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

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Abstract

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 Skagerak, 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.

Keywords: PCB, PAH, flux, sink, air, water, sediment

Capsule: The magnitude and direction of vertical fluxes of PCBs and PAHs in a coupled air-water-sediment system were simultaneously measured and compared.

1. Introduction

The world's oceans are thought to play an important role in both the cycling and removal of persistent organic pollutants (POPs) (key processes are illustrated in Figure 1). Atmospheric deposition delivers a large proportion of the POPs present in the oceans and once deposited, semi-volatile POPs may cycle between the ocean surface water and the atmosphere (see e.g. Totten et al., 2001).

The behaviour of less volatile, more hydrophobic POPs (e.g. PAHs) in marine waters is often closely related to the transport and loss of particles in the water column (Gschwend and Hites, 1981; Baker et al., 1991; Gustafsson et al., 1997a). Particulate material in the surface waters can be atmospherically derived, but is often dominated by biogenic particles including bacteria, phytoplankton, zooplankton, and their remains. Hydrophobic organic compounds tend to sorb to these particles, and are removed from the surface ocean on settling particles to be deposited in deep waters and bottom sediments.

Both transport on sinking particles to the deep ocean and burial in ocean shelf sediments have been hypothesized to be important global sinks for PCBs (Schulz et al., 1988; Schulz-Bull et al., 1998; Gustafsson et al., 1997b; Axelman and Broman, 2001; Dachs et al., 2002; Jönsson et al., 2003), and PAHs (Windsor and Hites, 1978; Gustafsson et al., 1997a), and for many other compounds with similar physical-chemical characteristics.

[INSERT FIGURE 1]

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. Estimation techniques are often used in place of real measurements because they are cheaper and faster to perform. For example, two recently published studies have attempted to estimate the global POP fluxes between the atmosphere and the world's oceans (Wania et al., 2002; Dachs et al., 2002). The accuracy of these modelling efforts is not known because there is such a paucity of flux measurements for comparison. The study presented here provides a rare opportunity to contrast actual measurements of POP fluxes with predictions of key processes borne out from modelling exercises. 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 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 and winter and during the day and night. 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.

2. Materials and Methods

2.1. Sampling site

The sampling site is located in the Koster Fjord north of the island Nordkoster (Figure 2). The fjord is 3 km wide and separates the Koster islands from the near-shore archipelago. The Koster-Väderö trough is a 62 km long depression in the sea floor, running parallel to the northern part of the Swedish west coast, and inside the Koster- and Väderö groups of islands. The trough is a fault fissure that is connected to the Atlantic deep water through the Norwegian Trough, over a 100 m deep sill. This connection makes for prevailing marine conditions in the area, i.e. high salinity. The site is representative of environmental background conditions with no known local point sources.

Lateral advection of POPs to the sampling site is thought to be insignificant with the majority of loading resulting from atmospheric deposition. This is supported by rather invariant concentrations of both PAHs and PCBs in coastal sediments reported from a large-scale monitoring exercise covering the whole eastern Skagerak region (Cato, 1997).

[INSERT FIGURE 2]

2.2. *Sampling methodology*

Sampling of air and surface water was carried out on three separate occasions during two different seasons covering both day- and night-time conditions. The first sampling exercise was undertaken on 8 July 1999 (day and night), the second on 28 July 1999 (day and night) and the third on 14 February 2001 (only daytime as diurnal temperature variation is small in the winter)

The methods used for air and deposition sampling have been described in detail elsewhere (Brorström-Lundén et al., 1994; Brorström-Lundén, 1996). Briefly, the particulate compounds in the atmosphere were trapped on a GF/F glass fibre filter and gaseous compounds were collected with two polyurethane foam (PUF) plugs, which were coupled in series. A high-volume sampler (HVS) was used to measure diurnal variations and for flux estimates, at a flow rate of approximately $20 \text{ m}^3 \text{ h}^{-1}$. In order to obtain representative air concentration data integrated over a longer time period, a low-volume sampler (LVS) was used, at a flow rate of $1.5 \text{ m}^3 \text{ h}^{-1}$. Atmospheric deposition was collected using an open sampler consisting of a 1 m^2 Teflon coated surface with 10 cm edges combined with a PUF containing cassette and thus includes both wet and dry deposition. The sampler was deployed for two separate three-week periods (7 – 28 July 1999 and 13 February – 6 March 2001).

Collection of surface ocean water samples for POPs, separated into particulate and dissolved phases, largely followed previously described methods (Broman et al., 1990, Naes et al., 1998). Briefly, for each water sample, 600-1400 L of water was pumped on-board from the centre of the mixed layer (15 m below the surface in

summer and 20 m in winter) through silicone-coated tubing at $>15 \text{ L min}^{-1}$ and split to a lower flow rate of 8 L min^{-1} .

