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THE USE OF DATA AND MODELS FOR ASSESSING THE EQUILIBRIUM PARTITIONING APPROACH FOR ANALYSING ENVIRONMENTAL QUALITY STANDARDS IN THE WATER COLUMN AND IN THE SEDIMENTS

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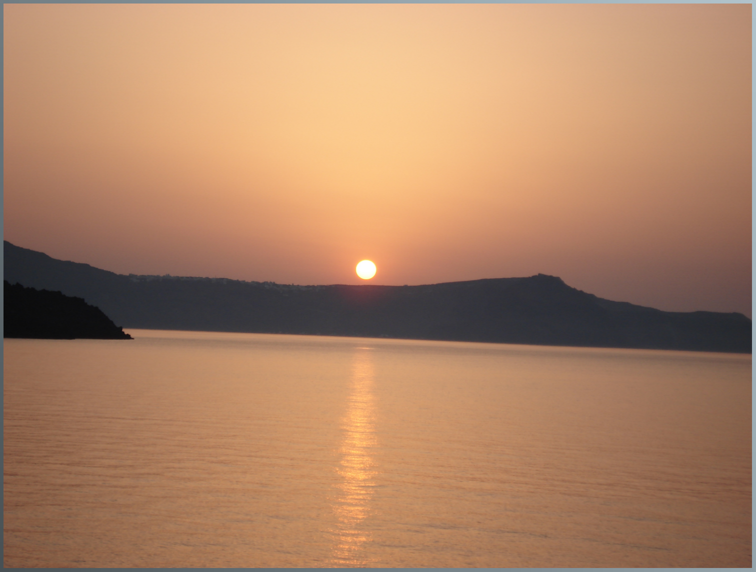

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1. INTRODUCTION

Article 16 of the Water Framework Directive (EC 2000) mandates the European Commission (EC) to select priority substances (PS) and identify priority hazardous substances (PHS) with a provision to review the list of PS at the latest four years after the entry into force of the WFD. Furthermore, the EC has to propose measures to control and reduce point and diffuse sources for the progressive reduction of PS and the cessation of PHS within 20 years after the adoption of the EC proposal. In addition quality standards applicable to the PS concentrations in surface water, sediments and biota have to be developed.

In 2001, a list of PS was adopted (Decision 2455/2001/EC) identifying 33 substances of priority concern at EU level, including a subset of PHS (11 and 14 as 'PS under review' for possible classification as PHS) that require the cessation or phase-out of discharges, emissions and losses within 20 years of adopting measures for that purpose.

A proposed Daughter Directive (COM (2006) 397) was developed by the EC and published in July 2006 in order to comply with the requirements of Article 16 of the WFD. The Directive has two objectives:

- to ensure a high level of protection of the aquatic environment by setting environmental quality standards (EQS) for the PS and certain other pollutants;
- to define good chemical status in surface water bodies through compliance with EQS.

Environmental Quality Standards (EQS) are concentrations of pollutants which should not be exceeded in order to protect human health and the environment (COM (2006) 397). There were already defined EQS at community level, also most Member States had their own EQS. However, all these EQS varied considerably across the EU. Therefore the EC decided to harmonise the EQS values based on toxicity and ecotoxicity data as well as bioaccumulation potential, environmental contamination and human risk. The EQS were derived from aquatic NOEC (No observed effect concentration) data (Lepper, 2005).

Finally, the 33 identified substances of priority concern were classified as follows:

- Priority substances (PS): Alachlor, atrazine, benzene, chlorofenvinphos, chloropyrifos, 1,2-dichloroethane, dichloromethane, di(2-ethylhexyl)phthalate (DEHP), diuron, fluoranthene, isoproturon, lead and compounds, naphthalene, nickel and compounds, octylphenol, pentachlorophenol, simazine, trichlorobenzenes, trichloromethane and trifluralin.

- Priority Hazardous Substances (PHS): Anthracene, brominated diphenylether (PentaDBE), cadmium and compounds, chloroalkanes (C_{10-13}), endosulfan, hexachlorobenzene, hexachlorobutadiene, hexachlorocyclohexane, mercury and compounds, nonylphenols, pentachlorobenzene, polyaromatic hydrocarbons (PAHs)[1] and tributylin (TBT) compounds.

