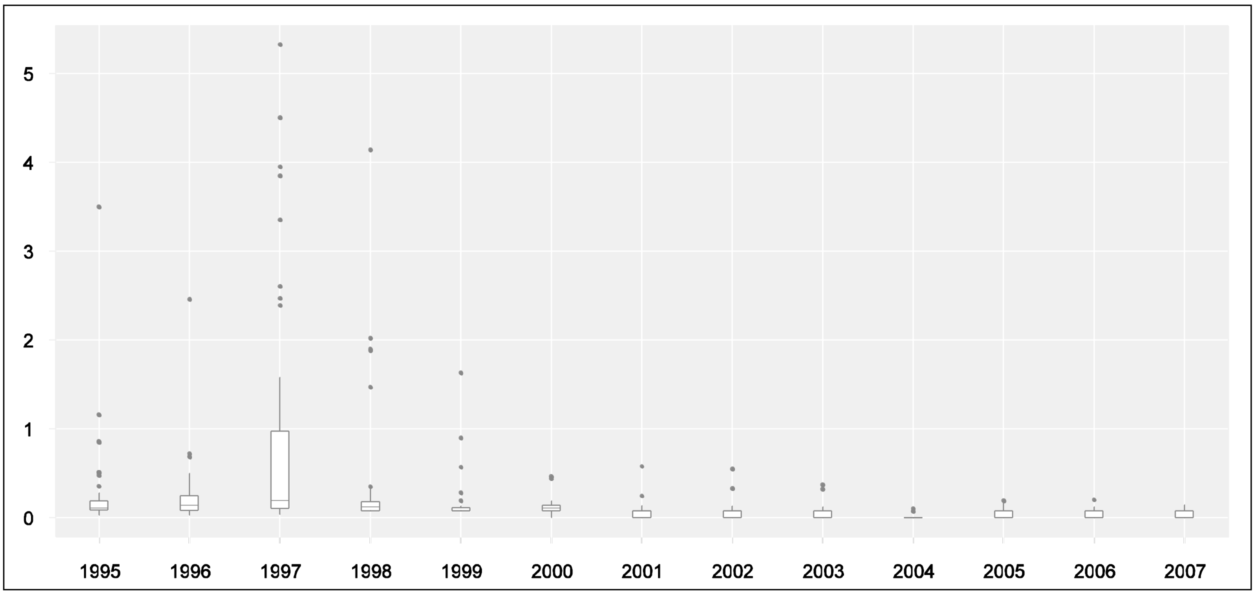
year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1995	48	9	2	110.1	55.1	25.0	53.0	78.3	98.0	130.3	189.8	277.0
1996	38	4	2	158.6	115.7	25.0	25.0	78.5	131.0	224.5	309.1	500.0
1997	35	6	1	543.9	864.1	37.5	70.4	96.4	173.0	338.5	2065	3354
1998	32	7	2	135.8	80.1	75.0	75.0	75.0	110.0	162.5	261.0	350.0
1999	20	5	2	80.8	14.9	75.0	75.0	75.0	75.0	75.0	101.0	130.0
2000	23	2	0	98.7	43.9	n.d.	75.0	75.0	106.0	128.3	137.8	188.0
2001	23	2	2	43.1	44.3	–	–	n.d.	75.0	75.0	75.0	136.0
2002	24	2	0	42.9	41.8	–	–	n.d.	75.0	75.0	75.0	130.0
2003	24	2	0	30.0	40.5	–	–		n.d.	75.0	75.0	120.0
2004	21	4	1	n.d.	–	–	–	–	–	–	–	n.d.
2005	24	1	2	40.0	56.8	–	–	–	n.d.	75.0	120.0	170.0
2006	24	1	1	28.3	42.2	–	–	–	n.d.	75.0	75.0	122.0
2007	26	0	1	34.3	42.9	–	–	–	n.d.	75.0	75.0	142.5
1995–2007	**362**	**45**	**16**	**82.2**	**77.3**	**–**	**–**	**n.d.**	**75.0**	**112.8**	**188.0**	**354.0**

note units of ng l^{-1}

Table 33: Cadmium concentration in canopy throughfall on the deciduous plot IP2.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1997	40	2	0	87.9	59.6	37.5	37.5	37.5	63.9	130.3	151.0	250.0
1998	36	3	1	91.9	31.1	75.0	75.0	75.0	75.0	102.5	135.0	180.0
1999	20	4	4	75.0	0.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0
2000	25	0	0	33.9	43.6	–	–	–	n.d.	75.0	87.6	121.0
2001	20	6	1	n.d.	–	–	–	–	–	–	–	n.d.
2002	22	4	0	n.d.	–	–	–	–	–	–	–	n.d.
2003	23	3	0	n.d.	–	–	–	–	–	–	–	n.d.
2004	24	1	1	n.d.	–	–	–	–	–	–	–	n.d.
2005	25	0	2	24.0	35.7	–	–	–	n.d.	75.0	75.0	75.0
2006	20	5	1	n.d.	–	–	–	–	–	–	–	n.d.
2007	26	0	0	24.6	38.4	–	–	–	n.d.	75.0	75.0	115.6
1997–2007	**298**	**11**	**10**	**38.3**	**45.5**	**–**	**–**	**–**	**n.d.**	**75.0**	**83.5**	**180.0**

note units of ng l^{-1}



four values > 8 (1997: 9.66, 19.87, 1998: 7.42, 7.61) not shown.

Figure 45: Cadmium concentration [µg l^{-1}] in canopy throughfall on plot IP1 on the coniferous plot IP1.

Table 34: Annual cadmium loads from canopy troughfall.

	coniferous	deciduous
1994	1.532	
1995	2.859	
1996	5.830	11.47
1997	21.28	1.118
1998	11.08	3.081
1999	1.685	0.711
2000	4.413	3.174
2001	0.706	0.114
2002	0.888	0.211
2003	0.598	0.040
2004	2.841	2.765
2005	0.570	0.191
2006	0.360	0.146
2007	0.333	0.183
2008	2.889	2.784

unit: g ha^{-1} a^{-1}; grey font: annual values including more than 35 days of interpolated data

4.4.3.4 Chromium (Cr)

The additional trace metal contamination observed during 2000–2003 became particularly manifest in chromium concentrations which in 2000 increased by two orders of magnitude at the coniferous stand (Table 35–Table 36).

Table 35: Chromium concentration in canopy throughfall on the coniferous plot IP1.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1995	47	0	12	1.25	n.d.	1.25	1.25	1.25	1.25	1.25	1.25	1.25
1996	42	0	2	1.25	n.d.	1.25	1.25	1.25	1.25	1.25	1.25	1.25
1997	41	0	1	1.88	n.d.	1.88	1.88	1.88	1.88	1.88	1.88	1.88
1998	39	0	2	0.75	n.d.	0.75	0.75	0.75	0.75	0.75	0.75	0.75
1999	25	0	2	0.75	n.d.	0.75	0.75	0.75	0.75	0.75	0.75	0.75
2000	24	1	0	112.1	81.76	–	n.d.	39.92	117.2	175.5	204.1	253.2
2001	25	0	2	71.24	55.78	1.89	11.91	35.09	55.25	110.2	147.7	203.8
2002	23	3	0	67.91	30.49	2.80	29.64	52.20	70.60	87.80	96.40	129.0
2003	26	0	0	99.20	77.66	17.40	21.20	43.10	63.75	157.3	195.5	287.0
2004	20	5	1	0.46	1.30	n.d.	n.d.	n.d.	n.d.	n.d.	1.05	4.70
2005	25	0	2	0.23	0.39	n.d.	n.d.	n.d.	n.d.	0.75	0.75	1.24
2006	25	0	1	n.d.	–	–	–	–	–	–	–	n.d.
2007	24	2	1	n.d.	–	–	–	–	–	–	–	n.d.
1995–2007	**299**	**98**	**26**	**0.89**	**0.76**	**–**	**–**	**n.d.**	**0.75**	**1.25**	**1.88**	**4.70**

unit: µg l^{-1}

Table 36: Chromium concentration in canopy throughfall on the deciduous plot IP2.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1997	42	0	0	1.88	0.00	1.88	1.88	1.88	1.88	1.88	1.88	1.88
1998	38	1	1	0.75	0.00	0.75	0.75	0.75	0.75	0.75	0.75	0.75
1999	24	0	4	0.75	0.00	0.75	0.75	0.75	0.75	0.75	0.75	0.75
2000	24	1	0	53.72	40.59	n.d.	n.d.	25.70	50.89	79.23	104.7	146.3
2001	24	2	1	35.54	22.23	3.32	6.86	20.89	37.37	45.48	62.26	86.49
2002	25	1	0	48.93	24.65	4.30	21.62	32.00	47.80	63.00	80.66	103.0
2003	25	1	0	37.92	23.43	5.60	8.72	15.60	39.20	55.50	67.54	74.60
2004	20	5	1	0.40	1.13	–	–	–	–	n.d.	1.00	4.10
2005	22	3	2	n.d.	–	–	–	–	–	–	–	n.d.
2006	24	1	1	n.d.	–	–	–	–	–	–	–	n.d.
2007	25	1	0	n.d.	–	–	–	–	–	–	–	n.d.
1997–2007	**278**	**31**	**10**	**8.89**	**16.24**	**n.d.**	**n.d.**	**n.d.**	**0.75**	**4.25**	**38.30**	**61.77**

unit: µg l^{-1}

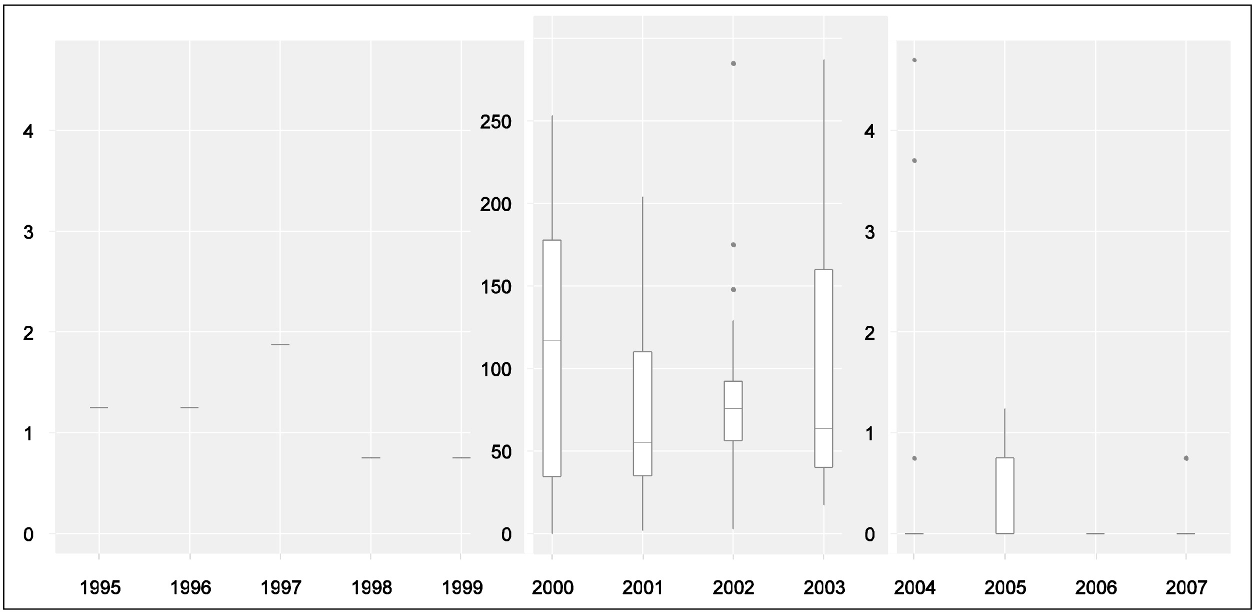


Figure 46: Chromium concentration [µg l^{-1}] in canopy throughfall on the coniferous plot IP1 (note reduced scale for years 2000–03); four values > 8 (1997: 9.66, 19.87, 1998: 7.42, 7.61) not shown.