The sample was filtered in-line first through a pre-combusted GF/F glass fibre filter held in a stainless-steel holder and then a pre-extracted PUF adsorbent (diameter 7 cm, length 12 cm) in a stainless steel housing. The GF/F filter is employed to trap particulate matter and the PUF adsorbent to trap dissolved-phase PCBs and PAHs. Filters were folded in half inwards and then both the filters and adsorbents were wrapped in pre-combusted aluminium foil and stored cold frozen in double layers of plastic bags until analysis. Sampling was undertaken on 8 and 28 July (day and night) and on the 14 February.

High-volume water column sampling (500 – 800 L) for short-lived ^{234}Th was afforded by in situ pumping from the middle of the mixed surface layer to a deck-board filtration and extraction unit, largely following previously described methodology (Gustafsson et al., 2000). Briefly, water was passed at a flow rate of 5-8 L/min through a 100 μm nylon screen, a glass fibre filter (GF/F; Whatman Inc., $\approx 0.7 \mu\text{m}$ cut-off), and two serially coupled MnO_2 -impregnated adsorbents (prepared according to Hartman and Buesseler, 1994; here using 10 μm twined cellulose filter cartridges) to adsorb dissolved ^{234}Th . The activity of ^{238}U was estimated from salinity, as it is well known to mix conservatively in seawater (Chen et al., 1986; Andersson et al., 1995).

Settling material in the lower water column was collected using three self-buoyant, bottom-anchored (approx. 25 m above the bottom) sediment traps (100-130 m depth),

which comprised eight 10-cm-diameter glass cylinders (10 cm diameter and 50 cm high) mounted in PVC cylinders. A detailed description of these sediment traps and sampling procedures is presented elsewhere (Broman et al., 1990). The sediment traps were deployed for 20 days, from 8 – 28 July 1999.

The sediment core sampling is discussed in detail elsewhere (Elmquist et al., in press). Briefly, two sediment cores were taken out in July 1999 using a modified Kayak corer (Blomqvist et al. 1985) at 113 and 126 m water depths, respectively. The cores were transported to the Marine Biological Laboratory at Tjärnö where they were cut into slices of 1 cm. The slices were put in polypropene containers, which were stored frozen until analysis.

One field blank was sampled for every four actual samples taken, for each sample type.

2.3. *Analysis*

After addition of internal standards (¹³C-labelled PCB-52, PCB-101, PCB-118, PCB-138 and PCB-180, and D₁₂-perylene and D₁₂-picene), GF/F filters, PUF adsorbents and sediment sample aliquots (0.5-1.5 g) were wet extracted with toluene for 24 h in pre-washed cellulose thimbles in a Soxhlet set-up with Dean-Stark trap for water removal (Zebühr et al., 1993; Bandh et al., 1996). The extracts were reduced in volume to near dryness by rotary evaporation and eluted with hexane through a silica column 10% deactivated with water, followed by separation of the PAHs from the PCBs by preparative HPLC on an amino column (Zebühr et al., 1993; Bandh et al., 1996). The PCB fractions were further cleaned up on column containing three layers

of modified silica: bottom, 10% deactivated silica; middle, KOH impregnated (33% w/w) silica; and top, H₂SO₄ impregnated (40% w/w) silica (Bandh et al., 1996). The PAH fractions was subjected to a dimethylformamide (DMF) clean-up in two steps (Näf et al., 1992). The cleaned-up extracts were reduced in volume and quantified on a Fisons GCMS MD800 instrument (Supelco 30 m x 0.25 mm x 0.25 µm PtE-5 fused silica capillary column) with on-column injection. The PCBs were quantified against their ¹³C-labelled compounds and PAHs against their perdeuterated internal standards. Concentrations were not blank corrected.

The short-lived isotope ²³⁴Th was radiochemically purified from the filters, MnO₂-impregnated adsorbers and quantified by either low-level beta or gamma counting techniques. The procedures largely followed that described by Buesseler et al. (1992a,b) with modifications for more organic-rich waters outlined in Gustafsson et al. (2000). The measured ²³⁴Th activities were corrected for detector background, method recovery, and U in growth and reported values were decay-corrected to the mid-point of sample collection. Errors (2-5% at the 95% confidence limit) were constrained by the goodness of the fit of the raw counts to the ²³⁴Th decay curves.

