Comparison of Atmospheric Emission and Deposition of POPs and heavy metals in Germany

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Introduction

Emission inventories are commonly applied to quantify the amount of pollutants released to the atmosphere [1]. These inventories are based on activity data and related emission factors [2]. Because of the large number of sources and the high uncertainty of emissions for some sources, particularly natural sources, it is often unknown how well these inventories represent the true emissions [3].

Measurements of atmospheric deposition also offer the opportunity to quantify the release of persistent pollutants into the atmosphere. Sediment contamination together with accumulation rates give an indication of the amount of pollutant released into the environment. If a sediment core is only contaminated by atmospheric deposition with no other pollutant inflow (run-off, etc.) and without known anthropogenic sources in the surroundings, the pollutant deposition to the sediments can be attributed only to atmospheric emissions. The derived deposition rates form a comprehensive basis for comparison with emission inventories.

The sediment core of Bugsinsee is in line with these criteria: only atmospheric deposition as pollutant source and no known anthropogenic sources in the surroundings. Bugsinsee is located in Brandenburg, North-East of Berlin (52.99 °N, 13.84 °E). The pollutant sedimentation rates of Bugsinsee are here compared with published atmospheric emission inventories for Germany.

Comparing emissions and deposition follows the mass balance approach. Deposition equals the emission plus the import from abroad minus the export plus the balance of formation and destruction in the environment. Assuming that the resulting import-export balance and the formation-destruction balance is small compared to the formation is a simplification, but for the POPs and heavy metals investigated here and for a large country like Germany this is not an unrealistic assumption. The overall goal of this work is to critically evaluate the quality of atmospheric emission inventories, to check the validity of the inventory data and to search for explanations if substantial differences occur.

Methods and Materials

The pollutant levels of PCDD/F, PAH, PCB, pesticides and selected heavy metals in sediment cores of Bugsinsee have been determined within a comprehensive study of sediment contamination in N-E Germany [4]. Sampling and analysis have been described in detail elsewhere [5-7]. Analytical blanks were determined during analysis and their pollutant levels usually remained far below the levels in the samples. The deposition rate and the sediment density of Bugsinsee were estimated 1 mm/a and 1 g/cm^3, respectively.

Atmospheric emission inventories of European countries are regularly compiled by EMEP [8, 9]. The emission inventories include a range of persistent organic pollutants (POPs) and heavy metals. The deposition rates were obtained with the following simplifications: The German transboundary pollutant transport (both import and export) was negligible compared to the German emissions. Pollutants formed or transformed in the environment can be neglected compared to the emissions. The pollutants are deposited equally over the whole area of Germany.

The deposition rates derived from the most recent sediment layer were compared with the inventory data for 1990. The cumulative deposition of the last 100-150 years was compared with the inventory data for the period since 1970 (POPs) and since 1985 (heavy metals).

The concentrations in sediment deposition refer to the following compounds: All 2,3,7,8-substituted and non-2,3,7,8-substituted PCDD/F were analysed. Total PCDD/F concentrations refer to the sum of all 2,3,7,8-substituted and non-substituted PCDD/F congeners. PCDD/F I-TEq concentrations take all 2,3,7,8-substituted congeners into account, the NATO-CCMS toxic equivalency factors are applied [10]. The sum PAH concentration are the total of 39 detectable PAH. Thirty different PCB congeners were analysed in the sediment samples. α-HCH, β-HCH, γ-HCH and δ-HCH were analysed and sum HCH concentrations are the total of all four HCH isomers. DDX includes 2,4´-DDE, 4,4´-DDE, 4,4´-DDMU, 2,4´-DDMS, 4,4´-DDMS, 2,4´-DDD, 4,4´-DDD and 4,4´-DDT. Total CBz are the sum of 1,2,4,5-TeCBz, 1,2,3,4-TeCBz, PeCBz and HCB.

The corresponding emission data are reported according to the following guidelines [2, 11, 12]: It is recommended that PCDD/F is reported as toxic equivalents according to [10]. The following indicator compounds should be used for PAHs: benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, and indeno[1,2,3-cd]pyrene. It is expected that the pollutant groups of the emission data usually cover similar if not the same compounds for the deposition data. If the coverage of compounds is known to be different, this is mentioned explicitly.

Results and Discussion

The pollutant sedimentation rates of Bugsinsee are in the following compared with the atmospheric emissions of Germany. The annual pollutant deposition rates are shown in Table 1.

Table 1: Annual deposition rates of POPs and Pb in the sediment core of Bugsinsee.

