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Distribution of Heavy Metals in a Woodland Food Web

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Often investigations deal with the residue situation in contaminated areas and their effects on ecosystems, however, information are rare concerning relatively uncontaminated areas -so called "reference areas".
In such areas we can assume an insignificant influence of pollutants and we can measure the metal flux under relatively natural conditions. Since 1988 we have investigated the nutrient and energy flow as well as the metal flux in an area which is hardly influenced by anthropogenic activities besides some agro-chemical compounds. For example, the depostion and contamination of some plants is relatively low in comparison to other places in North Germany. Also the average of geological background concentrations of soil from Schleswig-Holstein are higher than soil concentrations from Bornhöved. With this investigation we demonstrate the flux of metals through selected biotic compartments of a relatively uncontaminatedwoodland. Good indicators accumulating the non essential metals Cd and Pb are beetles and isopods. In contrast ground spiders, although predators, show only low metal concentrations. The essential metals Cu and Zn were relatively homogenous in concentration in the animals. Zn showed the highest values and beetles seem to accumulate it.

MATERIALS AND METHODS

We selected samples from an area in Schleswig-Holstein, Germany (10.20 E, 54.10 N). Following species were analyzed: Vertebrates - Common shrew (Sorex araneaus, n=13), Yellow necked mouse (Apodemus flavicollis, n=12), Bank vole (Clethrionomys glareolus, n=13); invertebrates

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- isopods (Oniscidae, pool of n=25), beetles (Carabus spec., pool of n=15), earthworms (Lumbricus rubellus and Dendrobaena octaedra, pool of n=15; animals lived without food for one day), different species of ground spiders (pool of n=30), snail (Arion spec., n=l); plants - different fractions of litter (beech, Fagus silvatica): leaves (n=ll), seedshells (n=5), seeds (n=3), wood (n=2). Samples were collected during the period from autumn 1991 till autumn 1993. Soil samples (Cambic Arenosol, ph 3,3-4,0 at 5 cm; collected 1994) were taken from 9 different soil horizons (3 samples each horizon). All samples were dried and homogenized. We used carcasses (body without fur, head, outer extremities and intestine) of vertebrates as is usual for determinating body burdens of organochlorine residues. For the invertebrates we analyzed whole animals, because they present the food for the next tropic level. (Because we had to use earthworms for further monitoring programs, we had to investigate them without gut). Whole body burdens were the basis for determining the metals fixed in the biomass and for metal flux estimations.

Soil samples were dried at 40° C and dry mass was corrected to 105° C dried samples. 250 mg of dried soil was dissolved with HNO_3 (1 ml) + HCl (3 ml) + HF (4 ml) in closed teflon vessels at 160° C for 12 h. Then 1 ml $HClO_4$ was added and samples evaporated to dryness in open vessels at 180° C and then dissolved in HNO_3 and destilled water at 100° C. For the analysis of biological samples dried material (max. 200mg) was dissolved in concentrated HNO_3 (1 ml) under pressure (190° C, 4h). For analysis samples were evaporated to dryness (90° C) and again diluted in HNO_3. For the Hg analysis we added 8.5 ml distilled water and 0.4 ml $K_2Cr_2O_7$. Samples were analyzedby atomic absorption spectrometry:

- graphite furnace: Perkin Elmer Zeeman 3030 with background correction (Pb)
- graphite furnace: Perkin Elmer 5100 with background correction (Cd, Cu)
- flame: Perkin Elmer 2100 (Zn)
- cold vapour: Perkin Elmer 1l00B equipped with FIAS 400 (Hg).

Recovery and accuracywas determinated by measuring blanks and standard reference material (Fa. Promochem: Bovine liver BCR 185 for animal samples: Plancton CRM 414 for plant samples; Reference soil sample SO-2 from "Canada Centre for Mineral and Energy Technology" for soil samples).

Detection limits were as follows (µg/g dry weight): Cd 0.002, Cu 0.03, Hg 0.02, Pb 0.1, and Zn 2.

RESULTS AND DISCUSSION

Table 1 shows the concentrations in the soil. Hg was below the detection limit in almost all horizons. Pb shows the smallest mobilety with relatively high concentration in the Ah1-horizon.

Table 1. Metal concentrations in soil samples of different horizons. Values are given in mg/kg dry matter. n.d. = not detectable.