2.4. *Flux measurements*

2.4.1. *Water-air exchange.* The dissolved/gaseous water-air transport of individual compounds was determined using the two-film theory (Whitman, 1923) adopting the fugacity approach as described in Mackay (2001). This method involves the conversion of dissolved/gaseous water and air concentrations to fugacities f (Pa), through the formula:

$$f = C / Z \tag{1}$$

where C is the concentration (mol m^{-3}) of a chemical in a particular phase and Z ($\text{mol m}^{-3} \text{ Pa}^{-1}$) is the fugacity capacity of that phase ($Z_{air} = 1/RT$, where $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ and T is the water temperature in degrees Kelvin, and $Z_{water} = 1/H$, where H = Henry's Law constant in $\text{Pa m}^{-3} \text{ mol}^{-1}$). Temperature dependent equations for H were obtained from Paasivirta et al. (1999). The net flux N (mol/h) from water to air is then determined through:

$$N = D_{VOL} (f_W - f_A) \quad (2)$$

where D_{VOL} ($\text{mol Pa}^{-1} \text{ h}^{-1}$) is the overall rate constant and f_W and f_A are the fugacities (Pa) in water and air, respectively. D_{VOL} is calculated through

$$D_{VOL} = \frac{1}{\frac{1}{D_A} + \frac{1}{D_W}} \quad (3)$$

where D_A is the rate constant for the air-side transport ($\text{mol Pa}^{-1} \text{ h}^{-1}$) and D_W is the water-side rate constant ($\text{mol Pa}^{-1} \text{ h}^{-1}$), which were calculated using estimated mass transfer coefficients $k_{A,chem}$ and $k_{W,chem}$ (m h^{-1}) as outlined in Mackay, (2001). The mass transfer coefficients were obtained using the equations suggested by Schwarzenbach et al. (1993)

$$k_{A, chem} = k_{A, H_2O} \cdot ((M_{H_2O} / M_{chem})^{1/2})^{0.67} \quad (4)$$

$$k_{W, chem} = k_{W, O_2} \cdot ((M_{O_2} / M_{chem})^{1/2})^{0.57} \quad (5)$$

where M is the molecular weight (g mol^{-1}) and k_{A,H_2O} and k_{W,O_2} (m h^{-1}) can be determined through

$$k_{A, H_2O} = (0.2 \cdot w_{10} + 0.3) \cdot 36 \quad (6)$$

$$k_{W, O_2} = (0.0004 + 0.00004 \cdot w_{10}^2) \cdot 36 \quad (7)$$

where w_{10} is the wind speed at 10 meters above the surface and is related to w_z measured at 3 m above the surface through equation (8) taken from Schwarzenbach et al. (1993)

$$w_{10} \text{ (m/s)} = w_z / ((\ln z + 8.1) / 10.4) \quad (8)$$

w_z , the wind speed 3 metres above the surface, measured with an anemometer was on average 5 m s^{-1} .

2.4.2. *²³⁴Th-derived particle settling rates.* Vertical particle-bound surface water export was calculated using the ²³⁴Th proxy method. The procedure has been described in detail by Gustafsson et al. (1997a,b). The basic principle is that the radioactivity of ²³⁴Th in the surface water is balanced between its formation from decaying ²³⁸U and its own decay plus the vertical removal transport on particles. This can be described through

$$\frac{\partial [^{234}\text{Th}_{tot}]}{\partial t} = \lambda [^{238}\text{U}_{tot}] - \lambda [^{234}\text{Th}_{tot}] - k_{settle} [^{234}\text{Th}_{part}] \quad (9)$$

where $^{234}\text{Th}_{tot}$ and $^{238}\text{U}_{tot}$ are the total radioactivities (dpm/m³), λ is the radioactive decay constant of ²³⁴Th (0.0288 d⁻¹) and k_{settle} (d⁻¹) is the vertical transport rate constant.

The removal rate of a certain chemical from the surface water can thus be calculated from:

$$F_{chem} = k_{settle} z_{mix} C_{chem,part,surface} \quad (10)$$

where F_{chem} is the vertical net removal flux of a chemical, z_{mix} is the depth of the surface mixed layer (determined by temperature and salinity depth profiles at the time of sampling to be 30 m in July and 40 m in February) and $C_{chem,part,surface}$ is the concentration of the chemical in the particle phase of the surface water.