1.1. Environmental Quality Standards for Priority Substances in surface water

The established EQS for the priority substances list taken from the Directive proposal have been summarized bellow. The units are in µg/l and refer to the total concentrations in the whole water sample; AA refers to Annual average and MAC to maximum allowable concentration. In the case of metals the EQS refers to the dissolved concentration, i.e. the dissolved phase of a water sample obtained by filtration through a 0.45 µm filter or any equivalent pre-treatment.

Name of substance	**AA-EQS Inland surface waters**	**AA-EQS Other surface waters**	**MAC- EQS Inland surface waters**	**MAC-EQS Other surface waters**
Alachlor	0.3	0.3	0.7	0.7
Anthracene	0.1	0.1	0.4	0.4
Atrazine	0.6	0.6	2.0	2.0
Benzene	10	8	50	50
Pentabromodiphenylether	0.0005	0.0002	*not applicable*	*not applicable*
Cadmium and its compounds *(depending on water hardness classes[2])*	≤ 0.08 (Class 1) 0.08 (Class 2) 0.09 (Class 3) 0.15 (Class 4) 0.25 (Class 5)	0.2	≤ 0.45 (Class 1) 0.45 (Class 2) 0.6 (Class 3) 0.9 (Class 4) 1.5 (Class 5)	
C10-13 Chloroalkanes	0.4	0.4	1.4	1.4
Chlorfenvinphos	0.1	0.1	0.3	0.3
Chlorpyrifos	0.03	0.03	0.1	0.1
1,2-Dichloroethane	10	10	*not applicable*	*not applicable*
Dichloromethane	20	20	*not applicable*	*not applicable*
Di(2-ethylhexyl)phthalate (DEHP)	1.3	1.3	*not applicable*	*not applicable*
Diuron	0.2	0.2	1.8	1.8
Endosulfan	0.005	0.0005	0.01	0.004
Fluoranthene	0.1	0.1	1	1
Hexachlorobenzene	0.01	0.01	0.05	0.05
Hexachlorobutadiene	0.1	0.1	0.6	0.6
Hexachlorocyclohexane	0.02	0.002	0.04	0.02
Isoproturon	0.3	0.3	1.0	1.0
Lead and its compounds	7.2	7.2	*not applicable*	*not applicable*
Mercury and its compounds	0.05	0.05	0.07	0.07
Naphthalene	2.4	1.2	*not applicable*	*not applicable*
Nickel and its compounds	20	20	*not applicable*	*not applicable*

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[1] Benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene,benzo[g,h,i]perylene, indeno[1,2,3-cd]pyrene

[2] For Cadmium and its compounds (No. 6) the EQS values vary dependent upon the hardness of the water as specified in five class categories (Class 1: <40 mg $CaCO_3$/l, Class 2: 40 to <50 mg $CaCO_3$/l, Class 3: 50 to <100 mg $CaCO_3$/l, Class 4: 100 to <200 mg $CaCO_3$/l and Class 5: ≥200 mg $CaCO_3$/l).

Nonylphenol	0.3	0.3	2.0	2.0
Octylphenol	0.1	0.01	*not applicable*	*not applicable*
Pentachlorobenzene	0.007	0.0007	*not applicable*	*not applicable*
Pentachlorophenol	0.4	0.4	1	1
Polyaromatic hydrocarbons (PAH)[3]	*not applicable*	*not applicable*	*not applicable*	*not applicable*
Benzo(a)pyrene	0.05	0.05	0.1	0.1
Benzo(b)fluoranthene	$\Sigma=0.03$	$\Sigma=0.03$	*not applicable*	*not applicable*
Benzo(k)fluoranthene				
Benzo(g,h,i)perylene	$\Sigma=0.002$	$\Sigma=0.002$	*not applicable*	*not applicable*
Indeno(1,2,3-cd)pyrene				
Simazine	1	1	4	4
Tributyltin compounds	0.0002	0.0002	0.0015	0.0015
Trichlorobenzenes (all isomers)	0.4	0.4	*not applicable*	*not applicable*
Trichloromethane	2.5	2.5	*not applicable*	*not applicable*
Trifluralin	0.03	0.03	*not applicable*	*not applicable*

