

# Role of Soot Carbon and Other Carbon Matrices in the Distribution of PAHs among Particles, DOC, and the Dissolved Phase in the Effluent and Recipient Waters of an Aluminum Reduction Plant

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The speciation of polycyclic aromatic hydrocarbons (PAHs) in natural waters affects both the chemical fate and the bioavailability of these compounds. PAHs may be dissolved or sorbed to particles or dissolved organic carbon (DOC). Furthermore, soot carbon has recently been shown to control the sorption of PAHs onto particles in natural waters. The present study investigated the distribution of individual PAHs among these three phases by examining the effluent and recipient waters of a Söderberg aluminum plant and evaluating the importance of soot carbon partitioning. The results showed that soot carbon may control partitioning between the dissolved and particulate phases and that the partition coefficients were orders of magnitude higher than would be expected on the basis of organic carbon–water partitioning alone. The carbon-normalized partition coefficient for the distribution of individual PAHs between DOC and the dissolved phase ( $K_{DOC}$ ) exhibited no more than a weak correlation with hydrophobicity ( $K_{OW}$ ) as compared with what was found for the partition coefficients for particles. This indicates that there are different sorption mechanisms at work with DOC than with particulate organic carbon and soot. In the recipient water, up to 90% of the total concentration of individual PAHs was accounted for by a nonfilterable DOC-associated phase, which was not retained by the polyurethane foam (PUF) adsorbent.

## Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous contaminants of urban coastal marine environments. PAHs originate from both natural and anthropogenic sources such as forest fires, releases of combusted and uncombusted petroleum products, and emissions from the metallurgical industry. Due to the carcinogenic and mutagenic potential

of some PAHs (1, 2), they are of serious environmental concern and are considered to be priority pollutants.

The source of a contaminant affects its environmental behavior. Specifically, the initial environmental fate of PAHs derived from oil or noncombusted petroleum products would be expected to differ in terms of speciation from that of PAHs occluded in combustion particles. The physicochemical speciation will ultimately control the transport, fate, and biological availability of PAHs and thereby their environmental effects. Hence, these factors will play a major role in setting PAH discharge limits and for the design and implementation of waste treatment technology.

The production of primary aluminum based on the Söderberg technology represents an important anthropogenic source of combustion-derived PAHs. For example, in Norwegian fjords and coastal waters, concentrations of more than 1000 times background levels have been observed in sediments and organisms in the vicinity of some of these plants (3). The PAH problem is mainly related to the use of coal tar pitch as a binder in the production of ramming paste and anode paste and in the fabrication of anode and cathode blocks. In some cases, it also stems from the production of anodes. The PAHs are released through ventilation air and pot fumes and enter the recipient waters through subsequent seawater scrubbing of the emissions.

Numerous studies have shown a hydrophobicity-dependent particulate partitioning of PAHs between the dissolved and particulate phases in different marine environments (4–6). The equilibrium partitioning of PAHs is generally described by normalizing the distribution coefficient to organic carbon ( $K_{OC}$ ). However, field investigations have reported  $K_{OC}$  values for PAHs of pyrogenic origin to be far higher than predictions based on organic matter partitioning models (6–9). These results suggest the presence of a particulate phase, such as soot, to which PAHs sorb significantly more strongly than to natural organic matter, thereby affecting the environmental speciation and effects of the compounds.

Only a few studies on physicochemical speciation have been conducted in the immediate vicinity of an aluminum smelter. Bjørseth (10) and Thrane (11) suggested that PAHs in smelter effluents occurred both in solution and in association with particles. Næs and Oug (12, 13) reported a seaward shift in the PAH profile in fjord sediments near an aluminum smelter that indicated different particulate size fraction associations of individual PAHs.

Furthermore, PAHs and other hydrophobic compounds have been observed to be sorbed not only by particles but also by nonfilterable organic carbon (14–16). This fraction is normally operationally defined as dissolved organic carbon (DOC) but may contain small molecules, such as amino acids and sugars, to humic acid macromolecular aggregates. The relative sorbing capacities of the different subfractions of DOC have so far only been speculated. In this study, only the entire nonfilterable sorbed fraction of PAH will be considered and will be denoted as the DOC-associated fraction.

The DOC-associated fraction will have different properties than PAHs in the dissolved and particulate forms. DOC-associated PAHs will not be directly subjected to sedimentation in the same way as particles, so they can be transported over longer distances. Furthermore, the DOC will not be bioavailable for direct gill uptake by aquatic organisms in the same way as the dissolved PAHs (15). The overall environmental fate and effect of the released PAHs will

