A novel method for estimating sediment resuspension using stable carbon isotopes of individual compounds

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Introduction

The gravitational settling of particulate matter (SPM) is probably the major pathway of particles from the surface waters down to the sediments. This deposition, or flux, is important to estimate for mass balance calculations, since the sediments often serve as a sink for organic compounds like polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins (PCDDs) in the environment, through burial, mineralisation, etc. Sediment traps are commonly used to study the fluxes needed to estimate such deposition (1-9). The material collected in the traps comprises a mixture of primary settling matter, i.e. material which has not been in contact with the sediment, and resuspended sediment matter. An estimation of the magnitude of the resuspended fraction is essential for estimation of net fluxes, which are used for mass balance calculation, budgets, etc. The resuspension has previously been studied with the aid of sedimentary markers such as chlorophyll (10), sedimentary organisms (11) or bedrock elements (12), and by using a vertical gradient of sediment traps (9,13).

In this study, a method for estimation of resuspension is presented. The method is based on stable carbon isotope values of perylene and some polycyclic aromatic hydrocarbons (PAHs). Perylene is produced *in situ* in sediments (14-16). As this additional diagenetic source of perylene has a different formation path than has the perylene formed by anthropogenic processes such as combustion, it is likely that the signature of stable carbon isotopes must differ between perylene formed in sediments and in anthropogenic processes, due to isotopic fractionation processes (17-19). This fractionation has two causes; a bond involving a heavier carbon atom is stronger, and a compound with heavy carbon atoms is less mobile. The perylene found in sediment traps originates from anthropogenic sources through primary settling matter or from resuspension of surface sediments. While the primary input can be considered as originating from anthropogenic sources only, the resuspended perylene consists of both previously deposited anthropogenic perylene and perylene produced biogenically in the sediments.

The stable carbon isotope composition can be studied using gas chromatography - combustion - isotope ratio mass spectrometry (GC/C/IRMS), which facilitates determination of stable isotope ratios of individual, GC-separated compounds. The method was initially described in the late 1970's (20) and refined and further developed by Matthews and Hayes (21). The conventional single collector MS operating in selective ion monitoring (SIM) mode was replaced by a dedicated IRMS (22,23) and today, ten years after the advent of commercial systems, the applications of GC/C/IRMS are rapidly growing (24,25).

Materials and Methods
Sediment traps of a self-buoyant design (26) were deployed in the vicinity of Stockholm, Sweden, with chloroform as preservative. The water depth at the location was 45 m and the traps were placed 1, 20 and 35 m above the sediment surface. The traps were deployed during two periods; one covering a stratified summer period with low resuspension, and one covering a non-stratified autumn period with high resuspension (Table 1).

After recovery, evaporation of the chloroform and addition of 2,2'-dinaphtyl as internal standard, the samples were extracted wet with toluene for 24 h in pre-washed cellulose thimbles using a Soxhlet setup with a Dean-Stark trap for water removal (27). The extracts were volume reduced and eluted with hexane through a SiO_2 column (10 mm i.d. × 100 mm) 10% deactivated with water (28), followed by separation using a liquid-liquid phase extraction method (29), and further cleaned on a SiO_2 column (5 mm i.d. × 30 mm).

Analysis was performed using a Hewlett-Packard™ (HP) 5890 Series II GC (Supelco™ 30m x 0.25mm x 0.25μm PTE-5 fused silica capillary column) coupled to a Micromass™ Optima isotope ratio mass spectrometer (IRMS) via a Micromass™ Isochrom III combustion interface. Injections were made in splitless mode. Isotopic calibration was performed by adding an additional internal standard (*para*-quarterphenyl), which, together with the 2,2'-dinaphtyl, had a known isotopic composition, to the samples prior to injection. Obtained values were corrected using the internal standards. Isotopic ratios, $\delta^{13}C$ values, were calculated for benzo[e]pyrene (BeP), benzo[a]pyrene (BaP) and perylene (Per). $\delta^{13}C$ was calculated as:

$$\delta^{13}C\ (\text{‰}) = (R_{sample}/R_{standard} - 1)10^3 \qquad (1)$$

where R is the ratio $^{13}C/^{12}C$. The results are given according to the international Pee Dee Belemnite scale (PDB), with Craig corrections for oxygen (30).