Member States shall ensure that the following concentrations of hexachlorobenzene, hexachlorobutadiene and mercury are not exceeded in prey tissue (wet weight) of fish, molluscs, crustaceans and other biota:

a) 10 µg/kg for hexachlorobenzene,
b) 55 µg/kg for hexachlorobutadiene,
c) 20 µg/kg for methyl-mercury.

The discussions on lead, nickel and their compounds on the risk assessment have not yet been finalized. Therefore the proposed values are provisional.

1.2. Environmental Quality Standards (EQS) for other Pollutants

Name of substance	**AA-EQS Inland surface waters**	**AA-EQS Other surface waters**	**MAC- EQS Inland surface waters**	**MAC-EQS Other surface waters**
DDT total[4]	0.025	0.025	*not applicable*	*not applicable*
para-para-DDT	0.01	0.01	*not applicable*	*not applicable*
Aldrin	$\Sigma=0.010$	$\Sigma=0.005$	*not applicable*	*not applicable*
Dieldrin				
Endrin				
Isodrin				
Carbontetrachloride	12	12	*not applicable*	*not applicable*
Tetrachloroethylene	10	10	*not applicable*	*not applicable*
Trichloroethylene	10	10	*not applicable*	*not applicable*

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[3] For the group of priority substances of polyaromatic hydrocarbons (PAH), each individual EQS shall be complied with: the EQS for Benzo(a)pyrene and the EQS for the sum of Benzo(b)fluoranthene and Benzo(k)fluoranthene and the EQS for the sum of Benzo(g,h,i)perylene and Indeno(1,2,3-cd)pyrene must be met.

[4] DDT total comprises the sum of the isomers 1,1,1-trichloro-2,2 bis (*p*-chlorophenyl) ethane; 1,1,1-trichloro-2 (*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethane; 1,1-dichloro-2,2 bis (*p*-chlorophenyl) ethylene; and 1,1-dichloro-2,2 bis (*p*-chlorophenyl) ethane.

1.3. Environmental Quality Standards in sediments

The Directive proposal let to Member States to set up EQS for sediment or biota, with the exception of: hexachlorobenzene, hexachlorobutadiene and methyl-mercury were EQS values for surface waters will not ensure protection against indirect effects and secondary poisoning (COM (2006) 397). This was decided to allow Member States flexibility depending on their monitoring strategy. However, having set up EQS for the water column, it is necessary that EQS defined for sediments are in agreement with those EQS already defined. In fact in the original proposal of the EQS methodology (Lepper, 2005), it was suggested that due to the scarcity of toxicological tests the equilibrium partitioning method could be applied. The proposed EQS were (Lepper, 2005):

Name of substance	**EQS for Sediments (µg/kg wet wt)**	**EQS for Sediments (µg/Kg dry wt)**
Alachlor	*not applicable*	*not applicable*
Anthracene	67.4	310
Atrazine	1.12	5.2
Benzene	*not applicable*	*not applicable*
Pentabromodiphenylether		310 (fresh water sed.) 62 (marine sed.)
Cadmium and its compounds		2600 (fresh water sed.)
C10-13 Chloroalkanes	217	998
Chlorfenvinphos	*not applicable*	*not applicable*
Chlorpyrifos	*not applicable*	*not applicable*
1,2-Dichloroethane	*not applicable*	*not applicable*
Dichloromethane	*not applicable*	*not applicable*
Di(2-ethylhexyl)phthalate (DEHP)		100000
Diuron	*not applicable*	*not applicable*
Endosulfan		
Fluoranthene	37.7	173
Hexachlorobenzene	3.7	16.9
Hexachlorobutadiene	107	493
Hexachlorocyclohexane	2.4 (fresh water sed.) 0.24 (marine sed.)	10.3(fresh water sed.) 1.1 (marine sed.)
Isoproturon	*not applicable*	*not applicable*
Lead and its compounds		53400
Mercury and its compounds		670
Naphthalene	*not applicable*	*not applicable*
Nickel and its compounds		3000
Nonylphenol	39	180
Octylphenol	7.4 (fresh water sed.) 0.74 (marine sed.)	34 (fresh water sed.) 3.4 (marine sed.)
Pentachlorobenzene	87	400
Pentachlorophenol	25.9	119
Polyaromatic hydrocarbons (PAH)	543	2497
Simazine	3.4	15.5
Tributyltin compounds	0.0046	0.02
Trichlorobenzenes (all isomers)	*not applicable*	*not applicable*
Trichloromethane	12	
Trifluralin	3.14	