2.4.3. Sediment trap settling rates. The settling rate F_{dw} ($\text{g m}^{-2} \text{ day}^{-1}$) of particulate “dry-mass” equivalents through the lower water column was determined through the formula

$$F_{dw} = m_{dw} / (A \cdot t) \quad (11)$$

where m_{dw} is the total mass of dry substance collected in the sediment traps in g, A (m^2) the total surface area of the traps and t the time for deployment in days. The F_{dw} was calculated to be $3.14 \text{ g m}^{-2} \text{ day}^{-1}$, based on a total dry mass of 3.94 g, a surface area of 0.06 m^2 and a deployment time of 20 days. The calculated settling flux from this study is similar to the flux reported by Sanders et al. (1996) for a UK rural lake ($4.6 \text{ g m}^{-2} \text{ day}^{-1}$), and only slightly higher than those reported in the Great Lakes by Jeremiason et al. (1998) and Baker et al. (1991) of 0.6 and $1.05 \text{ g m}^{-2} \text{ day}^{-1}$, respectively.

The flux F_{chem} of each chemical in units of $\text{pmol m}^{-2} \text{ day}^{-1}$ was then determined through

$$F_{chem} = C_{chem} / M_{chem} \cdot F_{dw} \quad (12)$$

where C_{chem} (pg g⁻¹ dw) is the concentration of a chemical in the collected material, and M_{chem} is the molar mass (g mol⁻¹) of that chemical.

2.4.4. Sediment burial fluxes. The burial rate of the sediments in the Kosterfjord has been determined previously (Elmqvist et al., in press), using the ²¹⁰Pb method (Goldberg, 1963). While post-depositional mixing prevented establishment of a definitive geochronology in one core, the second core suggested a linear sedimentation rate of 2.1 ± 1.5 mm yr⁻¹ (Elmqvist et al., in press). This typical sedimentation rate was used to estimate mass burial fluxes F (g m⁻² day⁻¹) on an area basis through the formula

$$F = \omega \cdot \rho_{solids} (1 - \phi) \cdot 10000 \quad (13)$$

Where ω is the linear sedimentation rate converted into units of cm day⁻¹ (5.8 x 10⁻⁴ ± 4.1 x 10⁻⁴ cm day⁻¹), ρ_{solids} is the estimated density of the dry solids (2.4 g cm⁻³) and ϕ is the porosity of the sediment, which was on average 0.70 (cm³_{waterspace}/cm³_{total}) in the top 5 cm of the core (Elmqvist et al., in press). The resulting average sedimentation rate for the core is thus 4.14 ± 2.96 g m⁻² day⁻¹. This rate is comparable to sedimentation rates reported from lakes in the UK (Sanders et al., 1992; Gevaio et al., 2000) and in the Great Lakes region in the US (Schneider et al., 2001; Pearson et al., 1997; Baker et al., 1991).

Chemical-specific fluxes F_{chem} ($\text{pmol m}^{-2} \text{ day}^{-1}$) were obtained using

$$F_{chem} = F \cdot C_{chem,dw} / M_{chem} \quad (14)$$

where $C_{chem,dw}$ is the concentration ($\text{pg g}^{-1} \text{ dw}$) of the chemical in the surface sediment (average of the upper 5 cm) and M_{chem} is the molar mass (g mol^{-1}).

2.5. *Selected compounds*

A total of six PAH and six PCB compounds were selected for presentation in this paper, 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). These compounds were selected because they represent a wide variety of molecular weights and physical-chemical properties and, since they are commonly studied, physical-chemical properties were available for all compounds. The PCB congeners 180 and 193 were not chromatographically separated, thus they are treated together. In the calculation of fluxes, however, the physical-chemical properties for PCB 180 have been used, since this congener has been shown to be more abundant than PCB 193 (Schulz et al., 1989).

3. **Results and Discussion**

3.1. *Environmental concentrations*

The concentrations in the various sample matrices are summarised in Table 1.

[INSERT TABLE 1]

3.1.1. Air concentrations. Total air concentrations (gas + particle) measured with the LVS for individual target PAHs varied from 2 to 7900 pg m⁻³. Phenanthrene was the most abundant PAH detected, coinciding with fluoranthene in the summer. The samples taken with a high-volume sampler revealed that daytime summer concentrations were about ten times lower than daytime winter levels and also lower than night-time summer levels. Levels of individual PAH compounds were about ten times higher than the levels usually observed at the EMEP (Co-operative programme for monitoring and evaluation of the long-range transmissions of air pollutants in Europe, website: www.emep.int) monitoring station at Rörvik on the Swedish west coast (2-2500 pg m⁻³ in the summer 1999 and 180-1700 pg m⁻³ in the winter 2000; Swedish EPA, 2002).

The seasonal pattern in PAH air concentrations is usually observed and is thought to result from an increased emission of these compounds from combustion processes during winter months (Hoff et al., 1992), but could also be explained by more efficient atmospheric oxidation with hydroxyl radicals in the summer. PAHs of lower molecular weight predominantly occurred in the gas phase, whereas heavier compounds, such as B(a)P and Per were almost exclusively found in the particulate phase. The observed diurnal trend in atmospheric concentration with much higher concentrations in the daytime is evidence for temperature-controlled diurnal air-water exchange of the lighter PAH compounds. The three-fold increase in daytime concentrations is almost completely controlled by an increase in the gas-phase concentration of Phe, Flu, and Pyr.