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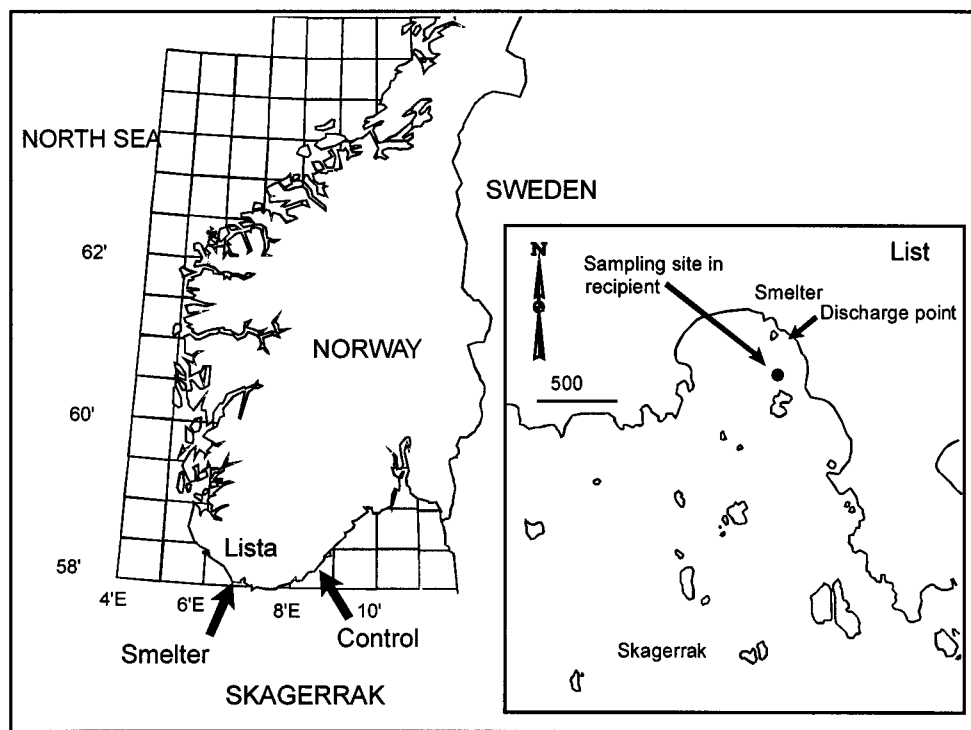


FIGURE 1. Map of the investigation area.

therefore be dependent on the distribution among all three phases.

The objective of the present study was to quantify the distribution of PAHs in the dissolved, DOC-associated, and particulate phases in the effluent and recipient waters of a Söderberg aluminum plant. Recently, a method was developed to separate organic carbon from soot carbon in sediments (17). This method was applied to suspended particles in the present study, making it possible to assess the impact of a stronger sorbing phase than what occurs in natural organic matter in these waters. Thus, the partition coefficients between the dissolved phase and the two sorbed phases (particulate and DOC-associated) could be calculated, and the relative influence of the DOC on the speciation of PAHs in these waters could be shown.

## Materials and Methods

**Sampling Site Characteristics and Water Sampling.** The aluminum smelter at Lista in southern Norway has a production capacity for primary aluminum of 80 000 ton per year based on Söderberg technology. The seawater scrubbers used to clean ventilation air produce an effluent flow of approximately  $9000 \text{ m}^3 \text{ h}^{-1}$ . This volume also includes a small amount of water used for general purposes within the plant. The effluent is piped into the recipient water, an open coastal embayment (Figure 1), at a depth of 1.5 m. Water samples were drawn on three occasions in June 1996 from the effluent and recipient waters ( $58^\circ 04.0' \text{ N}$ ,  $06^\circ 46.3' \text{ E}$ ) and from a control station ( $58^\circ 22.1' \text{ N}$ ,  $08^\circ 40.5' \text{ E}$ ). The control station was situated in coastal waters influenced by general human activities, but by no point sources. The samples from the control and recipient waters were all drawn from a depth of 0.5 m. The samples of the effluent were drawn directly from the pipeline, immediately before the effluent entered the recipient water.

An on-line filtration system was used to collect PAHs (Figure 2). It consisted of precleaned 142 mm i.d. borosilicate glass microfilter (Whatman GF/F) in a stainless steel holder for the retention of particulate matter (nominal cut off  $0.7 \mu\text{m}$ ). It was followed by two polyurethane foam (PUF)

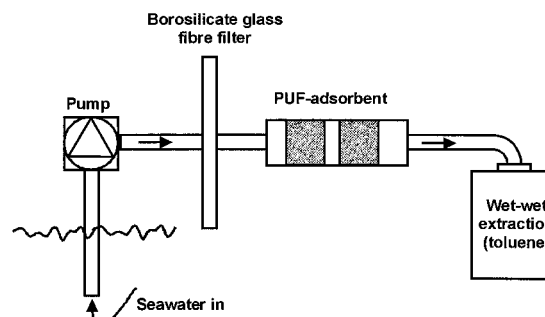


FIGURE 2. Flow diagram of the system used for sampling of the particulate, the dissolved, and the DOC-associated fraction of PAHs.

adsorbents (30 mm diameter, 45 mm length) in stainless steel casing for the control and recipient sites and a glass casing for the effluent water. The PUF is assumed to retain PAHs in the dissolved fraction (18). The filtrate from the PUF adsorbent, containing the DOC-associated fraction, was collected in 5- (for effluent water) or 10-L glass containers, after which toluene (Burdick and Jackson, glass distilled quality) was immediately added to prevent loss of PAHs. Water supply to the on-line filtration system was provided at a flow of  $1 \text{ L min}^{-1}$  by a modified Flojet pump equipped with a silicone tube. Five liter of effluent water, 30 L of recipient water, and 40 L of control station water were pumped through the system at each sampling. The filters, casings, and containers were washed with toluene and heated to  $480^\circ \text{C}$  prior to use.