However, in the CSTEE (Committee on Toxicity, Ecotoxicity and the Environment) opinion (CSTEE, 2004) as general conclusions they believed that specific quality standards should be developed for sediment and biota by producing the required ecotoxicological information due to the reduced number of priority substances and they were critic to the use of partitioning models as those suggested in the TGD (1993) due to the site-specific sensitivity of partition coefficients and the fact that the approach proposed there considered a specific sediment type and did not take into account differences in SPM (suspended particular matter) and organic carbon content which could over- or under-estimate the EQS_s values.

It is well-known (Di Toro *et al.*, 1987) that the development of sediment quality criteria, opposite to the water quality criteria, faces several difficulties. While water quality criteria are based on direct measurement of the total concentration and can be directly related to toxicological effects, the use of total sediment concentration as quality criteria is not supported by a direct link with toxicological effects. In fact several studies have pointed out that different sediments can differ by factors of one order of magnitude or more in toxicity (e.g. Luoma 1983) and have the same total concentration of contaminant. This may pose a major obstacle since without a quantitative estimate of biovailable chemical concentration it is not possible to estimate its toxicity. Also, in a recent study (Verweij et al., 2004) in which PAH, PCB and OCP concentrations in sediments were analysed and compared with caged carps, it was concluded that the use of just sediment quality criteria cannot be used to reliably estimate bioavailability of hydrophobic compounds and the toxicological effects of environmental pollution on aquatic animals.

To solve this problem, it was proposed (Di Toro, 1989) that the dose-response curve for the biological effect of concern should not be correlated to the total sediment chemical concentration (μg/g sediment) but to the interstitial water (pore water) concentration. Several experimental results confirmed that pore-water toxicity tests are more sensitive and better predictor than whole sediment tests (Adams et al., 1985; Swartz et al., 1987; Nebeker and Schuytema; 1988, Scott and Chapman, 1992). These observations suggested that if we are able to measure the chemical concentration in pore water or predict it from the total concentration in the sediment and its properties we can then define relevant quality criteria and connect EQS_w with EQS_s. This approach was adopted by the US Environmental Protection Agency that decided to use chronic water-quality criteria for water-column species to determine acceptable porewater concentrations and then to apply K_{OC} to estimate the corresponding contaminant concentration in sediment organic-carbon at equilibrium (Nowell and Resek,1994). They also requested that the uncertainty associated with the methods should be incorporated in the EQS. This is also the approach followed in the REBECCA Project where the OMEGA modelling framework was developed to assess the combined effects of contaminant mixtures (Wijdeveld, 2006).

The relationship between sediment contamination, pore-water concentration and bioavailability of hydrophobic organic contaminants has been recently studied by exposing deposit-feeder, that live within the sediment, to contaminated sediments (Kraaij et al 2003, Lu et al.2004, Lu et al. 2006). The results of these experiments showed that bioaccumulation is correlated to pore-water concentration and not to sediment concentration.

It is important to stress that the pore water concentration of a contaminant may be different from that of the water column and that in this context the hydrodynamic regime of the water body plays an important role. Therefore the measurement of a concentration of a chemical in the water column below the EQS_w does not imply that the pore water concentration will be also below the same EQS_w. In fact, it may be possible in the case of contaminated sediments, to have a pore water concentration in the sediment higher than the EQS_w and to have in the water column concentrations lower than the EQS_w (a typical example would be a river with historical contaminated sediments).