PCDD/F	PCB	PAH	DDX	CBz	HCH	Pb
pg/cm^2/a	ng/cm^2/a	ng/cm^2/a	ng/cm^2/a	ng/cm^2/a	ng/cm^2/a	µg/cm^2/a
0.15 - 12	≤ 0.01	4.7 - 41	< 0.003 - 1.3	< 0.001 - 0.03	< 0.002	0.3 - 5.1

Compared to other German sediment cores, the deposition rates at Bugsinsee are towards the lower end of deposition rates measured elsewhere. Other sediments of N-E Germany closer to anthropogenic activities show deposition rates one or several orders of magnitude higher.

Based on the pollutant depth profile in the sediment core of Bugsinsee, the amount of pollutants deposited over the last 100-150 years was investigated. Table 2 summarises the amount of pollutants deposited per area at Bugsinsee up to a depth of 40 cm.

Table 2: Per area deposited amounts of POPs and Pb in the sediment core of Bugsinsee.

PCDD/F	PCB	PAH	DDX	CBz	HCH	Pb
ng/cm^2	ng/cm^2	µg/cm^2	µg/cm^2	ng/cm^2	ng/cm^2	mg/cm^2
0.9	0.09	5.3	0.08	2	< 0.1	0.4

The amount of pollutants deposited in Bugsinsee are usually much lower than for other sediments. Sediments of the Baltic Sea show one (PCDD/F, PAH, Pb) to several (PCB) orders of magnitude higher pollutant amounts, but may also show lower amounts for selected pesticides (DDX, CBz). The higher levels in the Baltic Sea are caused by additional input from river water inflow. The high pesticide levels at Bugsinsee probably originate from adjacent agricultural emissions. The amounts of pollutants deposited in sediments in the region of Berlin are several orders of magnitude higher for all pollutants.

The comparison of deposition rates and per area deposited pollutant amounts confirm the low contamination levels of the sediments of Bugsinsee (except pesticides) and the importance of water inflow as pollutant source for other sediments.

The annual pollutant deposition rates derived from the measurements in the sediments and from the German atmospheric emission inventory are shown in Table 3. The deposition rates of both approaches are similar and of the same order of magnitude. The deposition rates of the heavy metals are throughout higher for the sediment measurements, while these are lower for PCDD/F and PAH compared to inventory data.

The differences in the annual deposition can be explained by:

- an emphasis of the EMEP inventories on anthropogenic sources and the neglect of natural sources,
- an under- or overrepresentation of pollutant sources in the surroundings of the Bugsinsee compared to German average,
- a larger influence of Eastern Europe on the deposition rates of the Bugsinsee than the assumption of the input-output balance indicates.

The cumulative deposition of heavy metals and POPs based on inventory data was calculated for the years 1985-2000 and 1970-2000, respectively. In Table 4, these are compared with the corresponding sediment data, integrating over the whole depth of the sampled core.

For most pollutants, the sediment cores show a substantially higher cumulative deposition than the inventory data. The difference reaches several orders of magnitude for heavy metals, while the cumulative deposition for PCDD/F and PAH is less than one order of magnitude higher for the sediment measurements than for the inventories.

The differences in the cumulative depositions are caused by:

- the difference in the period covered: inventories for 15-30 years compared to more than 100 years for the sediment measurements,
- a heavy metal peak contamination at a depth of 6-12 cm in the Bugsinsee originating from local rather than national pollution.

Conclusions

The comparison of the deposition rates based on the sediment measurements and the inventories showed very similar results for the recent pollutant emission and deposition. This indicates that the current inventories cover the actual atmospheric emissions reasonably well.

In contrast, the cumulative depositions are substantially higher for the sediment measurements than for the inventories. This can be explained by differences in the time span covered and local historical pollution.

Overall, this comparison shows to be a fruitful exercise for quality assurance and quality control of emission inventories where independent information is otherwise rarely available.

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Table 3: Annual deposition rates of POPs and Pb in the sediment core of Bugsinsee.

	Pb	Cd	Cr	Cu	Zn	HCH	DDX	PCB	PCDD/F	PAH	CBz / HCB
Unit	$mg/m^2/a$					$\mu g/m^2/a$			ng I-TEq/m^2/a	$mg/m^2/a$	$\mu g/m^2/a$
Sediment	10	0.2	0.9	2.0	18	mainly n.d.	13	mainly n.d.	1.6	0.4	0.3
Emission inventory	6.5	0.09	0.7	1.0	3.7	42	n/a	120	3.4	1.2	0.24

Table 4: Cumulative deposition of POPs and Pb in the sediment core of Bugsinsee.

	Pb	Cd	Cr	Cu	Zn	HCH	DDX	PCB	PCDD/F	PAH / B-a-P	CBz / HCB
Inventory period	1985-2000					1970-2000					
Unit	mg/m^2								μg I-TEq/m^2	mg/m^2	
Sediment	4500	60	480	1200	13000	mainly n.d.	0.8	mainly n.d.	1.9	53.4	0.02
Emission inventory	110	1.2	10	13	52	3.7	n/a	16	0.35	14	0.95