Results and Discussion
If the sources of perylene would be the same as for the other PAHs, we could expect the perylene $\delta^{13}C$ to be within the range of the $\delta^{13}C$ of the other PAHs, or more specific close to the other compounds with mw 252 and five benzene rings (i.e. BeP and BaP). This was verified on samples from combustion of wood and fossil fuels, where the Perylene differed less than 0.2 $\delta^{13}C$ units from that of the other mw 252 compounds. Since the measured values were more than one per mil lower than any of the other PAHs in the lower traps, we must have another source of perylene to the SPM in this area.

The biogenic formation of PAHs has been suggested as a aromatization process of triterpenoids (31), and the triterpenoids in turn suggested to be formed from C_{27-33} *n*-alkanes

Table 1. The SPM samples used, with the anthropogenic- and measured $\delta^{13}C$ for perylene, and the calculated degree of resuspended material in the traps.

Sediment trap		Perylene in sediment trap		
Deployment	From bottom *m*	Antropogenic *calculated* $\delta^{13}C$	Actual *measured* $\delta^{13}C$	Biogenic %
13/7/96-10/9/96	20	-26.7	-27.0	12
- " -	1	-25.3	-26.8	34
10/9/96-3/12/96	35	-26.2	-26.7	15
- " -	20	-25.2	-26.7	34
- " -	1	-25.1	-26.4	30

(32). The formation of triterpenoids from *n*-alkanes gives a rise in $\delta^{13}C$ of approx. 1.5‰ (19), whereas the aromatization of triterpenoids does not include any significant isotopic changes (33). Thus, having $\delta^{13}C$ values of sedimentary *n*-alkanes or triterpenoids, the expected $\delta^{13}C$ for biogenically produced PAHs such as perylene can be calculated. Using this reasoning and an average C_{27-33} *n*-alkane $\delta^{13}C$ value of -31‰ from marine literature data (34-37), we can approximate a $\delta^{13}C$ value of -29.5‰ for biogenetically produced perylene. By using the average $\delta^{13}C$ values for perylene, the anthropogenic values calculated as the average between BeP and BaP and the biogenic value estimated from literature data, a simple linear mixing model can be used to assess the fraction of perylene in the sediment traps that is of biogenic origin:

$$\text{Biogenic perylene in traps (\%)} = 100(\delta_M - \delta_A)/(\delta_B - \delta_A) \qquad (2)$$

where δ_M is the observed $\delta^{13}C$ of perylene in the trap, δ_A the estimated $\delta^{13}C$ of anthropogenic perylene, and δ_B the estimated $\delta^{13}C$ of biogenic perylene (32). The results, presented in Table 1, show that in the traps closest to the bottom, a resuspension of approx. 30% is prevailing all year round. During the first period, Jul-Sep, when the water is stratified, the resuspension is lower higher up in the water mass. The second period, Sep-Dec, shows no difference in resuspension between the two lower traps, indicating a high degree of resuspension due to the lack of stratification of the water. A decrease in resuspension is however observed for the topmost trap.

As described, this method is not capable of differentiating between the biogenically- and anthropogenically produced perylene introduced into the traps by resuspension. In studies where the purpose is to estimate fluxes down to the sediments, it is still important to make a correct placement of the traps, i.e. as far from the bottom as possible but still below the productive zone. Care also has to be taken while using this method for particles in general or other compounds than perylene, depending on their different degree of association with particles. This must be investigated further by studying the correlations between perylene and compounds like PCBs and PCDDs in sediment traps.

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