

NMR project “POP Multi-Flux Intercomparison (PMFI)”

Final report title:

Evaluation of sequentially-coupled POP fluxes estimated from simultaneous measurements in multiple compartments of an air-water-sediment system

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Summary

Bulk atmospheric deposition fluxes, air-water exchange fluxes, particle settling fluxes out of the upper water column, sediment trap fluxes in deep waters, and sediment burial fluxes of polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) were simultaneously measured in the Koster Fjord, eastern Skagerrak, on the Swedish west coast. The aim of the study was to compare the magnitude and direction of the compound fluxes in the system in order to diagnose key fate processes. The PCB and PAH fluxes via net atmospheric deposition, settling particles out of the surface and through deep waters, as well as into the accreting underlying sediments were shown to be remarkably similar, agreeing within a factor of a few for any given target compound. Fluxes of all PCB and PAH target compounds remained fairly constant with water column depth. Thus, there was no evidence for net desorption from sinking particles. The net unidirectional and near balancing of vertical fluxes suggests a net transport of PCBs and PAHs from the atmosphere to the continental shelf sediments in the Koster Fjord, which is consistent with the hypothesis that the shelf sediments are important sinks for these compounds.

Introduction

Although it is now becoming clear that oceans play a key role in the fate and removal of POPs from the rapidly cycling atmosphere - terrestrial biosphere - surface ocean biosphere system, there are still few measurements of POP fluxes in these systems. Furthermore, available flux measurements were usually performed at different sampling sites and at different times and tended to focus on one vertical flux at a time. This study attempts to measure and contrast multiple vertical fluxes of PCBs and PAHs at a relatively unpolluted background site on the Swedish west coast. A multiple, simultaneous flux measurement study of the kind presented here is rare and will provide a valuable insight into the cycling of PCBs and PAHs between air, water and sediments providing useful information on the key fate processes.

This report is a succinct summary of the work undertaken. A more detailed report of the work is provided in a publication by Palm et al. (in press).

Materials and Methods

The sampling site is located in the Koster Fjord, eastern Skagerek, on the Swedish west coast close to the border with Norway.

A variety of measurement techniques were simultaneously employed, namely: bulk atmospheric deposition sampling (Brorström-Lundén et al., 1994), a ^{234}Th -based method to estimate particle settling fluxes in the upper water column (Gustafsson et al., 1997a,b), sediment traps for measuring settling particles in the lower water column (Broman et al., 1988), and sediment burial fluxes using sediment cores dated by ^{210}Pb and ^{137}Cs radioisotope techniques (Elmqvist et al., in press). The two-film theory and water concentration measurements have also been used to estimate air-water exchange fluxes (Whitman, 1923; Mackay, 2001). To obtain fluxes representative for various seasonal conditions as well as to monitor diurnal variations, sampling was undertaken separately in the summer (July 1999) and winter (February to March, 2001) and during the day and night.

After addition of stable-isotope labelled internal standards, all samples were extracted with toluene and cleaned up using various chromatographic techniques. Analysis of cleaned-up sample extracts was undertaken by GC-MS. A total of six PAH and six

PCB compounds were selected for flux calculations, namely; phenanthrene (Phe), fluoranthene (Fth), pyrene (Pyr), benzo(a)anthracene (B(a)A), benzo(a)pyrene (B(a)P), perylene (Per), PCB IUPAC numbers: 28, 52, 138, 153 and (180+193).

Results and Discussion

Measured concentrations and estimated fluxes are compiled in Tables 1 and 2. Having established vertical fluxes for the target compounds into or out of the four sequential compartments (air, surface water, deep water and sediments), “mass balance” vertical flux diagrams were constructed for two selected compounds (PCB-28 and B(a)P) for July and February, respectively (Figure 1). These compounds were selected for presentation here because they represent the extremes in physical-chemical properties. PCB-28 is relatively volatile and does not associate appreciably to particles in the atmosphere, whereas B(a)P is almost 100% associated to particles in the atmosphere and water column. The four separate flux estimates made in July 1999 (8 and 28 July 1999, day and night) for air-water exchange fluxes and surface particle settling fluxes were averaged for comparison with the single estimate of these fluxes undertaken in February 2001.