Table 37: Annual chromium loads from canopy throughfall.

	coniferous	deciduous
1994	17.10	
1995	12.57	
1996	20.12	26.05
1997	27.63	21.10
1998	10.07	6.762
1999	8.353	6.405
2000	1827	574.3
2001	862.2	436.2
2002	1082	675.8
2003	1115	406.5
2004	220.5	46.10
2005	2.454	0.347
2006	0.000	1.024
2007	0.063	0.013
2008	2.740	2.740

unit: g ha^{-1} a^{-1}; grey font: annual values including more than 35 days of interpolated data

4.4.3.5 Lead (Pb)

Lead concentrations decreased steadily from 1995 on (with, like cadmium, transiently higher values in 1997).

Table 38: Lead concentration in canopy throughfall on the coniferous stand IP1.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1995	57	0	2	2.25	1.78	0.50	0.50	0.50	1.80	3.22	5.11	6.30
1996	37	5	2	1.70	1.48	0.50	0.50	0.50	1.33	2.49	3.69	6.03
1997	40	1	1	2.33	1.05	0.75	1.25	1.56	1.98	2.98	3.97	4.59
1998	36	3	2	1.48	0.73	0.75	0.75	0.97	1.26	1.80	2.60	3.40
1999	23	2	2	1.42	0.52	0.75	0.75	1.09	1.35	1.55	2.16	2.60
2000	23	2	0	1.33	0.36	0.75	0.81	1.10	1.35	1.52	1.71	2.18
2001	20	5	2	1.09	0.25	0.75	0.75	0.93	1.09	1.23	1.35	1.58
2002	24	2	0	1.01	0.30	0.75	0.75	0.75	1.01	1.13	1.50	1.62
2003	24	2	0	0.99	0.43	0.30	0.57	0.67	0.90	1.23	1.62	1.85
2004	24	1	1	0.72	0.35	0.30	0.30	0.47	0.69	0.94	1.12	1.58
2005	22	3	2	0.47	0.29	< .5	0.30	0.30	0.30	0.64	0.84	1.11
2006	25	0	1	0.78	0.46	0.30	0.30	0.30	0.71	1.09	1.32	1.97
2007	24	2	1	0.44	0.23	0.30	0.30	0.30	0.30	0.60	0.70	1.09
1995–2007	**371**	**36**	**16**	**1.21**	**0.78**	**< .5**	**0.30**	**0.61**	**1.10**	**1.58**	**2.40**	**3.64**

unit: µg l^{-1}

Table 39: Lead concentration in canopy throughfall.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1997	40	2	0	1.71	0.81	0.75	0.75	1.05	1.62	2.38	2.66	3.72
1998	34	5	1	1.05	0.42	0.75	0.75	0.75	0.75	1.17	1.59	2.34
1999	22	2	4	1.06	0.44	0.75	0.75	0.75	0.75	1.30	1.55	2.20
2000	23	2	0	0.95	0.28	0.75	0.75	0.75	0.75	1.15	1.33	1.63
2001	23	3	1	0.92	0.42	0.00	0.75	0.75	0.75	1.23	1.47	1.58
2002	18	8	0	0.75	0.00	0.75	0.75	0.75	0.75	0.75	0.75	0.75
2003	25	1	0	0.60	0.36	0.30	0.30	0.30	0.54	0.81	1.17	1.39
2004	23	2	1	0.48	0.25	0.30	0.30	0.30	0.30	0.62	0.90	1.01
2005	19	6	2	0.30	0.09	n.d.	0.30	0.30	0.30	0.30	0.30	0.52
2006	24	1	1	0.70	0.42	0.30	0.30	0.30	0.63	0.92	1.35	1.54
2007	25	1	0	0.44	0.22	0.30	0.30	0.30	0.30	0.59	0.80	0.96
1997–2007	**284**	**25**	**10**	**0.83**	**0.50**	**0.00**	**0.30**	**0.30**	**0.75**	**1.10**	**1.54**	**2.37**

unit: µg l^{-1}

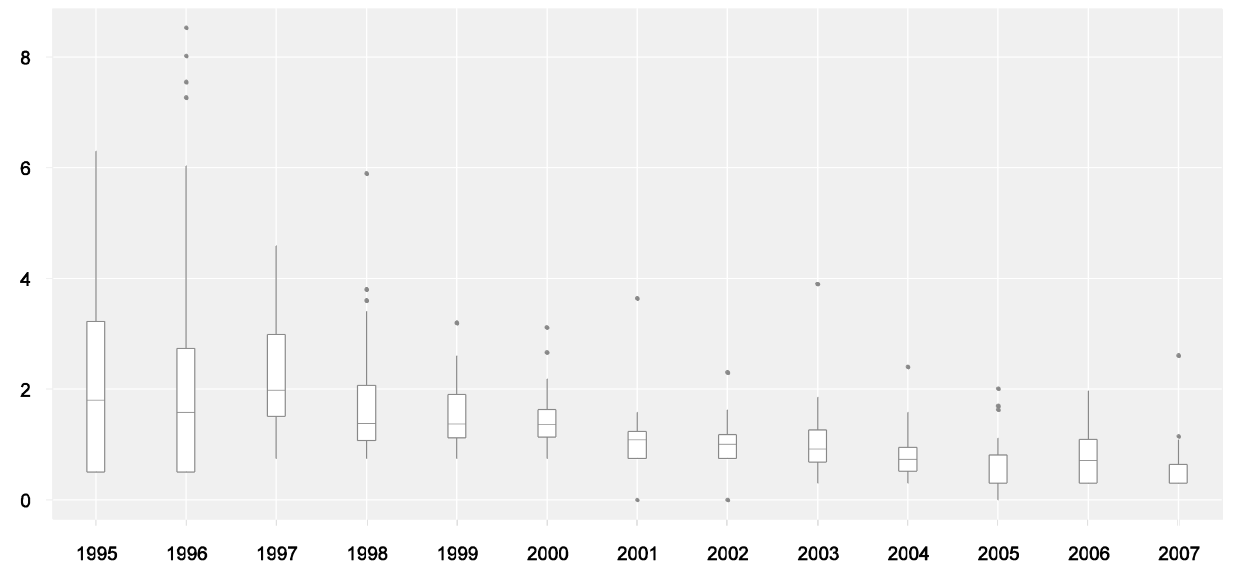


Figure 47: Lead concentration [µg l^{-1}] in canopy throughfall on the coniferous plot IP1; six values > 10 (1996 : 12.4, 1997 : 11.5, 2001: 19.4, 25.4, 107.0, 2003 : 10.4) not shown.

Table 40: Annual lead loads from canopy throughfall.

	coniferous	deciduous
1994	12.68	
1995	17.36	
1996	27.97	25.01
1997	32.34	21.23
1998	19.60	9.579
1999	15.11	9.345
2000	19.62	11.98

	coniferous	deciduous
2001	62.12	21.23
2002	11.68	8.927
2003	20.09	5.206
2004	10.82	7.628
2005	6.528	3.995
2006	9.540	7.757
2007	5.155	4.190
2008	5.869	4.717

unit: g ha^{-1} a^{-1}; grey font: annual values including more than 35 days of interpolated data

4.4.3.6 Copper (Cu)

Copper concentrations peaked during 2000–2003, but (unlike observed for Fe, Cr and Mn) already increased in 1999 (Figure 48). As found for the other elements, concentrations of Cu were higher (up to a factor of 1.8) in canopy throughfall of the coniferous stand (Table 41–Table 42).

Table 41: Copper concentration in canopy throughfall.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1995	44	3	12	4.44	3.04	1.25	1.25	2.32	3.90	5.92	8.33	13.51
1996	40	2	2	5.66	4.44	1.25	1.25	3.02	3.86	7.02	12.51	16.58
1997	36	5	1	4.29	2.56	1.88	1.88	1.88	3.80	5.33	6.98	11.73
1998	38	1	2	8.90	5.33	1.00	2.89	5.13	8.05	11.83	15.83	22.60
1999	25	0	2	13.96	8.27	3.90	5.36	6.50	13.50	18.30	24.36	32.40
2000	23	2	0	31.52	15.68	7.34	14.74	18.67	29.45	39.29	57.37	63.72
2001	25	0	2	25.77	14.21	3.86	8.23	18.19	21.27	35.83	42.34	58.51
2002	24	2	0	13.54	6.72	2.60	6.44	8.43	11.65	19.78	21.22	28.90
2003	25	1	0	14.85	9.23	1.87	4.70	7.40	14.40	20.90	26.96	36.10
2004	23	2	1	4.15	2.41	0.75	1.51	2.15	3.90	5.75	7.94	8.90
2005	24	1	2	4.33	2.82	1.57	1.61	2.04	3.20	6.48	7.39	11.20
2006	25	0	1	6.82	4.54	1.81	2.34	3.40	4.97	10.62	13.61	16.50
2007	26	0	1	14.93	12.63	0.75	1.60	3.98	13.35	21.39	33.25	43.05
1995–2007	**368**	**29**	**26**	**9.09**	**7.44**	**0.75**	**1.88**	**3.27**	**6.55**	**13.50**	**20.59**	**32.70**