Water samples were kept dark in sealed containers. Immediately after collection, they were extracted with 50 mL of toluene per liter of sample and spiked with picene and perylene- $d_{12}$  to serve as internal standards. They were subsequently shaken for 24 h and then left for phase separation for another 24 h. Most of the seawater was siphoned off, and the remaining solution was kept cool ( $4^\circ \text{C}$ ) until analysis. Filters and PUF adsorbents were stored frozen at  $-20^\circ \text{C}$  prior to chemical analysis.

From each of the 142-mm filters, four subsamples (16 mm i.d.) were drawn to determine total particulate carbon

(PC), particulate organic carbon (POC), and particulate soot carbon (PSC). Samples were also taken to determine DOC concentrations. Filters were stored in a frozen state, and filtrates were stored at +4 °C.

**Chemical Analysis.** The following PAHs (abbreviations in parentheses) were analyzed: phenanthrene (Phe), anthracene (Ant), 3-methylphenanthrene (3-mePhe), 1-methylphenanthrene (1-mePhe), fluoranthene (Flu), pyrene (Pyr), 2-methylpyrene (2-mePyr), 1-methylpyrene (1-mePyr), benzo[ghi]fluoranthene (B[ghi]F), cyclopenta[cd]pyrene (Cp[cd]P), benzo[a]anthracene (B[a]A), chrysene (Chr), benzo[k]fluoranthene (B[k]F), benzo[e]pyrene (B[e]P), benzo[a]pyrene (B[a]P), perylene (Per), indeno[1,2,3-cd]pyrene (Ind), benzo[ghi]perylene (B[ghi]P), and coronene (Cor). Filters and PUF adsorbents were spiked with two PAHs (perylene- $d_{12}$  and picene) and then Soxhlet extracted for 24 h in toluene with a Dean–Stark trap for water removal. Water was removed from the liquid–liquid extracts with precombusted  $\text{Na}_2\text{SO}_4$ . The volume-reduced extracts of all the samples were treated by a dimethylformamide (DMF) cleanup procedure. The hexane solution containing the PAHs was then finally eluted on  $100 \times 10$  mm columns containing deactivated  $\text{SiO}_2$  (10% water w/w) with hexane as the mobile phase. The extracts were analyzed on a gas chromatograph/mass spectrometer (Hewlett-Packard 5890/5971A). Response factors and retention times were determined by analyzing a standard mixture containing all the PAH compounds analyzed, including the internal standards. This mixture was extracted and cleaned up following the same procedure as the samples. All the solvents used (toluene and hexane; Burdick & Jackson; pentane; Merck) were of glass distilled quality. Blanks were found to contain nondetectable amounts of high molecular weight ( $W_m$ ) PAHs and negligible amounts of low  $W_m$  PAHs in relation to the amounts found in the samples.

**Particulate Carbon and Dissolved Organic Carbon.** Prior to the analyses, the filters for particulate carbon analyses were treated with HCl vapor to remove inorganic carbonates. Thermal oxidation in an excess of air at 375 °C for 24 h removed POC from the filters. The remaining carbon was thereby soot-like carbon (PSC). This method has been shown quantitatively to separate the two carbon fractions in particulate standard matrixes and in sediments (17). It has, however, not previously been applied on suspended particles. The filters were analyzed on a CHN element analyzer (Carlo Erba CHN). The total particulate carbon (PC) was determined from the nontreated filters. POC was determined from the carbon content difference between the thermally treated filters and the nontreated filters. DOC samplers were acidified and determined using a Dohrman TOC analyzer.

## Results and Discussion

**Total Concentrations.** The average sums of the concentrations in all three phases [filter ( $C_{\text{filter}}$ ), PUF ( $C_{\text{PUF}}$ ), and liquid–liquid extraction ( $C_{\text{wet}}$ ),  $C_{\text{tot}}$ , at the three locations are presented in Figure 3. However, at the control location, the filtered volume was too small to accurately quantify the high molecular weight PAHs. The dilution factor from the effluent to the recipient was  $34 \pm 23$  and did not correlate with hydrophobicity ( $\log K_{\text{ow}}$ , values taken from ref 19) ( $r^2 = 0.0408$ ,  $p < 0.20$ ), indicating that the only process involved was the mixing of water, which is a process that affects all three phases equally. Any process significantly affecting a specific phase, such as the sedimentation of particles, would result in a dilution factor that correlates with hydrophobicity. The total concentrations at the control station were almost 3 orders of magnitude lower than in the recipient area, showing that the PAH load deposited in the recipient water by this aluminum smelter is substantial.