An important conclusion from this study is that PCB and PAH fluxes via net atmospheric deposition, settling particles out of the surface and through deep waters, as well as into the accreting underlying sediments were shown to be remarkably similar, agreeing within a factor of a few for any given target compound. Concentrations and sinking fluxes of all PCB and PAH compounds remained fairly constant with water column depth, thus net desorption from sinking particles is likely of minor importance for all but the most soluble compounds. The near balancing of vertical fluxes suggests a net transport of PCBs from the atmosphere to the ocean shelf sediments in the Koster Fjord. These measurement-based findings are consistent with the hypothesis that sediments are important sinks for these types of compounds (Jönsson et al., 2003).

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Table 1. Measured concentrations in different media.

Medium	Date	Description	Phe	Fth	Pyr	B(a) A	B(a)P	Per	PCB 28	PCB 52	PCB 153	PCB 138	PCB 180+193
Air (pg m ⁻³)	8 July 1999, day	Gas	160	34	20	2.6	0.19	0.021	0.20	1.3	1.0	1.1	0.080
		Part	4.5	3.0	6.1	1.6	4.9	5.3	0.075	0.026	0.045	0.075	0.18
	8 July 1999, night	Gas	1100	94	160	2.4	0.66	0.46	3.1	0.86	0.25	1.2	0.087
		Part	5.5	3.8	6.8	2.2	14	13	0.12	0.029	0.22	0.87	0.18
	28 July 1999, day	Gas	75	39	8.8	0.70	0.85	0.91	0.21	0.20	0.20	0.22	0.055
		Part	19	6.1	7.0	1.0	4.8	3.5	0.098	0.083	0.25	0.29	0.10
	28 July 1999, night	Gas	91	40	24	0.69	0.59	0.72	0.30	0.23	0.41	0.54	0.16
		Part	15	5.4	6.6	1.3	5.8	4.9	0.12	0.099	0.29	0.34	0.11
	14 February 2001, day	Gas	3500	1100	1800	9.4	7.7	1.2	2.5	2.64	1.4	0.77	0.091
		Part	43	120	49	82	93	14	0.022	0.038	0.30	0.22	0.069
	7 July – 28 July 1999, low volume sampler	Gas	7700	7900	2600	56	0.71	0.84	2.1	2.1	2.2	2.4	0.15
		Part	10	12	7.8	3.0	4.9	1.5	0.038	0.017	0.050	0.055	9.4 × 10 ⁻³
Atmospheric deposition (ng m ⁻² day ⁻¹)	8-28 July 1999	Gas	1700	370	380	1.8	0.21	0.013	7.1	4.0	1.1	0.78	0.25
		Part	180	310	130	4.6	68	6.4	2.0	0.018	0.18	0.16	0.082
	13 February – 6 March 2001	Wet+dry	50	23	28	3.2	9.4	2.4	0.65	0.18	5.5	5.1	0.34
		Wet+ dry	130	140	58	11	72	52	3.7	0.079	0.57	0.47	0.15
Water (pg L ⁻¹)	8 July 1999, day	Diss.	150	79	41	17	0.63	0.78	0.35	0.23	0.085	0.37	0.093
		Part	3.1	3.1	4.7	0.91	1.0	0.70	0.12	0.11	0.10	0.70	0.16
	8 July 1999, night	Diss.	150	77	18	1.6	0.49	0.96	0.62	0.26	0.24	0.28	0.044
		Part	16	8.5	5.3	1.5	3.0	6.9	0.36	0.13	0.63	0.82	0.15
	28 July 1999, day	Diss.	2600	480	930	28	8.9	5.4	2.1	1.7	0.37	1.3	0.44

NMR project “POP Multi-Flux Intercomparison (PMFI)”