For PCBs, the atmospheric concentration (gas + particle) measured with the LVS for individual target congeners was between 0.2-8.1 pg m⁻³, which is comparable to levels measured at Rörvik in 2000 (0.5-11 pg m⁻³; Swedish EPA, 2002). Higher concentrations were observed for the lighter molecular weight PCBs, which were almost exclusively in the gas phase. The higher molecular weight PCBs, were more evenly distributed between the particle and gas phases. There is no obvious seasonal or diurnal trend in atmospheric concentrations for PCBs in this study. Seasonal (Hoff et al., 1992) and diurnal (Hornbuckle et al., 1996) trends in the atmospheric concentration of PCBs have been observed previously at inland sites.

3.1.2. Water concentrations. The water concentrations ranged from 1.5 – 1900 pg L⁻¹ for individual target PAHs and from 0.2 - 6 pg L⁻¹ for target PCBs. Considerably higher levels of all compounds were detected in the winter, probably as a result of increased atmospheric deposition. The low molecular weight PAHs were found in the highest concentrations and were mainly detected in the dissolved phase. The heavier PAH compounds were mainly associated with particles. The hexa-chlorinated PCB congeners were the most abundant in the water samples. PCBs were mainly in the dissolved phase with a clear correlation between particle association and molecular weight of congeners.

There is a large variation both in the magnitude of concentrations and in the sediment-water distribution (K_D) of compounds between 8th and 28th July. The K_D for PCBs, for example, varies by a factor of 25 between these two sampling events. Variations in concentrations and speciation could be due to environmental variation in both

atmospheric input, as a result of rainfall events, and in the highly variability in the primary production of biogenic particles in marine surface waters.

The observed levels of PAHs and PCBs in ocean surface waters in this study are in good agreement with levels reported by other researchers from cruises undertaken in this geographical region (Witt, 2002; Bruhn and McLachlan, 2002). Witt (2002) reported concentration of individual PAH compounds in surface waters in the western central Baltic Sea of 5-1500 pg/L and Bruhn and McLachlan (2002) reported specific congener PCB concentrations in surface waters in the Southern open Baltic Sea of 0.2-10 pg/L.

3.1.3. Sediment concentrations. The concentrations of organic contaminants in bottom sediments (upper 5 cm) were comparable in the two different sediment cores and ranged from 21-100 ng g⁻¹ dry weight (dw) for PAHs and 0.087-0.99 ng g⁻¹ dw for PCBs. The congeners PCB-138 and PCB-153 were consistently the most abundant. The detected levels are in the same order of magnitude as measured concentrations in Baltic Sea sediments; 36-84 ng g⁻¹ dw for PAHs and 0.16 – 0.97 ng g⁻¹ dw for PCBs (Cato, 1995).

The concentrations in the bottom sediments compare well to the PAH and PCB concentrations in settling solids collected in the sediment traps which ranged from 9 - 61 ng g⁻¹ dw for PAHs and 0.08-1.6 ng g⁻¹ dw for PCBs. There is thus no obvious decrease in PCB and PAH concentrations with depth as has previously been observed in Lake Superior (Baker et al., 1991) and no obvious change in the pattern of compound abundances. This can be partly explained by the relatively small distance

between the sediment traps and the surface sediment in this study in comparison to the Lake Superior study. The lack of a concentration decline with depth suggests that the compounds remain largely intact on the particles as they sink through the water column and that there is negligible net desorption or compound degradation.

3.2. *Flux measurements*

All fluxes in units of $\text{pmol m}^{-2} \text{ day}^{-1}$ are summarised in Table 2.

[INSERT TABLE 2]

3.2.1. *Atmospheric deposition.* Bulk deposition of individual PAHs in the summer varied between 2.4 and $50 \text{ ng m}^{-2} \text{ day}^{-1}$ (10 - $280 \text{ pmol m}^{-2} \text{ day}^{-1}$) and between 12 and $130 \text{ ng m}^{-2} \text{ day}^{-1}$ (50 - $700 \text{ pmol m}^{-2} \text{ day}^{-1}$) in the winter. The higher winter values are consistent with the atmospheric concentration data, possibly reflecting higher emissions of these compounds from combustion sources in the winter. The observed deposition fluxes in the summer are about ten times higher than those routinely measured at Rörvik ($1.6 - 4.5 \text{ ng m}^{-2} \text{ day}^{-1}$) and the winter fluxes about two times higher compared to Rörvik values (25 - $85 \text{ ng m}^{-2} \text{ day}^{-1}$) (Swedish EPA, 2002). These observations are consistent with the ten times higher PAH air levels observed at the Koster site compared to the Rörvik site.