unit: µg l^{-1}

Table 42: Copper concentration in canopy throughfall.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1997	39	3	0	4.32	2.16	1.88	1.88	2.33	3.79	5.11	7.61	9.20
1998	38	1	1	6.49	3.87	1.55	2.29	3.62	5.48	9.00	11.53	18.26
1999	21	3	4	8.20	3.77	1.45	4.40	5.80	7.80	11.70	12.80	14.80
2000	24	1	0	19.62	9.22	5.96	10.62	12.77	17.16	24.56	32.67	42.96
2001	26	0	1	18.80	10.91	2.97	7.25	10.93	15.13	27.34	33.10	40.99
2002	24	2	0	10.21	5.64	3.40	5.05	6.58	8.20	12.58	16.81	28.11
2003	25	1	0	8.86	5.10	1.32	3.32	5.90	8.10	11.30	15.44	20.50
2004	23	2	1	3.16	1.67	0.75	1.09	1.75	3.30	4.20	4.78	7.12
2005	24	1	2	4.12	3.36	0.75	1.39	1.54	2.50	6.20	8.84	11.80
2006	23	2	1	5.07	3.41	1.69	1.92	2.39	4.25	5.86	10.15	13.26
2007	25	1	0	12.39	9.74	0.75	1.78	4.99	9.74	19.06	22.73	34.85
1997–2007	**288**	**21**	**10**	**8.09**	**6.06**	**0.75**	**1.88**	**3.38**	**6.32**	**11.43**	**17.76**	**26.40**

unit: µg l^{-1}

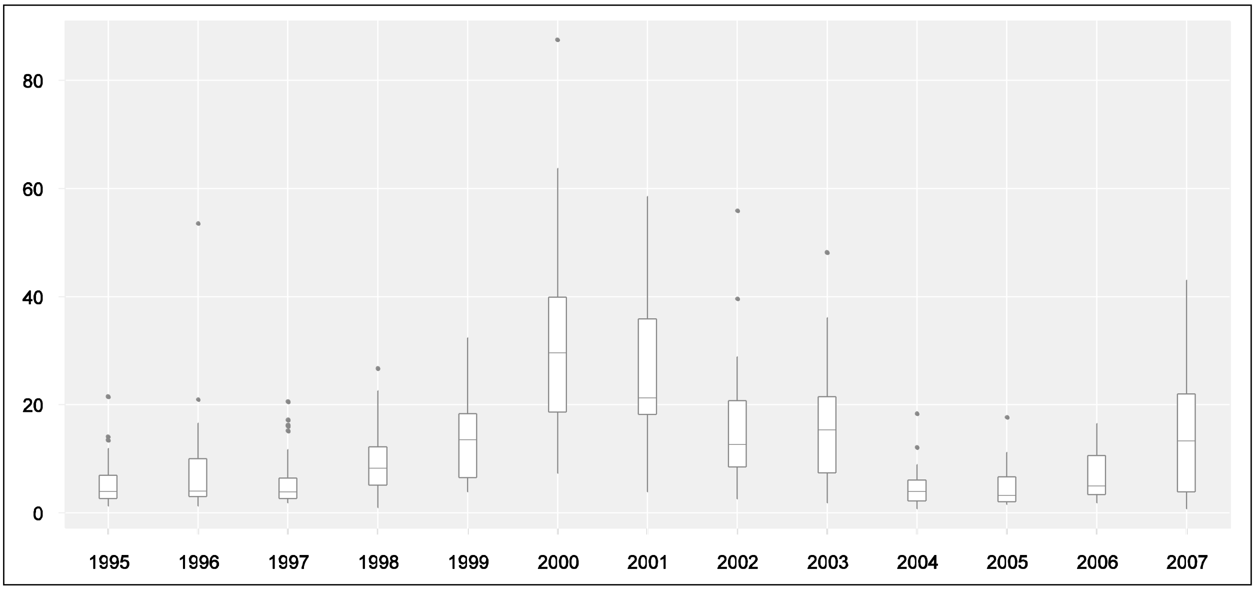


Figure 48: Copper concentration [µg l^{-1}] in canopy throughfall on the coniferous plot IP1; two values > 100 (1995: 311, 2000: 132) not shown.

Table 43: Annual copper loads from canopy throughfall.

	coniferous	deciduous
1994	69.16	
1995	38.98	
1996	52.81	41.86
1997	63.73	46.57
1998	97.39	48.97
1999	139.0	75.17
2000	357.4	187.19
2001	282.7	173.37
2002	174.2	124.71
2003	130.5	66.90
2004	55.77	37.12
2005	43.46	31.01
2006	60.59	41.39
2007	183.2	122.33
2008	93.32	58.44

unit: g ha^{-1} a^{-1}; grey font: annual values including more than 35 days of interpolated data

4.4.3.7 Zinc (Zn)

Zinc, besides chromium, was the characteristic element of the 2000–2003 period of markedly increased metal deposition. However, as observed for copper, zinc concentrations in canopy throughfall clearly went up already in 1999 (Table 44–Table 47, Figure 49). Zinc concentrations, as those of the other trace elements, were higher (annual medians differing by a factor of 1.1–2.6) in throughfall from the coniferous canopy.

Table 44: Zinc concentration in canopy throughfall on the coniferous plot IP1.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1995	44	3	12	19.75	10.31	2.000	10.48	12.56	16.25	26.34	28.97	48.71
1996	40	2	2	23.39	12.94	5.180	8.709	12.79	19.93	30.97	42.99	50.10
1997	39	2	1	25.82	12.72	9.885	14.65	16.21	21.49	32.63	42.22	62.22
1998	31	8	2	85.69	92.09	4.500	13.90	20.80	41.40	140.0	245.0	310.0
1999	20	5	2	599.0	482.0	17.30	49.92	210.1	489.0	864.0	1258	1730
2000	22	3	0	1822	1125	69.16	454.0	1072	1780	2400	2889	4310
2001	24	1	2	1581	1306	68.40	278.2	556.2	1072	2182	3640	4430
2002	24	2	0	925.3	599.5	24.10	276.2	469.5	745.5	1436	1799	1991
2003	25	1	0	725.8	702.3	34.30	73.36	207.0	510.0	960.0	1860	2353
2004	19	6	1	8.820	4.627	2.300	3.180	4.650	8.800	11.40	15.40	17.90
2005	24	1	2	10.58	6.972	2.400	3.560	4.800	9.400	16.00	19.93	27.10
2006	24	1	1	12.26	5.657	2.816	6.568	8.196	11.44	16.25	19.83	24.13
2007	25	1	1	22.28	11.38	5.055	8.143	15.15	19.19	30.74	38.26	42.26
1995–2007	**339**	**58**	**26**	**148.5**	**268.0**	**2.000**	**8.108**	**13.52**	**24.30**	**90.44**	**598.2**	**1170**

unit: µg l^{-1}

Table 45: Zinc concentration in canopy throughfall on the deciduous plot IP2.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1997	37	5	0	17.0	9.0	4.9	6.6	10.4	15.4	20.4	28.8	48.2
1998	35	4	1	72.2	88.6	4.8	8.5	15.5	28.6	95.6	231.4	291.0
1999	22	2	4	534	537	19	28	171	394	657	1223	1865
2000	25	0	0	1114	857	79	161	575	695	1630	2414	2820
2001	26	0	1	1058	925	92	176	259	805	1488	2540	3370
2002	22	4	0	434	240	25	156	263	484	533	738	976
2003	25	1	0	262	212	13	27	109	232	383	627	697
2004	22	3	1	9.2	9.1	2.1	2.8	3.4	5.4	10.4	20.2	35.5
2005	24	1	2	7.5	4.6	1.5	3.4	4.2	5.6	10.8	12.9	18.2
2006	24	1	1	9.5	4.4	2.3	4.5	5.8	9.8	12.2	15.5	16.6
2007	25	1	0	19.3	11.3	4.4	7.0	10.2	17.4	25.6	31.9	49.8
1997–2007	**277**	**32**	**10**	**159**	**239**	**1.5**	**5.2**	**10.4**	**25.9**	**226**	**587.6**	**976.0**

unit: µg l^{-1}

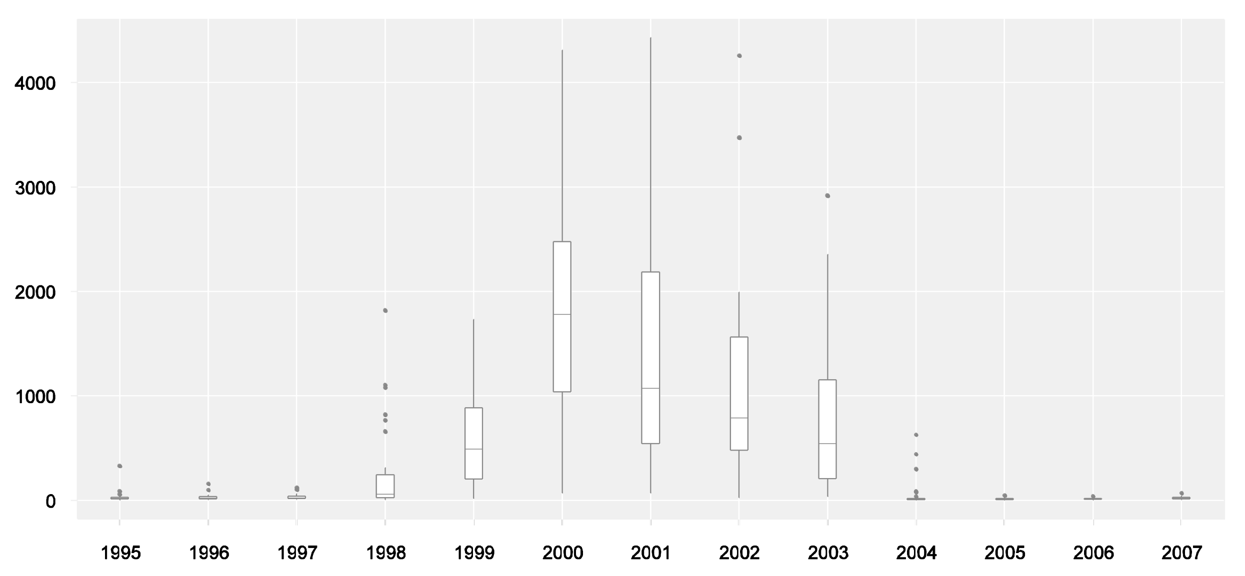


Figure 49: Zinc concentration [µg l^{-1}] in canopy throughfall on the coniferous plot IP1; six values > 5000 (1999: 5202, 7319, 2000: 7020, 5550, 5660, 2001: 7080) not shown.

Table 46: Annual zinc loads from canopy throughfall.

	coniferous	deciduous
1994	0.297	
1995	0.204	
1996	0.265	0.149
1997	0.337	0.196
1998	5.739	2.676
1999	15.67	5.501
2000	26.90	10.90

	coniferous	deciduous
2001	25.67	11.22
2002	15.92	11.71
2003	8.369	3.210
2004	1.127	0.253
2005	0.117	0.059
2006	0.129	0.079
2007	0.279	0.179
2008	0.136	0.089

note unit: kg ha^{-1} a^{-1}*; grey font: annual values including more than 35 days of interpolated data*

4.4.3.8 Nickel (Ni)

Nickel - like iron, chromium, copper and zinc - showed a pronounced increase of concentrations in canopy throughfall during the years 2000–2003, although this peak was not as drastic as for Fe, Cr and Zn. Outside this period and the following year 2004, zinc concentrations (annual medians) were only slightly higher – or even lower – in throughfall from the coniferous compared to the deciduous stand. This contrasts remarkably with the findings for the other trace elements investigated.