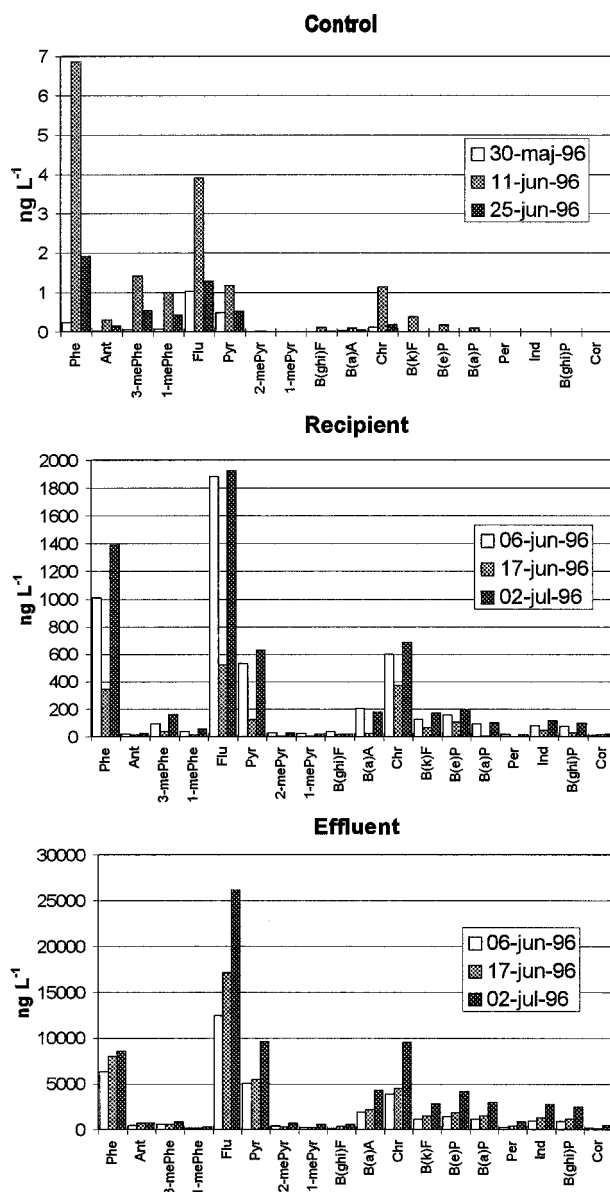


FIGURE 3. Total concentrations (sum of all three phases) of individual PAHs in the waters at the three different sampling locations.

**Relative Distribution of the Three Phases Collected with Filters, PUF Adsorbent, and Wet Extraction.** The relative distribution between particles, DOC, and the dissolved phase differed significantly between effluent and recipient waters. However, for each station individually the relative distribution between the phases was similar at all three sampling events (Figure 4). The variation in distribution during the different sampling occasions could not be evaluated at the control station because it was only possible to detect a few of the compounds in all three phases. The relative distribution for this station is therefore based on the total data available from all sampling occasions (Figure 4).

The pattern in the recipient waters differed from both the effluent and the control sites. It appears that the DOC in the recipient waters has a much higher sorbing capacity than the DOC at the other two locations (see also the section on partition coefficients below). The DOC concentrations were relatively similar at both locations (Figure 5), so the relative amount of the sorbing phase cannot account for the difference.