For PCBs, the bulk deposition fluxes were $0.2 - 5.5 \text{ ng m}^{-2} \text{ day}^{-1}$ ($0.6 - 15 \text{ pmol m}^{-2} \text{ day}^{-1}$) in the summer and $0.08 - 3.7 \text{ ng m}^{-2} \text{ day}^{-1}$ (0.3 - $14 \text{ pmol m}^{-2} \text{ day}^{-1}$) in the winter, thus showing little seasonal variation. These PCB fluxes are about ten times higher than those measured at Rörvik (0.08 - $0.17 \text{ ng m}^{-2} \text{ day}^{-1}$ in the summer and 0.09 - 0.35

ng m⁻² day⁻¹ in the winter; Swedish EPA, 2002). Occasionally higher deposition rates have been observed previously for the Koster site compared to Rörvik (Brorström-Lundén, 1996). It was hypothesized that these higher fluxes at Koster may be due to local sources in the Norwegian region, combined with air masses being transported southwards, as higher PCB concentrations had been reported in the south of Norway (Oehme et al. 1995). Our measurements do not, however, indicate higher PCB levels in air at Koster than is observed at Rörvik.

3.2.2. *Water-air gaseous exchanges.* The measured concentrations (Table 1) were used to deduce the dissolved water-air transport of individual chemical. The magnitude and direction of air-water exchange processes are controlled by temperature, relative contaminant levels in air and water and the extent of association of POPs with particulate matter in the atmosphere and water column. The air-water exchange is largest for chemicals of low molecular weight with principal occurrence in the gaseous and dissolved phases of air and water. The direction of the gaseous flux is determined by the ratio of the fugacities of a chemical in the two phases (Figure 3). An f_W/f_A ratio >1 indicates net water-air transport and a ratio <1 implies that there is a net deposition of that chemical. If there is a net volatilisation, the flux is represented by a negative sign in Table 2.

[INSERT FIGURE 3]

In the daytime in summer, there is a net volatilisation of both PAHs and PCBs, with highest fluxes observed for the lower molecular weight species such as phenanthrene (280 pmol m⁻² day⁻¹) and PCB 28 (0.7 pmol m⁻² day⁻¹). For compounds of higher

molecular weight, i.e. B(a)P, Per and higher chlorinated PCBs, the fluxes are lower, due to the fact that these chemicals occur almost exclusively in the particulate phase in both air and water. In the winter, there is a net gaseous deposition of all PAHs except for B(a)A from air to water (not for BaA –or do I have an old Figure??), but for the PCBs a net volatilisation flux is observed, albeit of a lower magnitude than is observed in the summer.

The high seasonal variation in air-water gaseous exchanges for PAHs and consistent steady net volatilisation flux for PCBs in this study are identical to results from a study conducted in the northern San Francisco Bay (Tai et al., 2002). The PAHs show a clear diurnal trend in gaseous fluxes consistent with the observed diurnal trend in atmospheric concentrations. For the samples taken at night, the direction of the flux changes for most PAHs with a net gaseous deposition occurring. PCBs, however, show a net volatilisation for both day and night, which could explain why a clear diurnal trend in atmospheric concentrations was not observed for these compounds. It is noteworthy that it is extremely challenging to measure or estimate surface-air exchange fluxes for trace organics such as PCBs. Fluxes are low and slight changes in surface temperatures or meteorology can change the direction of the estimated flux because the compounds in the surface and atmosphere are close to thermodynamic equilibrium (i.e. equifugacity).

3.2.3. ²³⁴Th-derived particle settling rates. Table 3 shows the measured activities and rate constants used in the calculations and Table 2 contains the estimated PCB and PAH fluxes. The calculated PAH fluxes vary, for instance for Pyr, from 50-500 pmol m⁻² day⁻¹ (higher during the night) to 1400 pmol m⁻² day⁻¹ during the winter. For

PCBs the observed range was, for instance, for PCB 52, from 0.2-0.8 in the summer to 2 pmol m⁻² day⁻¹ in the winter. As the settling rate is linearly dependent on the concentration in water particles (See Eq 10), highest fluxes were obtained for compounds occurring in highest concentrations in the settling particles. The reported ²³⁴Th-derived surface water export was compared with ²³⁴Th-derived fluxes reported for the coastal and shelf stations in Gustafsson et al (1997a,b). On their 1994 expedition to the Gulf of Maine, they found average Pyr export fluxes of 1400 pmol m⁻² day⁻¹ (n = 3 locations) and average PCB 52 fluxes of 0.1 pmol m⁻² day⁻¹, which are both of the same order of magnitude as found in this study on the opposite margin of the North Atlantic. Gustafsson and co-workers found order of magnitude higher fluxes in urban waters and order of magnitude lower fluxes in the pelagic North Atlantic (Sargasso Sea), with a steeper drop-off for PAHs than for PCBs.