Table 47: Nickel concentration in canopy throughfall on the coniferous plot IP1.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1995	40	7	12	3.71	2.32	2.50	2.50	2.50	2.50	3.13	7.94	10.28
1996	38	4	2	5.75	4.06	1.25	1.25	3.09	4.66	7.89	12.72	16.25
1997	38	3	1	6.66	4.30	1.88	1.88	3.17	5.64	8.70	13.44	16.24
1998	38	1	2	7.06	6.19	0.75	1.39	2.81	4.71	11.48	16.87	24.50
1999	24	1	2	4.71	3.46	0.75	1.45	2.28	3.30	6.63	10.33	12.30
2000	24	1	0	66.74	46.50	0.75	4.20	28.76	68.57	104.1	127.7	154.56
2001	25	0	2	43.72	31.54	2.45	8.30	24.45	32.74	65.87	87.81	110.4
2002	25	1	0	46.31	22.03	1.91	18.94	34.70	48.90	55.60	70.36	93.50
2003	26	0	0	59.77	45.41	11.70	13.95	26.25	38.55	95.00	117.5	166.0
2004	20	5	1	1.56	0.96	n.d.	0.75	0.75	1.45	2.15	2.90	3.70
2005	21	4	2	1.03	0.55	n.d.	0.75	0.75	0.75	1.19	1.80	2.30
2006	22	3	1	1.46	1.05	n.d.	0.75	0.75	0.88	1.98	3.18	3.85
2007	24	2	1	2.15	1.98	–	n.d.	0.75	1.53	2.69	5.48	7.10
1995–2007	**349**	**48**	**26**	**9.49**	**12.23**	**n.d.**	**0.75**	**2.00**	**3.70**	**11.70**	**30.76**	**51.30**

unit: µg l^{-1}

Table 48: Nickel concentration in canopy throughfall on the deciduous plot IP2.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1997	39	3	0	7.06	5.26	1.88	1.88	3.15	5.51	8.32	16.88	19.86
1998	37	2	1	5.11	3.33	0.75	1.68	2.60	4.30	7.10	9.41	14.60
1999	23	1	4	4.05	2.98	0.75	1.15	2.02	2.70	5.30	8.40	10.70
2000	24	1	0	32.96	22.78	0.00	2.24	15.89	32.01	46.70	62.31	80.98
2001	25	1	1	24.73	15.53	2.86	5.98	14.24	22.74	32.78	43.94	66.96
2002	26	0	0	31.60	15.57	2.60	13.70	21.18	30.50	40.28	52.55	66.20
2003	25	1	0	22.82	13.11	4.40	6.24	9.60	23.20	33.90	40.28	44.10
2004	21	4	1	1.29	1.41	–	–	n.d.	0.75	1.74	2.90	5.00
2005	24	1	2	1.17	0.54	n.d.	0.75	0.75	1.06	1.55	1.88	2.10
2006	21	4	1	1.15	0.70	n.d.	0.00	0.75	1.21	1.45	1.78	2.53
2007	24	2	0	1.72	1.16	n.d.	0.23	1.02	1.52	2.31	3.14	4.24
1997–2007	**291**	**18**	**10**	**10.08**	**11.83**	**n.d.**	**0.75**	**1.71**	**4.30**	**15.86**	**29.30**	**44.70**

unit: µg l^{-1}

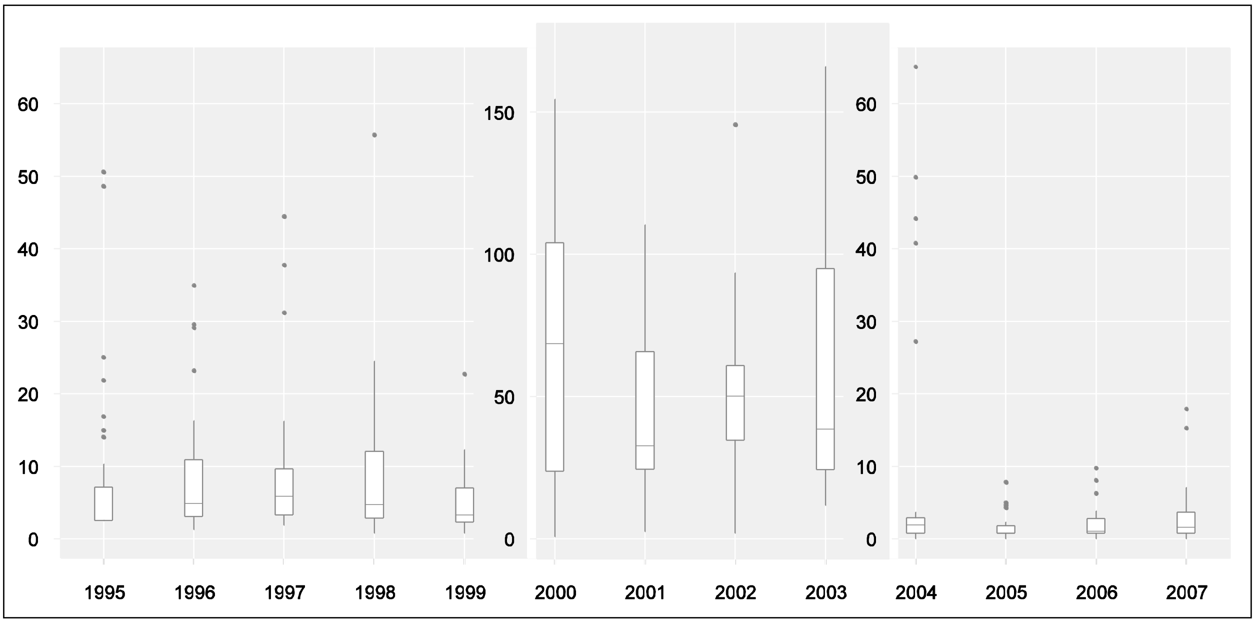


Figure 50: Nickel concentration [µg l^{-1}] in canopy throughfall on the coniferous plot IP1 (note reduced scale for years 2000–03); one value > 200 (933 from year 2000) not shown.

Table 49: Annual nickel loads from canopy throughfall.

	coniferous	deciduous
1994	213.8	
1995	60.47	
1996	98.27	148.3
1997	126.0	92.31
1998	101.9	49.96
1999	60.69	39.15
2000	1079	333.8
2001	525.7	272.9
2002	643.1	407.8
2003	665.2	237.7
2004	146.3	34.83
2005	19.09	10.51
2006	23.77	44.12
2007	55.86	22.93
2008	15.70	12.89

unit: g ha^{-1} a^{-1}; grey font: annual values including more than 35 days of interpolated data

4.4.3.9 Arsenic (As)

1995 was the only year with eight samples containing arsenic above the quantification limit of 0.25 µg l^{-1} with a maximum value of 1.02 µg l^{-1}.

4.4.3.10 Aluminium (Al)

Table 50: Aluminium concentration in canopy throughfall on the coniferous plot IP1.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1995	43	4	12	24.8	14.2	5.0	5.0	12.9	25.0	37.7	41.8	54.4
1996	40	2	2	23.5	14.8	5.0	5.0	12.7	20.9	32.6	41.5	63.6
1997	38	3	1	21.4	8.4	5.5	11.3	17.0	20.7	26.5	33.8	39.7
1998	37	2	2	57.0	41.1	10.3	20.1	30.3	42.8	87.1	111.2	180.0
1999	24	1	2	34.8	23.4	10.1	11.9	19.1	26.0	50.3	68.7	98.9
2000	23	2	0	72.7	35.0	8.5	26.4	52.1	70.4	94.9	120.6	132.4
2001	25	0	2	104.6	61.0	8.5	22.7	70.9	95.3	138.1	189.1	217.3
2002	25	1	0	68.1	39.7	5.2	24.1	40.5	57.2	97.8	128.6	148.0
2003	26	0	0	59.0	36.8	9.0	12.7	31.7	53.0	87.9	112.0	130.0
2004	23	2	1	17.8	8.7	2.8	7.8	13.2	16.6	23.0	25.3	41.5
2005	22	3	2	25.5	12.9	7.1	11.1	18.5	21.6	31.3	38.6	64.2
2006	24	1	1	32.8	10.9	14.7	16.9	26.7	33.5	40.5	46.6	50.4
2007	24	2	1	14.4	6.5	3.4	6.5	9.1	14.5	19.3	23.2	26.7
1995–2007	**360**	**37**	**26**	**34.8**	**25.3**	**2.8**	**10.1**	**16.9**	**27.1**	**44.8**	**77.8**	**109.0**

unit: µg l^{-1}

Table 51: Aluminium concentration in canopy throughfall on the deciduous plot IP2.

year	obs	out	na	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1997	39	3	0	16.6	7.2	3.8	9.6	11.3	15.4	20.3	26.7	36.9
1998	34	5	1	29.2	18.0	7.2	11.5	14.5	27.2	36.9	52.3	73.6
1999	22	2	4	22.4	12.0	6.7	9.2	11.7	20.7	31.5	37.3	47.7
2000	25	0	0	42.3	21.2	6.5	14.6	26.9	43.5	56.2	70.2	80.0
2001	23	3	1	54.7	34.8	7.8	15.4	38.7	47.9	64.3	86.3	144.8
2002	26	0	0	44.3	30.0	7.8	15.8	19.6	36.6	57.2	91.7	109.0
2003	23	3	0	20.3	11.5	5.4	8.2	11.7	17.1	29.0	36.5	44.7
2004	24	1	1	10.5	4.3	3.1	5.7	8.6	9.6	12.3	16.9	19.4
2005	24	1	2	19.2	8.5	7.9	9.2	11.2	17.9	25.3	30.0	37.0
2006	22	3	1	23.0	6.9	12.1	13.7	17.8	24.0	27.6	29.4	37.0
2007	22	4	0	10.7	4.7	3.5	5.8	7.4	10.4	12.8	14.7	24.2
1997–2007	**284**	**25**	**10**	**24.6**	**16.6**	**3.1**	**9.0**	**11.8**	**19.4**	**31.1**	**50.0**	**75.9**

unit: µg l^{-1}

Aluminium concentrations showed a transient peak during the period 2000–2003 although this temporary increase was far less pronounced than the increases observed for other trace elements (Fe, Cr, Cu, Zn, Ni): Figure 51. Again, concentrations in throughfall from the coniferous stand were (1.2–3.1 times) higher than on the deciduous plot (Table 50, Table 51).