28 July 1999, night	Part	22	58	51	5.7	28	4.5	0.047	0.047	0.025	0.13	0.11
	Diss.	500	100	190	4.6	1.9	1.7	2.0	1.7	0.31	1.2	0.51
	Part	51	31	19	2.4	75	17	0.021	0.033	0.070	0.088	0.056
	Diss.	470	1600	940	72	13	3.1	2.64	1.1	3.6	3.1	0.26
	Part	89	340	130	82	110	60	0.47	0.27	2.5	2.3	0.41
Settling material (ng g⁻¹ dw)												
8 - 28 July 1999	Sediment trap	33	30	30	8.9	35	61	0.36	0.19	1.6	1.5	0.079
July 1999	Core 1: 1-2 cm	39	92	40	29	40	39	0.13	0.096	0.64	0.67	0.087
	Core 1: 3-4 cm	47	77	71	36	49	43	0.18	0.11	0.58	0.78	0.091
	Core 1: 6-7 cm	63	81	100	51	55	44	0.11	0.12	0.61	0.78	0.10
	Core 1: 10-11 cm	33	57	61	28	36	41	0.12	0.095	0.44	0.55	0.080
	Core 2: 1-2 cm	62	97	96	39	58	64	0.23	0.14	0.76	0.99	0.13
	Core 2: 4-5 cm	58	92	100	21	56	58	0.31	0.12	0.69	0.93	0.12
	Core 2: 7-8 cm	61	73	48	40	59	56	0.28	0.15	0.79	0.11	0.12
	Core 2: 12-14 cm	42	45	47	23	72	44	0.10	0.11	0.49	0.62	0.11

*Average of two samples. Core 1 and 2 were sampled at 113 m and 126 m depth, respectively (Elmqvist et al., in press). Core 2 was used for calculation of sediment burial rates of PCBs and PAHs.

Table 2. Calculated fluxes in $\text{pmol m}^{-2} \text{day}^{-1}$.

Flux	Date	Phe	Fth	Pyr	B(a)A	B(a)P	Per	28	52	153	138	180+193
Bulk deposition	July	280	120	140	14	37	9.6	2.5	0.61	15	14	0.86
	February	700	690	290	50	290	200	14	0.27	1.6	1.3	0.38
Water-air transport	July 8 day	-280	-32	-64	-25	0.04	-0.20	-0.73	-0.32	1.1×10^{-4}	-0.14	-0.10
	July 28 day	-4600	-660	-1400	-35	-6.0	-5.8	-2.3	-1.6	-0.26	-0.89	-0.28
	July 8 night	220	29	48	-0.10	0.38	-0.21	-0.26	-0.19	-0.14	2.9×10^{-3}	-0.02
	July 28 night	-480	-81	-160	-3.3	-1.2	-0.96	-1.26	-0.88	-0.09	-0.46	-0.18
	February	4000	1400	1700	-37	12	0.38	-1.8	-0.56	-2.4	-1.1	-0.11
	July 8 day	7.3	84	75	-11	37	9.3	1.8	0.29	15	14	0.75
Air-water net transport (Bulk deposition plus Water-air transport)	July 28 day	-4300	-540	-1200	-21	31	3.7	0.23	-0.96	15	13	0.58
	July 8 night	498	145	187	14.0	37.7	9.28	2.3	0.42	15	14	0.84
	July 28 night	-199	34.8	-18.6	10.7	36.1	8.53	1.3	-0.27	15	14	0.68
	February	4690	2120	2020	13.6	300	205	13	-0.29	-0.85	0.23	0.27
Surface water particle transport	July 8 day	38	33	50	8.6	8.9	6.0	0.97	0.83	0.60	4.1	0.86
	July 28 day	270	610	540	54	240	39	0.39	0.34	0.15	0.77	0.58
	July 8 night	160	78	49	12	22	50	2.6	0.82	3.22	4.2	0.69
	July 28 night	530	280	170	19	550	130	0.15	0.21	0.36	0.45	0.26
Sediment traps settling rate	February	1100	3600	1400	780	910	510	3.9	2.0	15	14	2.2
	July	590	470	460	120	440	760	4.4	2.1	14	13	0.63
Sediment burial	July	1100	3600	1980	1200	1300	1100	2.4	1.4	5.6	7.2	0.89