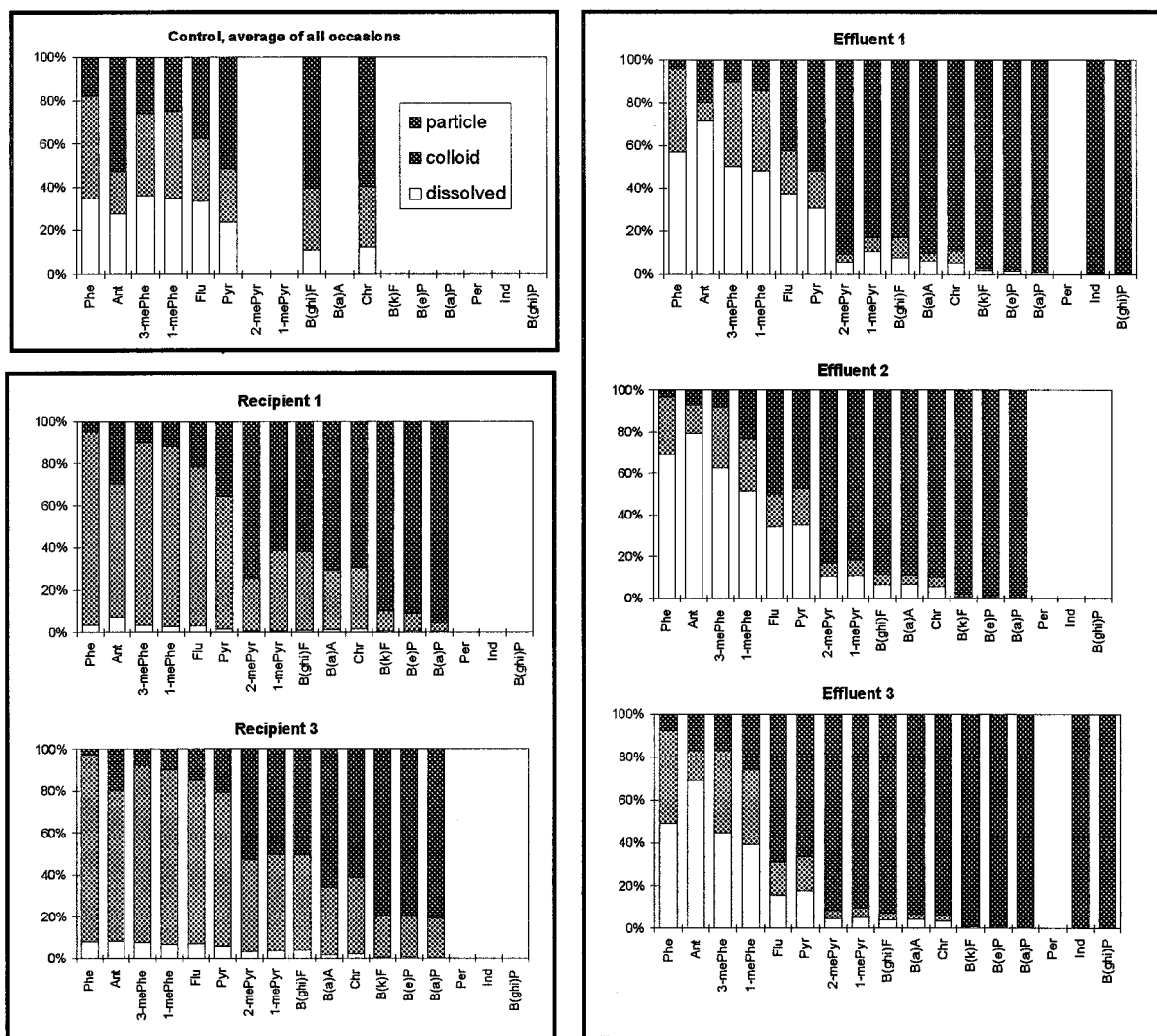


FIGURE 4. Relative distribution of individual PAHs between the three phases: dissolved, DOC-associated, and particulate. Only a few PAHs could be detected in all three phases at the control site, so all three sampling occasions were combined. On sampling occasion 2, the filter at the recipient station was damaged, so a significant portion of the particulate fraction was retained by the PUF adsorbent. These data were therefore excluded from this graph.

In regard to the recipient water, the results also indicate that the DOC-bound fraction is the dominating pool for PAHs with low  $W_m$ . A total of 60–90% of the low  $W_m$  PAHs and 10–30% of the high  $W_m$  PAHs passed through the filters and PUF adsorbent. This may have significant implications for the choice of sampling methods used to determine contaminant concentrations. In the event that only a few low  $W_m$  PAHs are selected for screening and conventional filter and PUF sampling techniques are used,  $C_{tot}$  could be underestimated by an order of magnitude.

**Partition Coefficients: Dissolved Phase—Particles.** It has been suggested that the partitioning of PAHs between particles and water in the aquatic environment is controlled by soot carbon rather than by organic carbon. This implies higher partition coefficients than those observed between organic carbon and water (9). In the present study, the partition coefficients were orders of magnitude higher than would be expected from the empirically derived relationship between  $\log K_{ow}$  and  $\log K_{oc}$ . The use of coal tar pitch in the Söderberg process implies that soot-like structures, i.e., large aromatic structures (20), may be released with the effluent water. Although the variation is high in the PSC analysis of the effluent and recipient waters, the results still imply that a large fraction of the total particulate organic carbon (PC) in these waters is not POC. Karickhoff (21) derived an

empirical relationship between  $\log K_{ow}$  and  $\log K_{oc}$ :

$$\log K_{oc} = \log K_{ow} - 0.39 \quad (1)$$

A method to estimate the partition coefficient of individual PAHs for the water to soot carbon partitioning ( $K_{sc}$ ) has been described by Gustafsson and Gschwend (9). This method takes the specific molecular sorbing mechanisms between soot and PAHs into account:

$$\log K_{sc} = \log \gamma_w - \log \gamma_s + \log (V_w/A_s) + \frac{\Delta S_\phi}{2.3R(T_m/T - 1)} \quad (2)$$

where  $\gamma_w$  and  $\gamma_s$  are the activity coefficients of the molecule in water and in the sorbed state at the soot surface, respectively;  $V_w$  is the molar volume of water;  $A_s$  is the specific area of soot carbon;  $\Delta S_\phi$  is the entropy of the phase transfer of the molecule;  $R$  is the gas constant;  $T_m$  is the melting point of the molecule; and  $T$  is the temperature of the system (approximately 10 °C in this study).  $\gamma_w$  is dependent on the subcooled liquid solubility in water ( $^{sat}C_L$ ). The sorption of a PAH onto soot is assumed to be thermodynamically similar to the association of a PAH with a pure PAH crystal (9).  $\gamma_s$  is therefore 1.  $K_{sc}$  was calculated for all PAHs in this study except B(ghi)F and Ind, for which no estimates of  $T_m$  and