[INSERT TABLE 3]

3.2.4. Sediment trap settling rates. Sediment trap settling fluxes ranged from 0.63 to 14.2 pmol m⁻² day⁻¹ for PCB compounds and 120 to 760 pmol m⁻² day⁻¹ for PAH compounds.

Sediment trap fluxes of PAHs in the oceans have previously been measured by, among many others, Broman et al. (1988), Näf et al., (1992), Takada et al., (1994), Lipiatou and Sailiot (1991) and Gustafsson et al., (1997a). Vertical Pyr fluxes from these studies vary from 20-24000 pmol m⁻² day⁻¹. A summary of vertical Pyr export fluxes in the marine environment based on available studies using sediment traps, the ²³⁴Th-coupled technique, and ²¹⁰Pb-dated surface sediments demonstrated a global

relationship between flux magnitude and distance to urban source region (Gustafsson et al., 1997a). The sediment trap and ^{234}Th -derived Pyr fluxes in this northeast Skagerak study correspond to a typical “urban source distance” of 30 – 100 km.

Dachs et al. (1996) and Tolosa et al., (1996) measured sediment trap fluxes of PCB-52 in the Mediterranean Sea of $1.5 - 3$ and $1.3 \text{ pmol m}^{-2} \text{ day}^{-1}$, respectively, which are very similar to those recorded in this study of $2.1 \text{ pmol m}^{-2} \text{ day}^{-1}$. PCB sediment trap fluxes for Lake Superior (Baker et al., 1991) are also comparable to this study.

3.2.5. Sediment burial rates. Sediment burial rates were estimated to be between 0.9 and $7.2 \text{ pmol m}^{-2} \text{ day}^{-1}$ for PCB congeners and 910 and $3600 \text{ pmol m}^{-2} \text{ day}^{-1}$ for PAH compounds.

Tolosa et al. (1995, 1996) have previously used sediment cores to calculate burial fluxes of PAHs and PCBs in the NW Mediterranean Sea and estimated fluxes of $1-1790 \text{ } \mu\text{g m}^{-2} \text{ year}^{-1}$ and $0.1-1340 \text{ } \mu\text{g m}^{-2} \text{ year}^{-1}$ for PAHs and PCBs, respectively (individual compound data was not given). The sediment burial fluxes measured in this study converted to the same units are $59-264 \text{ } \mu\text{g m}^{-2} \text{ year}^{-1}$ and $0.13-0.95 \text{ } \mu\text{g m}^{-2} \text{ year}^{-1}$ for PAHs and PCBs respectively, which are at the low end of the fluxes reported by Tolosa and colleagues.

Particle-associated POP settling fluxes in natural waters have previously been measured at different depths in the water column and sediments of both Lake Superior (Baker et al., 1991) and on the western North Atlantic shelf of the Gulf of Maine (Gustafsson et al., 1997a,b). Baker et al. (1991) compared settling fluxes in the water

column of Lake Superior with sediment burial fluxes and found that in some cases settling fluxes of PCBs and PAHs were 10-100 times greater than net accumulation in bottom sediments. It was hypothesized that PCBs and PAHs have a tendency to desorb from sinking particles and recycle in the water column, and that the tendency for desorption is directly related to compound hydrophobicity. Gustafsson found such decreasing fluxes into the bottom sediments relative to water column export fluxes only for the tetra-chlorinated and smaller PCB congeners (Gustafsson et al., 1997b), whereas the fluxes of more hydrophobic PCBs and the PAHs (Gustafsson et al., 1997a) were of equal magnitude in the water column and into the bottom sediments. Here we undertake similar calculations to those of Baker et al. and Gustafsson et al. for the Koster Fjord (Figure 4) by plotting water solubility against the ratio of compound fluxes measured using sediment traps over the fluxes deduced from the ^{234}Th -derived export. In contrast to previous studies (Baker et al., 1991; Gustafsson et al., 1997b), no obvious trend was observed between compound solubility in water and the ratio of the sediment settling fluxes of PCBs and PAHs in the surface ocean and in the sediment traps. However, a median ratio of surface export fluxes/sediment trap fluxes of 2.3 for the PAH compounds and 4.4 for the PCB compounds suggest that some attenuation with depth may be occurring for all these compounds in the Koster Fjord system.