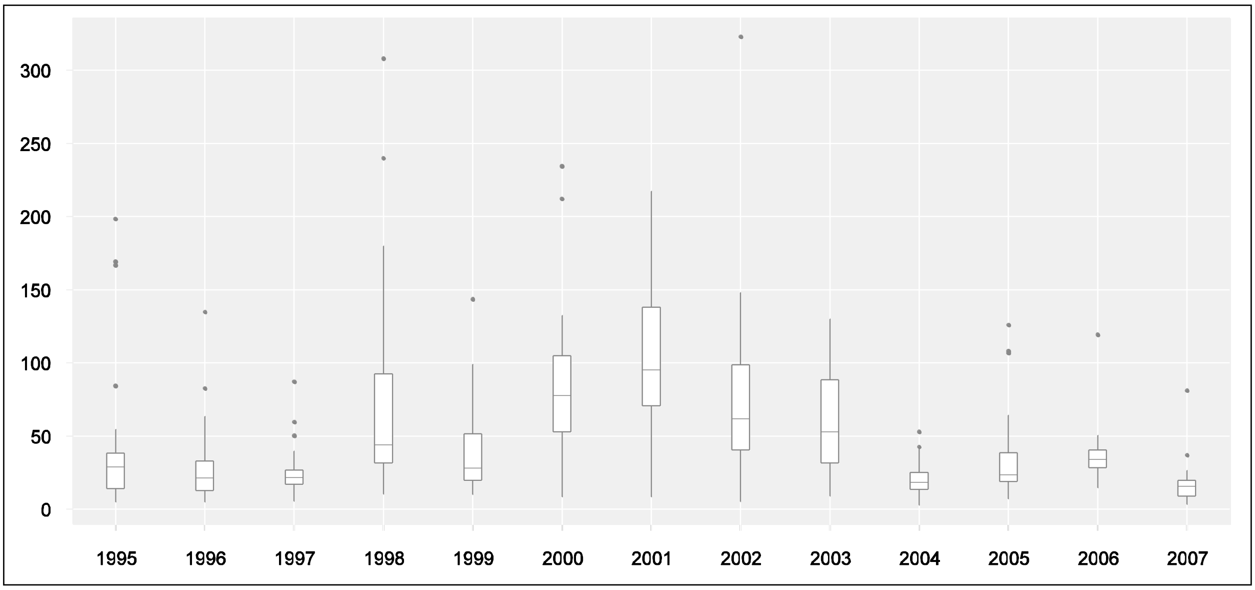


Figure 51: Aluminium concentration [µg l^{-1}] in canopy throughfall on the coniferous plot IP1.

Table 52: Annual aluminium loads from canopy throughfall.

	coniferous	deciduous
1994	662.2	
1995	361.2	
1996	300.5	252.8
1997	344.3	220.5
1998	1093	364.6
1999	429.3	212.2
2000	900.2	396.2
2001	1330	734.0
2002	1084	606.2
2003	584.4	221.1
2004	216.0	112.4
2005	388.1	185.9
2006	453.4	295.2
2007	173.6	245.7
2008	136.7	73.94

unit: g ha^{-1} a^{-1}; grey font: annual values including more than 35 days of interpolated data

4.4.3.11 Mercury (Hg)

Mercury was only detected in samples from 1995 but levels did not exceed the quantification limit of 0.5 mg l^{-1}.

4.4.4 Litterfall

4.4.4.1 Manganese (Mn)

Manganese concentrations in litterfall of the coniferous (Norway spruce) stand exceeded those of the broadleaf (mainly European beech) stand by one order of magnitude (Table 53, Table 54).

Table 53: Manganese concentration in litterfall on the coniferous plot IP1.

year	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1994	301.8	100.4	184.7	195.3	216.8	291.3	367.5	434.8	449.3
1995	266.6	73.7	183.4	195.7	216.6	260.8	292.9	343.4	389.4
1996	245.8	118.4	94.3	121.4	164.7	239.4	325.6	376.7	407.9
1997	339.9	61.1	270.8	270.8	301.5	333.0	362.3	397.1	448.2
1998	278.3	149.7	24.4	129.9	246.5	291.1	337.3	413.9	478.7
1999	256.7	60.3	198.8	213.2	232.1	246.1	247.9	311.0	373.6
2000	292.3	33.8	246.2	250.5	266.4	305.3	312.0	321.1	329.5
2001	255.6	93.3	178.5	178.8	191.9	235.8	265.9	352.3	430.4
2002	324.8	94.9	242.9	249.3	257.9	290.9	363.9	434.1	488.8
2003	279.8	80.3	142.5	190.0	248.6	280.7	324.8	355.8	407.6
2004	203.7	110.5	50.3	73.8	141.8	223.9	241.0	303.3	386.1
2005	210.7	91.8	112.0	123.3	147.4	205.6	234.2	303.1	369.1
2006	231.6	90.0	130.0	147.1	170.4	222.0	268.1	325.6	378.6
2007	284.2	90.7	224.3	229.9	238.5	252.7	270.1	370.1	466.1

unit: mg kg^{-1} d.m.

Table 54: Manganese concentration in litterfall on the deciduous plot IP2.

year	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1997	24.66	4.60	15.88	20.02	22.98	25.55	27.99	28.59	29.23
1998	80.95	121.6	29.35	29.41	29.59	30.41	35.41	183.0	329.1
1999	21.13	6.32	14.19	14.53	16.19	21.38	23.46	27.49	31.24
2000	27.23	2.89	22.93	24.38	26.00	27.17	28.60	30.14	31.44
2001	20.46	4.68	12.40	15.79	19.30	20.67	23.50	24.92	25.73
2002	27.74	11.13	19.01	19.85	21.38	23.97	28.32	39.40	49.21
2003	26.42	6.89	18.47	18.93	21.05	25.77	31.13	33.33	38.22
2004	27.65	5.51	21.48	22.17	22.97	27.32	31.32	33.51	36.16
2005	22.78	3.16	17.62	18.93	21.15	24.07	24.79	25.34	25.71
2006	21.28	9.97	12.25	14.12	16.35	19.39	20.93	30.02	42.73
2007	24.34	4.95	20.62	20.65	20.70	21.79	27.87	30.58	31.60

unit: mg kg^{-1} d.m.

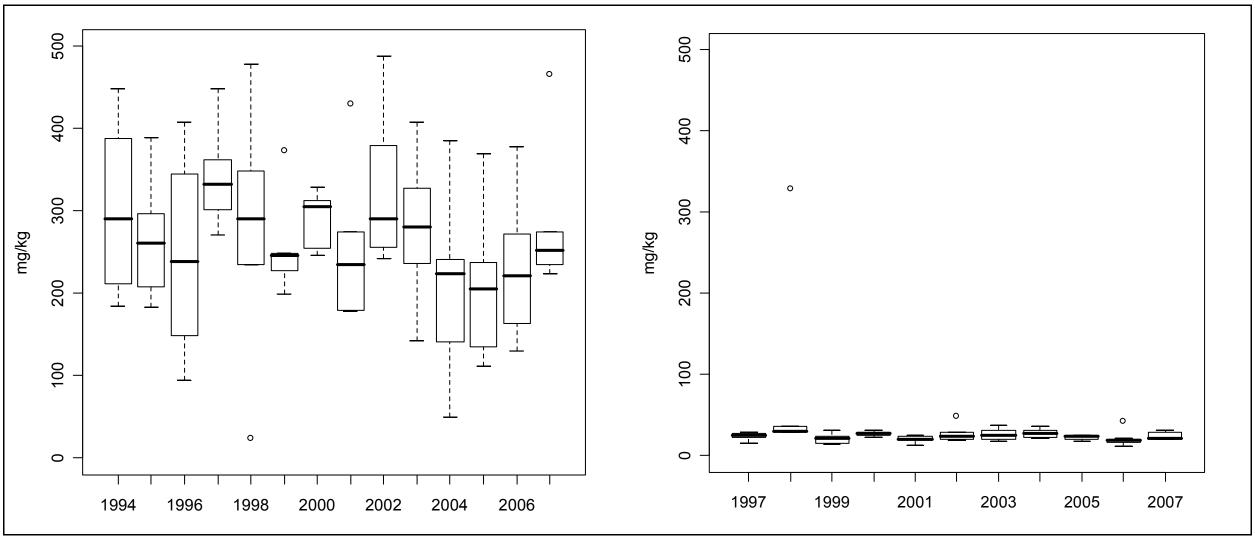


Figure 52: Manganese concentration [mg kg^{-1}] in litterfall of the Norway spruce stand IP1 (left) and the broadleaf stand IP2 (right).

4.4.4.2 Cadmium (Cd)

Cadmium concentrations in coniferous litterfall were higher than in the deciduous stand's litter (Table 55, Table 56), although the difference was not as pronounced as observed with manganese (p. 65 f).

Table 55: Cadmium concentration in litterfall on the coniferous plot IP1.

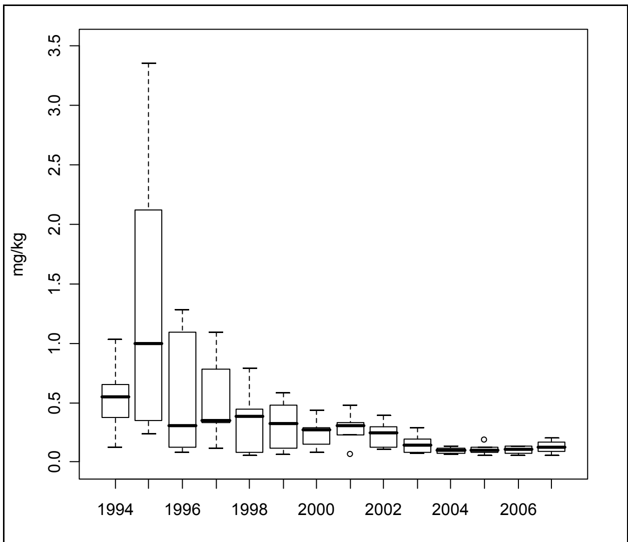
year	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1994	538.5	272.2	126.0	233.3	421.9	549.3	633.3	788.0	1036
1995	1342	1194	237.6	293.8	479.6	996.9	1870	2736	3355
1996	533.8	517.8	80.26	104.6	166.5	310.2	905.4	1186	1279
1997	542.2	364.5	118.9	240.3	336.4	351.5	780.4	1026	1092
1998	356.1	271.6	54.00	66.96	155.0	382.9	428.1	618.4	794.6
1999	317.1	199.9	67.63	93.89	164.1	327.2	446.6	530.1	584.4
2000	252.6	124.3	82.35	116.3	179.9	275.4	289.9	366.2	439.9
2001	285.3	135.1	68.14	147.4	242.4	303.5	327.5	404.9	479.1
2002	237.3	108.4	106.2	117.8	155.8	244.6	290.2	349.5	396.8
2003	149.6	76.85	72.06	72.11	80.96	143.2	190.8	233.5	287.9
2004	96.97	25.92	64.75	69.78	77.42	98.71	114.8	129.7	131.0
2005	109.1	45.68	53.65	68.71	87.06	101.7	120.3	156.8	188.6
2006	102.8	31.71	58.24	63.99	80.16	111.8	126.0	132.6	134.6
2007	127.7	55.12	52.01	71.90	99.07	122.5	158.3	188.6	207.4