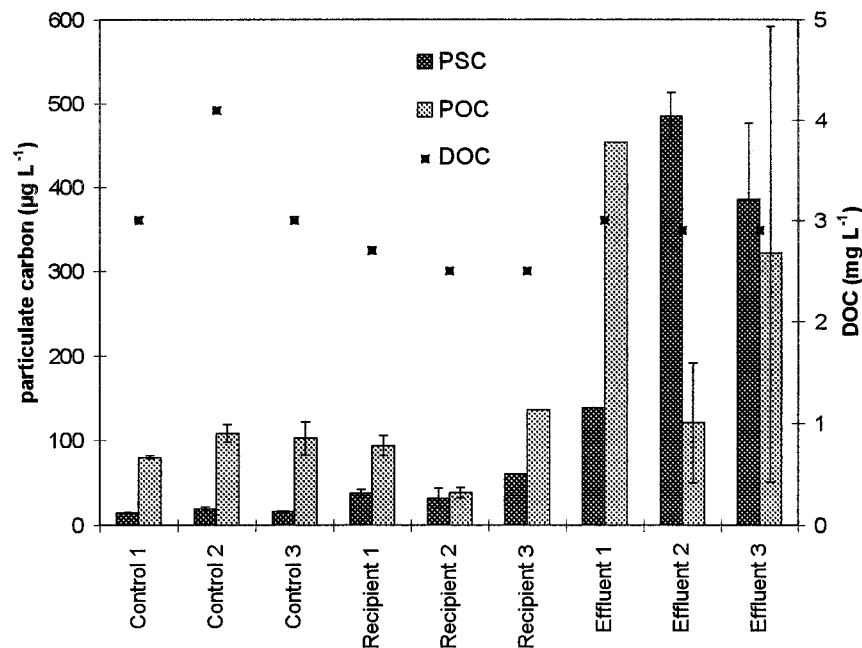


FIGURE 5. Concentrations of particulate soot-like carbon, particulate organic carbon, and dissolved organic carbon at the different locations on all three sampling occasions. The error bars indicate standard errors.

$^{sat}C_L$  was found. Literature values for  $^{sat}C_L$  and  $T_m$  was taken from Miller et al. (22), and literature values for PAHs not included in that study were from Mackay et al. (18). The addition of a methyl group (in the 9 position) to anthracene was found to give a 70% decrease in  $^{sat}C_L$  and a 135 K decrease in  $T_m$  (23). These effects were applied to the literature values of  $^{sat}C_L$  and  $T_m$  for Phe and Pyr to roughly calculate  $K_{sc}$  (also for the methylated PAHs included in this study).

Assuming that Karickhoff's relationship was derived for organic carbon, it is possible to assess the relative influence of the partitioning of these two phases. Using the fractions of PSC ( $f_{PSC}$ ) and the fraction of POC ( $f_{POC}$ ) of the total sorbing matrix PC, the total partition coefficient ( $^{est}K_c$ ), may be calculated by the following equation (17):

$$^{est}K_c = f_{POC}K_{oc} + f_{PSC}K_{sc} \quad (3)$$

The observed partition coefficient ( $\log^{obs}K_c$ ) exhibits a strong positive linear correlation with  $\log K_{ow}$  in the effluent and recipient waters, with slopes of 1.8 for the effluent ( $r^2 = 0.87$ ,  $p < 0.001$ ) and 1.4 for the recipient ( $r^2 = 0.62$ ,  $p < 0.001$ ). The slope was  $<1$  in the control water. However, this estimate was uncertain ( $r^2 = 0.30$ ,  $p < 0.10$ ). Both the slopes of the regression lines and  $^{obs}K_c$  values themselves were significantly higher than would be expected from the findings of Karickhoff (21) and Gustafsson et al. (17). An underestimated dissolved fraction could have caused such an effect. However, the PUF adsorbent has been thoroughly evaluated and found to efficiently trap dissolved hydrophobic compounds from seawater. The volumes sampled in the present study were far too small for any filtration breakthrough to occur (18).

The  $^{obs}K_c$  values of all PAHs lie much closer to  $^{est}K_c$  than to the coefficient based solely on organic carbon partitioning (eq 1; Figure 6). The term  $f_{sc}K_{sc}$  in eq 3 is the largest, and considering the observed partition coefficients, it appears that eq 3 is better suited than eq 1 to the partitioning of the particulate matter in these waters. The  $^{obs}K_c$  values are lower in the effluent water than in the other two types of water. The differences in average  $f_{PSC}$ , which ranged from 0.15 to 0.63, are not large enough to explain this discrepancy. It is evident from the dilution factors that most of the PSC in the recipient water did not originate from the effluent water. On

the contrary, it is most probably long-range, air-transported soot carbon and/or air emissions of coal tar volatiles that have emanated from the plant. The PSC measured in the effluent water might therefore differ in terms of sorbing capacity from the atmospherically deposited PSC at the recipient and control stations.