Horizon	(cm)	Cd	Pb	Cu	Zn	Hg
Ah1	(5)	0.07	40.4	4.6	22	0.02
Ah2	(28)	0.08	9.7	3.4	26	n.d.
AhBv	(38)	0.09	6.7	3.1	26	n.d.
IIBv1	(60)	0.08	7.2	5.8	31	n.d.
Bv2	(91)	0.05	4.0	3.2	15	n.d.
rGBv	(110)	0.06	3.4	2.7	11	n.d.
Bv3	(130)	0.09	4.1	3.1	13	n.d.
IIIBbsC	(154)	0.04	3.3	1.8	3	n.d.
IVBvC	(165)	0.10	4.3	3.2	23	n.d.

With the exception of Hg all metals were detectabale in all plant samples (Table 2). Within these samples all metals were relatively constantly distributed besides ten times higher concentrations of Pb in wood than in seeds.

Table 2. Metal residues in samples (homogenates) of different tropic levels. Values are given in mg/kg dry matter; Y.-n. mouse= Yellow necked mouse.

	Cd	Pb	Cu	Zn	Hg
Beech litter					
- leaves	0,27	2,4	5,3	68	0,06
- seeds	0,09	0,9	10,9	62	n.d.
- seedshell	0,11	2,9	8,2	47	0,02
- wood	0,22	9,6	5,8	88	0,02
Snail	3,62	0,5	51,2	320	0,15
Worm	6,62	2,4	18,3	312	0,15
Ground spider	0,43	1,3	26,1	151	0,09
Beetle	7,58	1,2	192,0	382	0,22
Isopod	11,14	29,7	140,0	168	0,11
Bank vole	0,05	0,5	9,9	121	0,01
Y.-n. mouse	0,16	0,9	13,5	122	0,08
Commom shrew	1,30	2,6	17,4	274	0,17

Animals were more highly contaminated with Cu, Hg and Zn than plants. Zn was relatively constantly accumulated in all animals while Cu was 20 times higher in isopods and beetles than in Bank voles.
Within the invertebrates isopods showed the highest concentrations of Cd, Cu and Pb. Cd showed the largest deviations.
In general Common shrews were more highly contaminated than rodents and within the rodents Yellow-necked mice were more highly contaminated than Bank voles.

The comparison of samples from producers up to tertiary consumers showed the following tendency: in most plant samples Pb is more highly concentrated than in consumers while the opposite is obvious for the other metals. Compared to other consumers rodents show low metal concentrations. Decomposers (isopods) and secondary consumers (beetles) contained higher concentrations than other consumers do. Final consumers like shrews did not contain the highest concentrations and ground spiders (secondary and tertiary consumers) show low metal concentrations.

Our investigation area shows relatively low heavy metal deposition as shown in a monitoring program from Schleswig-Holstein (pers. comm. Gewerbeaufsichtsamt Itzehoe).

In comparison to "averaged " background soil concentrations in Schleswig-Holstein, measured and calculated by Wiegmann (1994), the soil from our area can be characterized as follows: in general the values of the Bornhöved samples are lower than the Schleswig-Holstein average. Only Pb in the Ah1-horizon was slightly higher. The soil can be regarded as uncontaminated, the metals are of geological origin.

The metal concentrations of litter samples are also relatively low, often in the same range as sample concentrations from areas which were defined as uncontaminated or far away from industrial influence. For example samples of beech (leaves, wood and litter) from another woodland in Germany showed higher concentrations (Pb 8 fold, Cu 5 fold, Cd 3 fold), while Zn and Hg were similarly concentrated (Ulrich et al. 1986). Other authors quoted values of uncontaminated plant samples in the same range as our values. Only Zn is slightly higher in some samples from our investigation area.

Also invertebrates, often epi- or hypogeal living earthworms showed higher residues: this is also true for organisms from so called uncontaminated areas.
For example we compared our results with findings from different food-web species from an "industrial non influenced" woodland in Finnland (Nuorteva 1990). Leaves, mice, voles and worms showed comparable concentrations, metals in beetles (Carabidae) of the Bornhöved area are slightly higher concentrated and metals in spiders are slightly lower concentrated. In general, Zn concentrations in Bornhöved samples are slightly higher in comparison to the Finnish samples. In our investigation especially isopods show elavated concentrations of Pb and Cd.