*note unit: **µg** kg^{-1} d.m.*

Table 56: Cadmium concentration in litterfall of the deciduous plot IP2.

year	mean	sd	min	P10	P25	med	P75	P90	max
1997	346.0	292.2	41.48	73.61	158.8	277.7	502.8	747.3	779.5
1998	772.3	921.2	215.5	222.8	265.7	427.8	659.5	1666	2614
1999	318.1	224.3	33.44	37.70	119.4	413.0	492.2	503.5	508.7
2000	249.8	185.4	48.60	57.01	93.16	250.1	353.3	442.2	521.2
2001	185.7	133.5	60.50	61.61	75.72	172.0	238.6	323.5	405.2
2002	178.8	91.16	98.92	105.7	117.1	140.6	227.0	290.2	327.9
2003	124.2	73.89	36.42	38.94	58.81	125.9	195.7	201.1	206.9
2004	91.34	40.62	31.68	50.62	64.35	94.91	118.4	136.9	147.3
2005	85.59	38.61	40.05	43.54	55.82	90.83	100.0	122.4	144.5
2006	89.37	66.31	26.00	34.68	47.55	60.80	112.7	161.6	218.2
2007	68.76	36.07	26.82	27.82	36.08	74.00	98.18	104.5	108.0

*note unit: **µg** kg^{-1} d.m.*



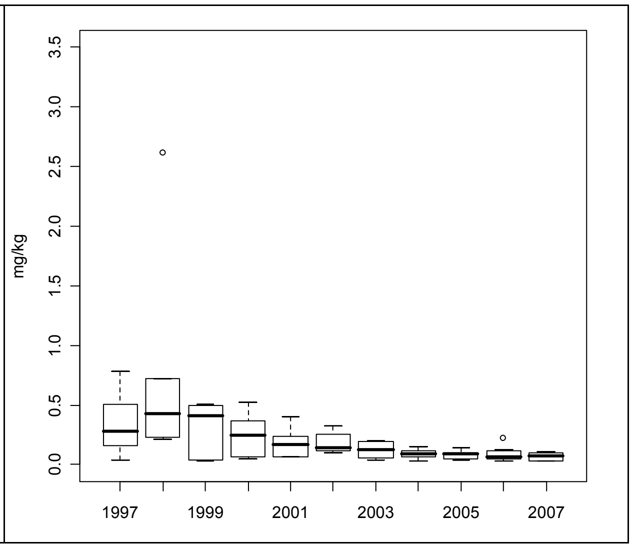


Figure 53: Cadmium concentration [mg kg^{-1}] in litterfall of the Norway spruce stand IP1 (left) and the deciduous stand IP2 (right).

4.4.4.3 Lead (Pb)

In contrast to manganese and cadmium which were highly mobile along the transfer path from soil to leaves, lead concentrations in litterfall were similar in the coniferous and the broadleaf stand (Table 57, Table 58). Litterfall from the coniferous stand showed a pronounced decline from 1994 to 2007 (Figure 54).

Table 57: Lead concentration in litterfall of the coniferous plot IP1.

year	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1994	10.87	7.44	2.44	3.32	5.65	9.16	15.59	19.45	23.60
1995	8.63	4.14	4.13	4.87	5.76	7.64	11.10	13.38	14.99
1996	6.09	3.71	2.69	2.74	2.94	5.67	8.00	9.86	11.72
1997	8.34	3.67	3.79	5.40	6.48	7.07	9.71	12.33	15.16
1998	8.34	5.01	3.02	3.03	3.80	8.19	12.54	13.82	14.34
1999	7.51	4.80	1.37	1.98	3.72	8.00	11.27	12.56	13.05
2000	6.61	3.76	1.64	2.62	4.21	6.74	8.40	10.47	12.21
2001	6.88	3.43	1.66	3.10	5.18	7.31	8.53	10.21	11.55
2002	6.64	3.24	2.83	3.83	4.95	5.46	9.34	10.62	10.64
2003	5.28	3.74	1.23	1.58	1.90	5.04	7.07	10.33	11.22
2004	3.04	1.83	1.03	1.17	1.51	3.18	4.30	5.39	5.44
2005	4.91	3.16	1.96	2.66	3.44	3.69	5.40	8.38	10.79
2006	3.91	1.73	1.54	1.82	2.64	4.37	5.00	5.54	5.92
2007	3.83	1.90	1.68	2.14	2.68	3.19	5.41	6.16	6.25

unit: mg kg^{-1} d.m.

Table 58: Lead concentration in litterfall of the deciduous plot IP2.

year	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1997	7.662	3.784	2.369	3.915	5.972	7.081	9.141	12.09	13.95
1998	11.34	5.268	6.628	6.736	7.014	9.753	15.04	17.54	19.03
1999	6.189	5.061	1.399	1.482	2.323	5.330	8.004	11.75	14.86
2000	6.099	4.421	1.048	1.363	2.727	6.488	7.638	10.45	13.08
2001	6.664	4.307	2.409	2.507	3.390	6.344	7.895	11.14	14.07
2002	7.897	3.914	2.911	3.864	5.179	7.611	10.83	12.22	12.97
2003	6.094	4.260	1.127	1.256	1.600	6.947	8.903	11.07	11.63
2004	8.288	5.506	1.573	3.698	5.528	6.863	10.59	15.48	17.34
2005	7.063	3.613	1.818	3.034	4.962	7.291	9.542	10.86	11.50
2006	6.652	5.277	1.679	2.902	3.781	5.771	6.900	11.80	17.75
2007	4.710	3.054	1.259	1.542	2.273	4.810	6.184	7.779	9.313

unit: mg kg^{-1} d.m.

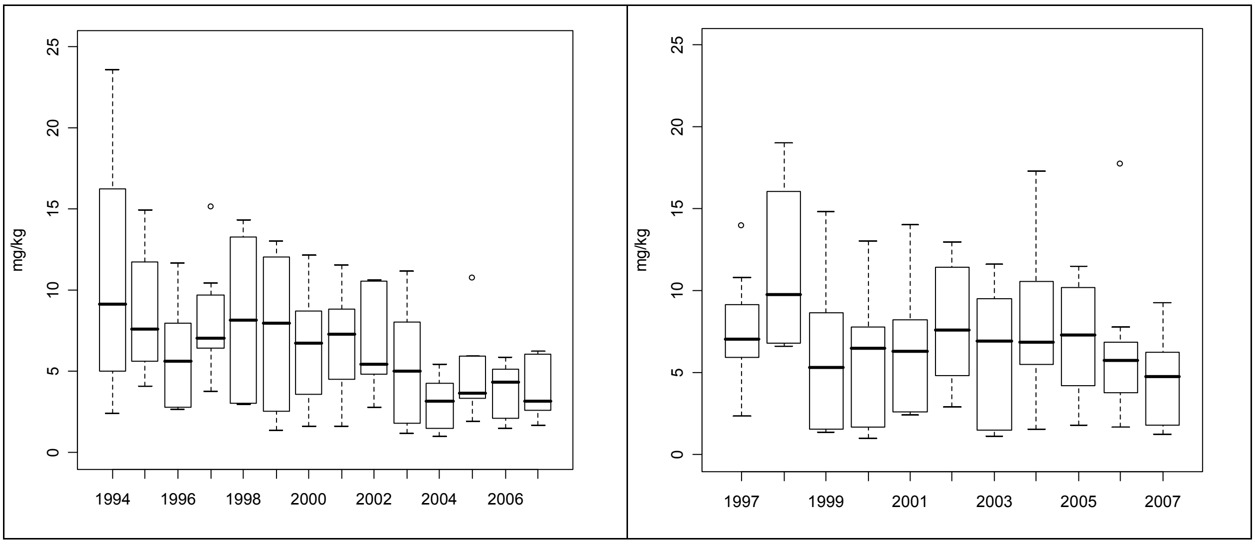


Figure 54: Lead concentration [mg kg^{-1}] in litterfall of the Norway spruce stand IP1 (left) and the deciduous stand IP2 (right).

4.4.4.4 Copper (Cu)

Similar to the case of lead, copper concentrations in litterfall did not show sizeable differences between broadleaf and coniferous stands (Table 59, Table 60). Remarkably, the 1999–2002 episode of increased copper and zinc inputs, mirrored in bulk/wet deposition (pages 25, 40, 58) and stand throughfall, did not lead to an increased copper (orzZinc) content in litterfall.

Table 59: Copper concentration in litterfall of the coniferous plot IP1.

year	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1994	3.883	1.549	2.072	2.443	2.685	3.805	4.465	5.465	6.869
1995	6.005	1.051	4.300	5.041	5.816	6.052	6.250	6.921	7.571
1996	6.478	3.146	4.385	4.438	4.608	5.335	6.423	9.660	12.66
1997	4.809	0.810	3.697	3.862	4.095	5.292	5.487	5.511	5.511
1998	5.618	1.200	3.240	4.449	5.712	6.046	6.276	6.361	6.425
1999	5.563	0.771	4.552	4.618	4.932	5.833	6.041	6.240	6.420
2000	5.475	1.327	3.647	4.098	4.743	5.473	6.087	6.855	7.468
2001	5.297	1.409	2.917	3.808	4.779	5.490	6.356	6.594	6.698
2002	5.014	0.836	3.779	4.046	4.487	5.227	5.481	5.769	6.045
2003	6.291	1.663	3.900	4.265	4.861	6.892	7.213	7.733	8.729
2004	5.590	2.170	3.667	4.048	4.351	5.200	5.684	7.655	10.19
2005	6.983	3.181	4.292	4.885	5.524	6.001	6.764	10.06	13.22
2006	5.177	1.091	3.505	4.140	4.792	5.028	5.945	6.363	6.537
2007	5.745	1.533	3.004	4.129	5.389	6.045	6.608	7.059	7.407

unit: mg kg^{-1} d.m.

Table 60: Copper concentration in litterfall of the deciduous plot IP2.

year	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1997	5.509	1.230	3.865	4.209	4.727	5.027	6.604	6.906	7.009
1998	7.556	1.048	6.692	6.755	6.834	7.093	8.070	8.820	9.313
1999	5.953	1.150	4.262	4.552	5.144	6.391	6.759	6.916	7.064
2000	6.404	1.576	3.942	4.632	5.566	6.609	7.691	7.970	7.993
2001	6.055	1.620	3.913	4.460	5.095	5.914	7.000	7.791	8.406
2002	7.300	3.649	5.322	5.376	5.436	5.837	6.588	10.69	14.66
2003	6.834	1.829	4.516	4.700	5.583	6.726	8.013	8.735	9.897
2004	7.234	1.223	5.618	5.669	6.202	7.929	8.013	8.290	8.661
2005	8.720	2.553	5.185	6.389	7.611	8.602	9.571	11.17	12.76
2006	6.778	2.235	4.587	4.595	4.992	6.888	7.525	9.014	10.93
2007	6.813	2.439	4.323	4.766	5.422	6.368	7.150	9.306	11.30

unit: mg kg^{-1} d.m.