**Partition Coefficients: Dissolved Phase—DOC.** By normalizing the fraction of PAHs to the DOC concentrations at the various locations, it is possible to determine the partition coefficients for the distribution between the truly dissolved fraction and the DOC-associated fraction,  $K_{DOC}$ . Plots of the observed  $\log K_{DOC}$  vs  $\log K_{ow}$  are given in Figure 7. Using new techniques that avoid the problems of phase separation, Gustafsson (23) recently showed that, based on carbon mass, the capacity of marine DOC to sorb hydrophobic compounds is lower than that of other carbon matrixes. Gustafsson (23) reported a  $\log K_{DOC}$  of 5.3 for methylperylene (a PAH component not included in this study), which has a  $\log K_{ow}$  of 6.9 (based on ref 24). The present study's measurements of benzo[a]pyrene ( $\log K_{ow} = 6.20$ ) gave an average  $\log K_{DOC}$  of 5.1 in the effluent water and 7.1 in the recipient water. Benzo[a]pyrene was not detected in any of the three phases at the control station. The most hydrophobic PAH for which a  $\log K_{DOC}$  could be estimated at the control station was chrysene ( $\log K_{ow} = 5.86$ ) for which the average  $\log K_{DOC}$  was 5.7. If the PUFs also trap the DOC-associated fraction of PAH, the true  $K_{DOC}$  values would be significantly higher than the measured ones. Considering that our measured  $K_{DOC}$  values were equal to or even higher than those reported by Gustafsson (23), this appears unlikely. This supports the assumption that PUFs exclusively trap the dissolved phase.

Interestingly, no correlation could be detected between hydrophobicity and  $K_{DOC}$  in the effluent and control waters (Figure 7). On the other hand, a significant correlation was found in the recipient water ( $r^2 = 0.58$ ,  $p < 0.001$ ), although the slope of the regression line was only 0.15 (Figure 7). If the sorption mechanism for DOC is the same as has been observed for organic pools of particles, it would be reasonable to expect a positive correlation between  $\log K_{ow}$  and  $\log K_{DOC}$  with the slope of the regression line near 1 (21). In this study, all  $\log K_{DOC}$  values for the control and effluent waters were within 1.5 log units (4.5–5.9), except for a single value of 6.3.