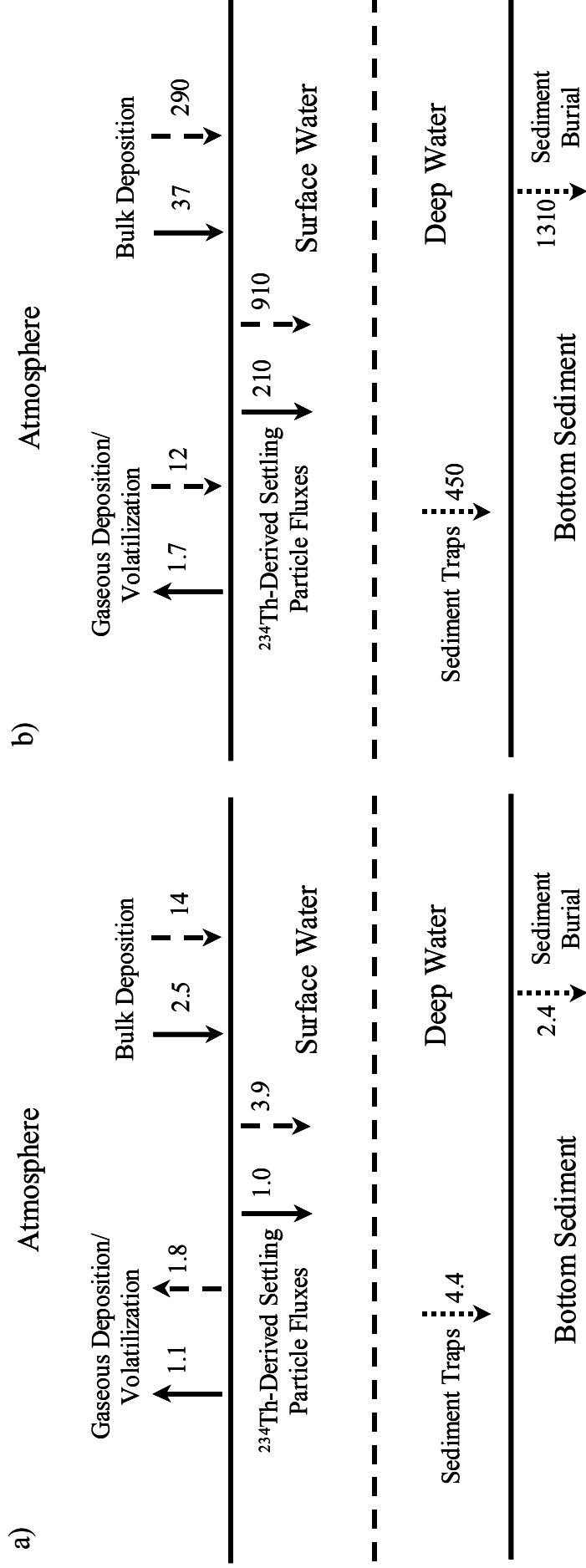


Figure 1. Mass balance diagram of fluxes in $\text{pmol m}^{-2} \text{ day}^{-1}$ for a) PCB-28, and b) B(a)P. The solid arrows represent summer flux estimates, the dashed lines represent winter flux estimates, and the dotted lines represent fluxes that are integrated over longer time periods. The air-water gaseous exchange flux estimates and the surface ^{234}Th -derived particle settling fluxes are the average of the four separate flux estimates made in July 1999 (see Table 2). Bulk atmospheric deposition fluxes and sediment trap fluxes were measured over a three-week period in July 1999. Sediment cores were collected in July 1999, but integrate fluxes over a longer time period.