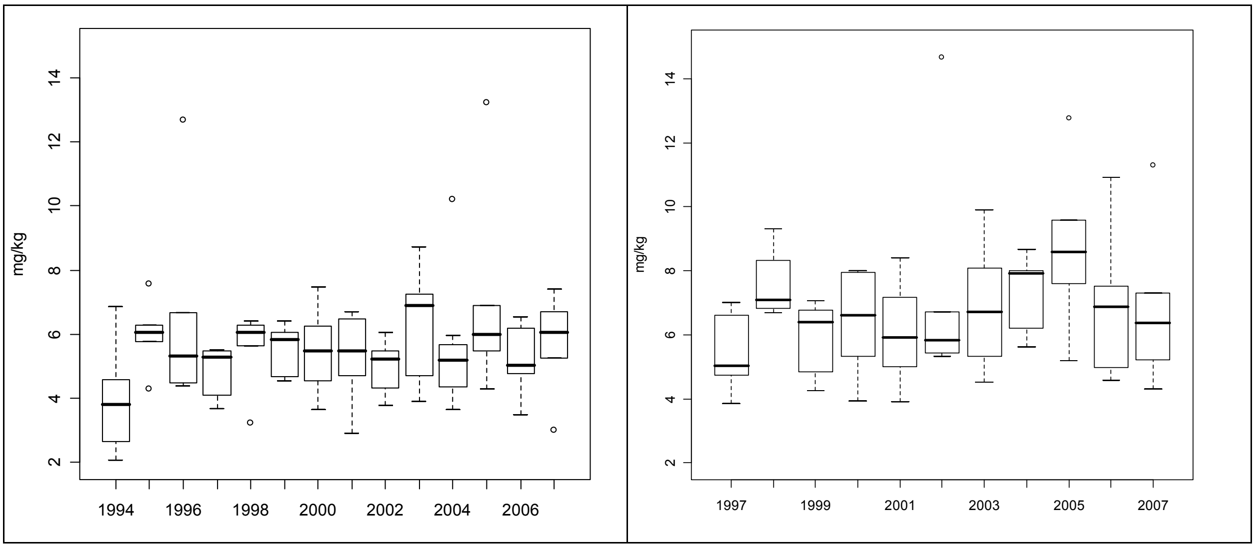


Figure 55: Copper concentration [mg kg^{-1}] in litterfall of the Norway spruce stand IP1 and the deciduous stand IP2 (right).

4.4.4.5 Zinc (Zn)

Zinc concentrations in litterfall were comparable between the coniferous and the broadleaf stand (Table 61, Table 62). As mentioned earlier, the 1999–2002 episode of increased copper and zinc inputs and stand throughfall (pages 27, 42, 60) was not reflected by a corresponding increase in litterfall zinc content.

Table 61: Zinc concentration in litterfall of the coniferous plot IP1.

year	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1994	118.5	73.20	49.94	65.29	83.11	88.92	125.7	232.6	241.2
1995	166.0	101.5	52.65	67.48	92.15	153.7	218.1	277.0	325.1
1996	101.6	63.75	44.40	47.31	54.14	75.66	156.0	181.8	184.0
1997	102.3	42.00	47.92	62.39	79.05	86.07	131.9	157.3	159.9
1998	95.05	52.95	31.25	38.00	55.40	94.05	127.2	153.1	170.2
1999	101.3	58.69	34.00	38.20	56.84	101.8	129.4	164.0	190.0
2000	93.11	42.81	39.42	46.85	65.01	98.06	106.3	134.4	160.0
2001	88.65	29.99	42.58	59.81	77.58	88.52	102.2	117.6	131.6
2002	99.12	30.40	58.87	62.36	75.71	107.9	116.2	127.1	136.1
2003	59.44	22.43	33.31	34.56	42.64	56.78	76.91	85.19	90.66
2004	46.74	13.92	24.79	34.23	41.54	43.24	53.60	62.00	68.85
2005	49.32	7.00	40.87	42.24	44.67	48.33	53.76	57.40	59.38
2006	47.70	7.27	36.70	40.28	44.45	47.20	53.70	55.63	55.72
2007	48.48	11.52	33.96	35.52	39.84	50.20	53.94	59.73	64.98

unit: mg kg^{-1} d.m.

Table 62 Zinc concentration in litterfall of the deciduous plot IP2.

year	mean	sd	min	P_{10}	P_{25}	med	P_{75}	P_{90}	max
1997	88.61	44.09	32.98	43.21	54.28	88.01	118.5	137.8	153.7
1998	222.5	246.4	75.37	78.48	87.55	117.3	205.8	471.7	712.0
1999	102.5	58.62	27.07	29.50	52.05	123.7	149.1	154.3	154.7
2000	107.7	71.46	31.44	34.68	47.88	109.2	142.5	179.3	215.5
2001	69.87	37.65	35.65	37.75	40.99	58.81	89.76	113.0	130.8
2002	95.70	58.98	47.52	54.18	62.41	71.47	106.5	161.4	206.2
2003	58.99	27.69	24.32	24.99	34.57	62.95	79.41	89.94	94.12
2004	64.63	18.36	32.72	41.95	56.20	68.17	78.04	81.91	83.04
2005	54.49	14.64	32.80	40.14	48.58	53.02	62.73	70.31	75.03
2006	69.91	76.21	29.15	30.46	32.86	35.11	59.89	138.1	239.6
2007	56.76	41.36	25.85	27.46	29.51	36.45	73.39	106.4	128.9

unit: mg kg^{-1} d.m.

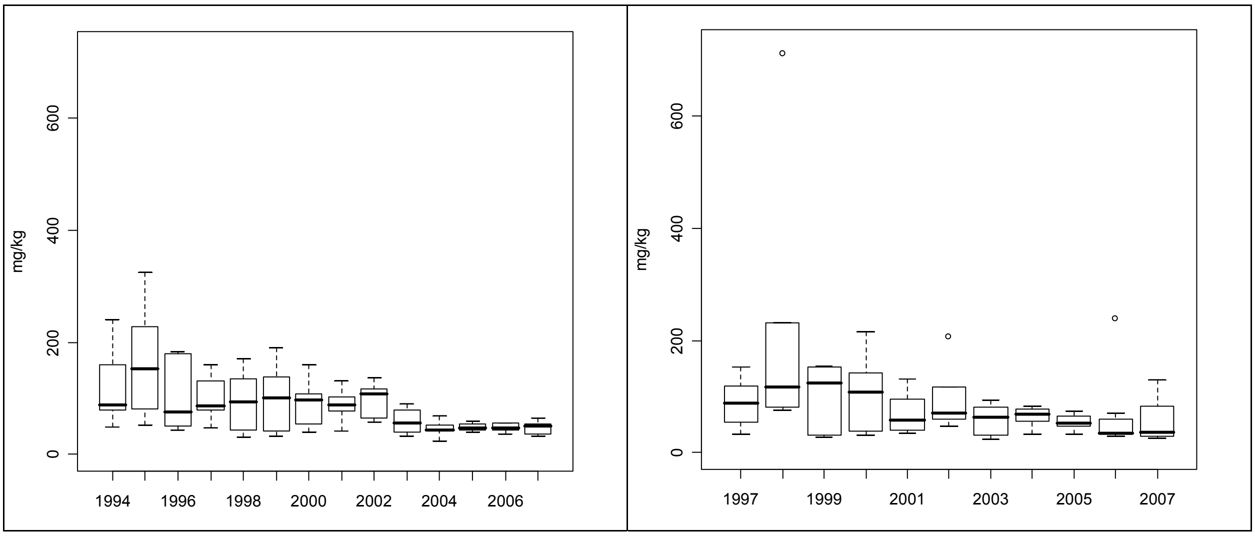


Figure 56: Zinc concentration [mg kg^{-1}] in litterfall of the Norway spruce stand IP1 (left) and the deciduous stand IP2 (right).

5 METHODS

5.1 Site description

The study site 'Zöbelboden', which is part of International Cooperation Programmes (ICP) of the 'Convention on Long-Range Transboundary Air Pollution' (CLRTAP) is located in the Northern limestone Alps (latitude: 47° 50' 30'', longitude 14° 26' 30'';
http://www.umweltbundesamt.at/en/umweltschutz/oekosystem/im/)

The 90 hectare study area forms part of the "Kalkalpen" national park in the federal province of Upper Austria. The bed rock consists of different carbonates, mainly Norian dolomite and limestone. Based on its geomorphology, the site can be divided into a plateau at 850–956 m a. s. l. and slopes forming a natural catchment (550–850 m, inclination 30–60 °, exposure E-NE-N-NW). The average annual temperature is 7.2 °C. Monthly temperature extremes at 900 m a. s. l. are –1 °C (January) and 15.5 °C (August). Annual rainfall ranges from 1500 to 1800 mm. Monthly precipitation ranges from 75 mm to 182 mm in February and July, respectively. Snowfall occurs between October and May with snow cover lasting about four months. The mixed forests found on the slopes are composed of European beech (*Fagus sylvatica*) as dominant tree species, Norway spruce (*Picea abies*), maple (*Acer pseudoplatanus*) and ash (*Fraxinus excelsior*). These forests are considered close to natural vegetation. By contrast, the tree species composition of the forest at the plateau was changed, after a clearcut in 1910, into a pure Norway spruce (*Picea abies*) plantation. Since 1992 forest management has been restricted to single tree harvest after bark beetle infestations (UMWELTBUNDESAMT, 2007). As the site was not covered with ice during the Würm glaciations, a more or less continuous layer of relict clayey soil material has remained on the plateau (KATZENSTEINER, 2000).

5.2 Sampling design

Samples were taken at a clearing area ("Wildwiese") and two instrumented plots ("Intensive Plots"). Intensive plot 1 (IP1) is located on the plateau with Chromic Cambisols and Hydromorphic Stagnosols. Intensive plot 2 (IP2) is situated on a slope and dominated by Lithic and Rendzic Leptosols (FAO/ISRIC/ISSS, 2006). IP1 is dominated by Norway spruce whereas a mixed mountain forest with European beech as the dominant species, Norway spruce, maple, and ash covers IP2.

Gross precipitation was collected in the clearing area with five to ten bulk collectors (∅ = 20 cm). Throughfall at each Intensive Plot was measured with 15 regularly spaced bulk deposition samplers (∅ = 20 cm). Since 2006, 17 samplers have been used at IP1.