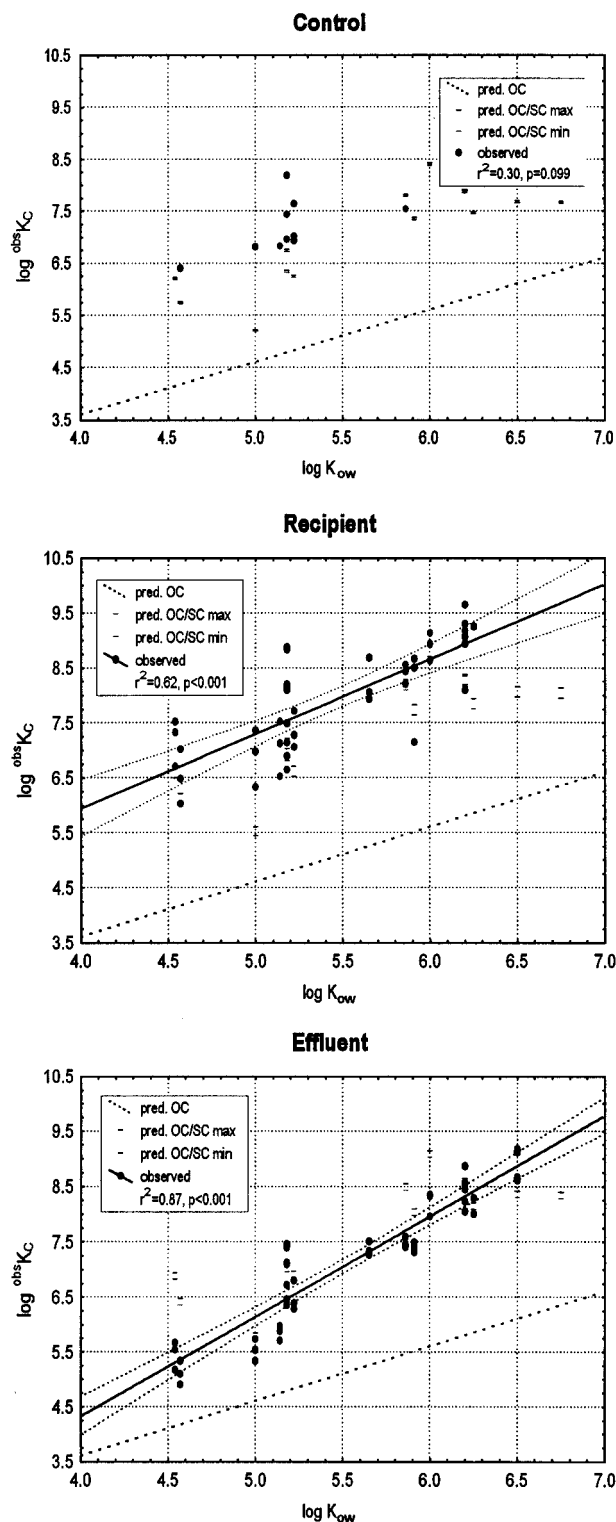


FIGURE 6. Logarithm of the observed partition coefficients ( $\log_{obs} K_c$ ) of individual PAHs plotted against the respective  $\log K_{ow}$ . The linear regression lines with 95% confidence bands have also been plotted. The predicted relationship between  $\log K_{ow}$  and  $\log K_c$  based solely on organic carbon partitioning (predicted OC) and based on both soot carbon and organic carbon (predicted SC and OC). The SC and OC prediction is stated as a range that takes the uncertainties in the PSC and POC measurements into account.

Similarly, there was a narrow range for all observed  $K_{DOC}$  values (6.6–7.7) in the recipient waters. In other words, the low dependence on hydrophobicity was similar for all locations, but the absolute values differed greatly. As pointed

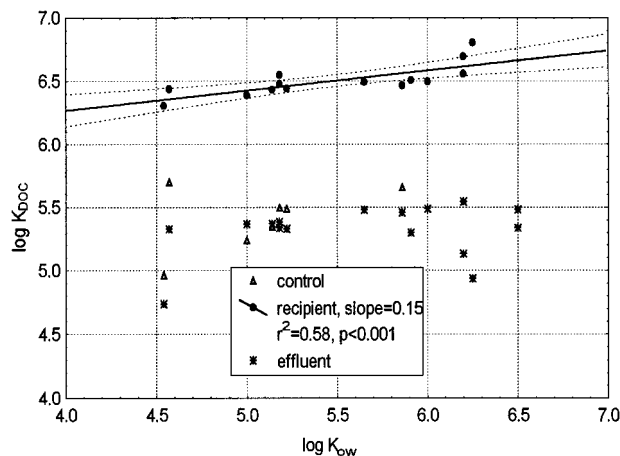


FIGURE 7. Observed  $K_{DOC}$  for individual PAHs at the three different sampling locations. The  $K_{DOC}$  values of the individual PAHs are averages from the different sampling occasions.

out, in the recipient water the DOC appears to have a very high sorbing capacity for PAHs. The reasons for these differences can only be speculated. The difference for the effluent can possibly be explained by the fact that there were very high concentrations of PAHs in the effluent water. The concentration of dissolved  $\Sigma$ PAH was 10–15  $\mu\text{g L}^{-1}$ , which in fact is as much as 0.5% of the total concentration of dissolved organic carbon. Considering that only part of the DOC is available for partitioning, it is possible that saturation effects may occur. The lower  $K_{DOC}$  in the effluent water could thus be caused by the fact that the most favorable sorbing sites at the DOC are saturated. However, this would still leave the difference between the recipient and control site unexplained.

The low dependence observed in this study of  $\log K_{DOC}$  on hydrophobicity indicates that DOC and particles have different sorption mechanisms. One possible explanation is as follows: The molecules in natural DOC are often small, with the largest mass fraction having molecular weights lower than 30 kDa, of which a large part are  $W_m < 1$  kDa (25). This may imply that the sites at which the PAHs can associate are also small in size. The decrease in aqueous solubility with increasing  $W_m$  that normally is accompanied by increasing hydrophobicity could, in the case of DOC, thus lead to a decreased compatibility with the small binding sites. As a result, an increase in  $\log K_{ow}$  will not result in the expected increase in  $\log K_{DOC}$ .

Again, there is a possibility that an unknown volume of the very small particles containing PAHs pass through the GF/F filters and are collected by the PUF. If there actually were a significant relationship between  $\log K_{ow}$  and  $\log K_{DOC}$ , these particles would lower the slope, since the particle's relative content of PAH would increase with increasing  $\log K_{ow}$ . In that case, the observed noncorrelation would be the result of a sampling error. However, that would mean that the  $obs K_c$  in the previous section, which also was based on  $C_{PUF}$ , would then also be too low. Moreover, the slope of the correlation between  $\log K_{ow}$  and  $\log K_c$  in the effluent and recipient waters would be higher. Considering that the observed slopes were already higher (1.8 and 1.4, respectively) than the frequently observed one-to-one relationship (e.g., ref 21) and that the partition coefficients were also high, a significant sampling error of that kind appears unlikely. Since the partition coefficients for the two phases were calculated from the same dissolved concentrations, the differences in terms of sorption mechanisms between particles and DOC would still be present in all three locations, regardless of the accuracy of the  $C_{PUF}$ .

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