3.3. *Mass balance of measured fluxes*

Having established vertical fluxes for the target POP compounds into or out of the four sequential compartments, “mass balance” vertical flux diagrams were constructed for four selected compounds (PCB-28, PCB-180/193, Phe and B(a)P) for July and February, respectively. The selected compounds represent a low and high

molecular weight compound from each compound class. 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.

[INSERT FIGURE 4]

An important conclusion from this study is that PCB and PAH fluxes in settling particles in surface and deep water and sediment burial fluxes are all remarkably similar. As diverse techniques were employed for measuring the vertical fluxes and the different flux measurement methods were integrated over different time periods, the differences between fluxes could be attributed to a combination of measurement error and natural variability. As discussed previously, there is no evidence for compounds being significantly desorbed from the particles (or degraded) as they sink through the water column.

Balancing atmospheric deposition fluxes with water column fluxes is complicated by the fact that compounds may redistribute between the free form and particle-bound form after deposition to the water surface. However, bulk atmospheric deposition measurements compare remarkably well (median factor of 1.9 lower) to settling particle fluxes for all compounds. There are strong seasonal variations in some flux estimates. For example, a net flux of Phe from water to air from volatilisation is estimated for the July sampling episode, whereas a net deposition flux is estimated in February. However, for all compounds an annual average net flux is shown to occur from air to water to sediment providing evidence that burial in sediments is a sink for

PCBs and PAHs in the atmosphere of this region. There is an estimated net downward flux for the PCBs despite the fact that water/air fugacity ratios are above 1.0 (Figure 3), suggesting that sequestration on particles and subsequent removal by downward transport is a faster transport process than volatilisation in this system.

4. Conclusion

PCB and PAH fluxes in net atmospheric deposition, on settling particles both in surface and deep water, as well as through burial into sediments were shown to be of similar orders of magnitude. 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 the shelf sediments are important sinks for these types of compounds (Jönsson et al., 2003). More empirical studies in which measured particle-settling fluxes of POPs are compared with air-surface exchange processes are needed to evaluate the reliability of predictions from the modelling studies that are being conducted (e.g. Dachs et al., 2002, Wania et al., 2002).

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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
	13 February – 6 March 2001, low volume sampler	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
Atmospheric deposition (ng m ⁻² day ⁻¹)	8-28 July 1999	Wet+dry	50	23	28	3.2	9.4	2.4	0.65	0.18	5.5	5.1	0.34
	13 February – 6 March 2001	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
		Part	22	58	51	5.7	28	4.5	0.047	0.047	0.025	0.13	0.11

28 July 1999, night		Diss.	500	100	190	4.6	1.9	1.7	2.0	1.7	0.31	1.2	0.51
14 February 2001, day*		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
Sediments (ng g⁻¹ dw)	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
Air-water net transport (Bulk deposition plus Water-air transport)	July 8 day	7.3	84	75	-11	37	9.3	1.8	0.29	15	14	0.75
	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
	February	1100	3600	1400	780	910	510	3.9	2.0	15	14	2.2
Sediment traps settling rate	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

Table 3. Radionuclide activities, settling rate constants and mixed layer depths

Sampling date	^{234}Th (dpm m ⁻³)		k_{settle} (d ⁻¹)	Z_{mix} (m)
	Particulate	Dissolved		
8/7/99, day	280 ± 12	1600 ± 140	0.023	30
8/7/99, night	290 ± 5	1400 ± 140	0.062	30
28/7/99, day	200 ± 6	1100 ± 110	0.120	30
14/02/01	330 ± 3	810 ± 9.0	0.054	40

Figure Captions.

Figure 1. Diagram showing the key processes affecting POP transport between the atmosphere, ocean and bottom sediments. (MLD is Mixed Layer Depth)

Figure 2. Map showing the sampling site in the Koster Fjord on the Swedish west coast.

Figure 3. Estimated water/air fugacity ratios in the Koster Fjord.

Figure 4. The ratio of fluxes deposited in sediment traps and fluxes deduced from ^{234}Th -derived export from the overlying surface ocean as a function of solubility in water. Water solubility data for the PAH compounds and PCB congeners was taken from Mackay et al. (1999). The July 1999 sediment trap fluxes were compared to the average of four surface settling rates measured during the same month.

Figures 5a-d. Mass balance diagram of fluxes in $\text{pmol m}^{-2} \text{ day}^{-1}$ for a) PCB-28, b) PCB-180/193, c) phenanthrene and d) 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.