Litter was collected at each Intensive Plot with 15 regularly spaced litterfall samplers (each 70 × 70 cm). Since 2006, 17 samplers have been used at IP1. Sampling was conducted monthly (± one week) during the snow free season (generally May to October) from 1993 to 2007 at Intensive Plot 1, and from 1997 to 2007 at Intensive Plot 2.

5.3 Sample preparation and chemical analysis

Aqueous samples were pooled and stored in a cool place at 4 °C. Successive weekly samples were mixed (volume weighted) biweekly, filtered (0.45 µm; Millipor Isopore™, USA) and acidified with 1 ml of HNO_3 (65%) before being transported to the laboratory. Mn, Cr, Cu, Zn, Ni and Al were measured with inductively coupled plasma optic emission spectrometry (ICP-OES, 1993–1995: Jobin-Yvon 70+, Fr; 1996–1997: Perkin-Elmer Optima 3000 XL, USA) and inductively coupled plasma mass spectrometry (ICP-MS, 1998–2005: Perkin-Elmer ELAN 6000, USA; 2005–2008: Perkin-Elmer ELAN DRC II, USA). Cd and Pb concentrations were determined with graphite furnace atomic absorption spectrometry (GF-AAS, 1993–1996: Perkin-Elmer 5100 PC with HGA, USA; 1997–1997: Perkin-Elmer SIMAA 6000 with THGA, USA) and inductively coupled plasma mass spectrometry (ICP-MS, 1998–2005: Perkin-Elmer ELAN 6000, USA; 2005-2008: Perkin-Elmer ELAN DRC II, USA). As was measured with hydride generated atomic absorption spectrometry (HG-AAS, 1993-1995: Perkin-Elmer 1100B with FIAS, USA). Hg was measured with cold vapour atomic absorption spectrometry (CV-AAS, 1993–1995: Perkin-Elmer 1100B with MHS20, USA).

All litter samples from each Intensive Plot were pooled, oven-dried at 30 °C until the weight was constant and ground with an ultra-centrifugal grinding mill (ZM1, Retsch, D). A subsample of 2 g was oven-dried at 105 °C to determine the dry mass at 105 °C. Another subsample of 1 g was digested (HNO_3/$HClO_4$) in glass vessels on a heating block (SMA 20 A, Gerhardt, D). Subsequent determination of Mn, Cu and Zn was carried out with inductively coupled plasma optic emission spectrometry (ICP-OES, 1993–1994: Jobin-Yvon 70+, Fr; 1994–1999: Perkin-Elmer Optima 3000 XL, USA; 1999–2007: Perkin-Elmer Optima 3000 DV, USA). Pb was determined with inductively coupled plasma optic emission spectrometry (ICP-OES, 1993–1994: Jobin-Yvon 70+, Fr; 1994–1996: Perkin-Elmer Optima 3000 XL, USA) and graphite furnace atomic absorption spectrometry (GF-AAS, 1997-2003: Perkin-Elmer SIMAA 6000 with THGA, USA; 2004–2007: Perkin-Elmer AA800, USA). Cd was determined with graphite furnace atomic absorption spectrometry (GF-AAS, 1993–1996: Perkin-Elmer 5100 with HGA600, USA; 1997–2003: Perkin-Elmer SIMAA 6000 with THGA, USA; 2004-2007: Perkin-Elmer AA800, USA).

5.4 Calculation of concentrations

5.4.1 Treatment of very low values

Concentrations below the analytical limit of detection were treated as zero. Values above the detection limit but below the limit for (accurate) quantification were replaced with 0.75 times the quantification limit for the subsequent calculations.

5.4.2 Treatment of very high values

Values whose distance from the P_{25}–P_{75} interval (= “box” in boxplots) exceeded 1.5 times this interval’s span (= “boxlength”) were considered outliers and excluded from the calculation of descriptive statistics. It should be noted that the number of outliers in a pluriannual sample will *not* equal the cumulative count of outliers returned by a yearwise inspection.

Descriptive statistics were calculated after the removal of outliers from the sample. Statistics for observation periods of several years can thus deviate from annual statistics. This might, at first sight, confuse the reader – especially when the maximum of a whole observation period exceeds that of any single year.

Yearly annual statistics were only calculated for unfragmented data sets, i.e. where sampling had been maintained over the entire year.

5.5 Calculation of loads

Loads were calculated by multiplying the measured liquid concentrations by the corresponding sample volume and dividing by the effective sampling area. Loads of each sampling interval were then aggregated by calendar year to give the annual load.

5.5.1 Treatment of very high values

In contrast to the statistical processing of concentrations, observations of extreme loads were included in the calculations of annual statistics: it was assumed that such observations indeed reflected events of extraordinarily high deposition and were not artifacts from manipulation or chemical analysis of the sampler content.

5.5.2 Treatment of missing values

To compensate for missing sampling periods, the calculated annual load was divided by the effective sampling duration per year and multiplied by 365 or 366 (leap years). Calculated annual loads of which more than one tenth (30 days) had to be interpolated are printed in grey font.

5.6 Element composition of deposition fluxes

The element composition was illustrated by taking the median of the annual median concentrations of each element, omitting the years 2000–03, during which a number of elements reached unusually high concentrations which probably were caused by industrial sources in the region. Each value was expressed as a fraction of the total of the nine trace elements considered.

6 LITERATURVERZEICHNIS

BAUER, H.; SMIDT, S.; STOPPER, S.; HERMAN, F.; PUXBAUM, H. (2008): Schwermetalleinträge in den Nordtiroler Kalkalpen. Austrian J. For. Sci. 125(2):103–120.

BUNDESMINISTERIUM FÜR UMWELT, NATURSCHUTZ UND REAKTORSICHERHEIT (2002): Technische Anleitung zur Reinhaltung der Luft – TA Luft. http://www.bmu.de/files/pdfs/allgemein/application/pdf/taluft.pdf

EEA (2008): Annual European Community LRTAP Convention emission inventory report 1990-2006. http://www.eea.europa.eu/publications/technical_report_2008_7

FAO/ISRIC/ISSS, 2006. World reference base for soil resources, in: FAO (Ed.), World soil resources reports, 2nd ed. FAO, Rome, p. 128.

HERCKES, P; MIRABEL, P; WORTHAM, H. (2002): Cloud water deposition at a high-elevation site in the Vosges Mountains (France). *Sci Tot Env.* 296:59–75.

KATZENSTEINER, K. (2000): Water and Nutrient Household of Forest Ecosystems in the Northern Limestone Alps. Forstliche Schriftenreihe 15:159.

MSC-E (2008): EMEP modelled deposition data. http://www.msceast.org/countries/Austria/index.html

MSC-E (2008): Heavy Metals: Transboundary Pollution of the Environment. EMEP Status Report 2/2008, http://www.msceast.org/reps/2_2008.zip

NEAL, C.; RYLAND, G. P.; CONWAY, T.; JEFFERY, H. A.; NEAL, M.; ROBSON, A. J., SMITH, C. J., WALLS, J., BHARDWAJ, C. L. (1994): Interception of chemicals at a forest edge for a rural low-lying site at Black Wood, Hampshire, Southern England. Sci. Tot. Env. 142:127–141.

RADEMACHER, P. (2003): Atmospheric Heavy Metals and Forest Ecosystems. Federal Research Centre for Forestry and Forest Products. Work Report. 2003. http://bfafh.de/bibl/pdf/i_03_12.pdf

SCHWEIZERISCHER BUNDESRAT. Luftreinhalte-Verordnung vom 16. Dezember 1985 (Stand am 1. Januar 2009). 1985, S. 89. http://www.admin.ch/ch/d/sr/8/814.318.142.1.de.pdf

SMIDT, S.; HERMAN, F. (2004): Evaluation of air pollution-related risks for Austrian mountain forests. Env Poll. 130: 99–112.

SMIDT, S; HERMAN, F. (2007): Blei- und Cadmiumeinträge mit dem Nebel. *Forstzeitung* 118(2): 32–33.

TESAR, M.; FISAK, J.; SIR, M; FOTTOVA, D. (2004) Time and space variability of the occult precipitation in the selected mountainous and urban areas of the Czech Republik. The Third International Conference on Fog, Fog Collection and Dew, Pretoria, 11–15 October 2004: Proceedings. http://www.up.ac.za/academic/geog/meteo/EVENTS/fogdew2003/PAPERS/C42.pdf.

UMWELTBUNDESAMT (2007): Dirnböck, T.; Willner, W.; Türk, R.: Effects of Nitrogen and Sulphur Deposition on Forests and Forest Biodiversity. Report, REP-0077. Umweltbundesamt, Wien.

UMWELTBUNDESAMT (2008): Spangl, W.; Nagl, C.; Moosmann, L.: Jahresbericht der Luftgütemessungen in Österreich 2007. Report, REP-0153. Umweltbundesamt, Wien 2008.

UKONMAANAHO, L.; STARR, M.; HIRVI, J.-P.; KOKKO, A.; LAHERMO, P.; MANNIO, J.; PAUKOLA, T.; RUOHO-AIROLA, T.; TANSKANEN, H. (1998): Heavy metal concentrations in various aqueous and biotic media in Finnish Integrated Monitoring catchments. Boreal Environment Research 3:235–249.
http://www.borenv.net/BER/pdfs/ber3/ber3-235-249.pdf

UKONMAANAHO, L.; STARR, M.; MANNIO, J.; RUOHO-AIROLA, T. (2001): Heavy metal budgets for two headwater forest catchments in background areas in Finland. Environ. Poll. 114:63–75.

ULRICH B, MAYER R, MATZNER, E. (1986): Vorräte und Flüsse der chemischen Elemente. In: MAYER R, SCHAUERMANN J ELLENBERG H. (Hrsg.): Ökosystemforschung. Ergebnisse des Sollingprojekts 1966–1986. Ulmer. Stuttgart, 1986.

UNECE (1998): Protocol on heavy metals to the 1979 Convention on Long-Range Transboundary Air Pollution.
http://www.unece.org/env/lrtap/full%20text/1998.Heavy.Metals.e.pdf

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Under the UN Convention on Long-Range Transboundary Air Pollution, the Environment Agency Austria has been operating the ICP Integrated Monitoring site Zöbelboden for 17 years. During this time, an invaluable inventory of environmental monitoring data has accumulated, permitting the assessment of the effectiveness of international emission reduction measures. Here, we provide a history of heavy metal pollution in a remote area of the Northern Limestone Alps since the 1990s. Declining background concentrations of most of the 11 trace metals monitored correspond to decreasing emissions and indicate the success of transnational abatement efforts. Measurements reveal that woodland receives higher and differently composed metal inputs than treeless terrain. Conspicuous peaks in pollutant trends demonstrate that activities of nearby sources do not go unnoticed in long-term monitoring.

ISBN 978-3-99004-046-1