In general residues in organs of vertebrates were higher than residues in homogenates from our investigation (Ma et al. 1991, Müller 1990, Fangmeier and Steubing 1986).

Hopkin and Hames (1994) measured lethal food residues (one year experiment) forisopods (Porcellio scaber) which were 200-250 times higher for Pb and Cd than residues in litter samples that we measured. For Cu and Zn these values only ranged between 10-15. But the authors pointed out, that one can find isopods in regions with higher residues in leaves than residues of their experiments. Spurgeon et al. (1994) determined LC 50 soil concentration for earthworms (Eisenia foetida) of 555 mg/kg (dryweight) for Cu, 745 mg/kg for Zn, > 1000 mg/kg for Cd and 3700 mg/kg for Pb. These values were far above those measured in soil samples of Bornhöved samples. Invertebrates seemed not to be endangered. At present Cu and Zn have the highest toxicological relevance.

Residues cited in the literature, which can endanger mammals, where also higher than residues of mammals from our area (Tull-Singleton et al. 1994).

There is no strict accumulation of heavy metals via the food chain, although in general (with the exception of Pb) samples from animals contain higher concentrations than plant samples. Hg and Zn are less concentrated in plants, higher but relatively homogenously concentrated in animals. Only Bank voles contain extremly low concentrations. Pb is highly concentrated in plants and especially in isopods, low in omnivorous mammals and without any tendency regarding the trophic level in the other samples. No tendency can be found concerning Cu, isopods and beetles contain the highest residues. With the exception of spiders Cd is more highly accumulated in invertebrates than in vertebrates even in shrews.

Concerning the accumulation one can differentiate between essential and non-essential metals: essential metals can be regulated, especially invertebrates and no differences can be recognized between herbivorous and carnivorous organisms (Roberts and Johnson 1978, Hunter and Johnson 1982). It is hardly possible to define "normal" concentrations of essential metals for invertebrates of a great variety of different species. There exist some ecotypes which were able to accumulate metals without any toxicological consequences. Especially concerning binding proteins for Cd, which can also bind Zn, it is not surprising to find higher concentrations of both metals in some species. Even in arthropods we cannot recognize a convincing tendency although there are some hints: carnivorous arthropods often contain higher residues than omnivorous ones. Some species tend to accumulate high amounts: isopods and snails -in our investigation beetles too.

Non-essential metals tend to accumulate. This is obvious for Cd especially in the system plant/herbivore (Hopkin and Hames 1994, Hunter and Johnson 1982, Roberts and Johnson 1978). For spiders the results are contradictory: while some authors assume spiders do accumulate metals (Hunter et al. 1987, Fangmeier and Steubing 1986) others do not (Hopkin 1990, Hopkin and Martin 1985, Van Hook and Yates 1975). Concerning small mammals the tendency, that carnivors accumulate higher amounts than herbivors, is obvious (Hunter et al. 1989, 1987; this investigation). Andrews et al. 1984 confirm this situation for contaminated areas, but not for uncontaminated areas.

The results for Pb are not without contradiction. In low contaminated areas Fangmeier and Steubing (1986) could not identify an accumulation with the exception of Arion spec. and Lumbricus spec.. The animals showed a high variability. In other investigations some carnivorous invertebrates were lower contaminated than herbivorous ones (Andrews et al. 1989, Roberts and Johnson 1978). On the other hand Beyer et al. (1985) found in ground living arthropods from metal contaminated areas relatively high concentrations, in some cases whole populations were missing. Also residues in small mammals showed a strict dependence on their trophic level (Ma et al. 1991, Ma 1989).

For Hg one can find accumulation tendencies in mammals and birds. Lubricides from contaminated areas also contained higher amounts than animals from uncontaminated areas (Bull et al. 1977). We cannot find any tendency.

Some authors consider the amount of food and the physiological situation to be responsible for the accumulation (Fanggmeier and Steubing 1986). Bioavailability in connection with soil ph is another important factor to be considered for hypogeal species. In animals from contaminated areas (especially soil contamination) in general we can find higher residues than in animals from uncontaminated areas while bioaccumulation via the food chain is not noticeably evident. We can agree with this last finding. Nevertheless some invertebrates are good accumulation indicators even in low contaminated areas; isopods and beetles should be mentioned.

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