In this work we have analyzed with the help of experimental data sets at JRC-IES as well as in literature, and with the application of dynamic fate models, the issue of the link between concentrations in the water column and in the sediments. Also, the application of the partitioning approach to calculate the expected distribution of a chemical compounds between several phases, i.e. dissolved, attached to dissolved organic carbon (DOC) and attached to particulate matter has been undertaken. The results of this exercise should be considered preliminary since an exhaustive data set for compounds, sediment type and water column characteristics, does not exists. However, it clearly emerges that water column and sediments are not always coupled, concentration in sediments does not reflect toxicity as porewater concentrations, and the partitioning approach for sediments gives values between 1-3 orders of magnitude and therefore is, at the present, not suitable for establishing EQS. Two proposed solution would consist on monitoring surface water as well as porewater and use the same EQS or on developing new soft extraction techniques that will allow extracting the bioavailable part from sediments. Finallly, good chemical status in surface waters does not imply good chemical status in sediments and *viceversa*.

2. PARTITIONING OF CHEMICALS

The process in which chemicals become associated with solid phases is generally referred to as sorption[5] (Schwarzenbach *et al.*, 2003). This process is extremely important for chemicals in the environment since it affects their biovailability, their degradation rates as well as their fate, e.g. chemical sorbed to a suspended particle can sink through the water column.

The equilibrium partitioning approach assumes a reversible linear equilibrium between the dissolved, C_{diss} (ng L^{-1}) and the sorbed, C_{part} (ng kg^{-1}), concentrations. Therefore, the general approach to describe the particle affinity is by means of the partition coefficient K_d (L kg^{-1}) which is defined as the ratio between the particulate and the dissolved phases as:

$$K_d = \frac{C_{part}}{C_{diss}} \qquad (1)$$

K_d represents a global value of several types of sorption processes. In the case of sediment C_{diss} will refer to porewater concentration. Let us assume that for nonpolar chemicals only sorption to natural organic matter is relevant. In that case we can express K_d as a function of the organic-carbon partition coefficient, K_{OC}:

$$K_d = f_{OC} \cdot K_{OC} \qquad (2)$$

where f_{OC} is the fraction of organic carbon for suspended solids or sediments:

$$f_{OC} = \frac{mass\ of\ organic\ carbon}{total\ mass\ of\ sorbent} \qquad (3)$$

Values of K_{OC} should take into account the structural properties of the POM (Particulate Organic Matter) present in the system under analysis. However, in practice this is quite difficult to analyze due to the large variability of POM. Therefore, what is assumed is that K_{OC} values can be fitted using the octanol-water partition coefficient, K_{OW} , as (Karickhoff *et al.*, 1979; Chiou *et al.* ,1998; amongst others):

$$\log K_{OC} = a \cdot \log K_{OW} + b \qquad (4)$$

Table 1 summarizes some values of the parameters *a* and *b* found in literature.

By combining Eqs. (1)-(4) we obtain:

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[5] Adsorption if the molecules attach to a 2D surface and absorption if the molecules penetrate into a 3D matrix

$$C_{part} = f_{OC} \cdot f(K_{OW}) \cdot C_{diss} \tag{5}$$

Therefore if we define (Di Toro, 1989)

$$C_{part}^{OC} = \frac{C_{part}}{f_{OC}} \tag{6}$$

as the organic carbon normalized sediment concentration (ng chemical/ kg organic carbon) then

$$C_{part}^{OC} = f(K_{OW}) \cdot C_{diss} \tag{7}$$

Therefore for a given chemical, the total normalized sediment concentration is proportional to the dissolved concentration in pore water. For this reason, it was proposed by Pavlou and Weston (1983), Pavlou (1987) and Di Toro (1989) to use the following correlation to define environmental quality standards for chemicals:

$$EQS_s = K_d \cdot EQS_w \tag{8}$$

This is the base of the partitioning approach to define EQS$_s$.

Table 1. Examples of proposed correlations between the organic carbon-water partition coefficient and the octanol-water partition coefficient.

	$\log K_{OC} = a \cdot \log K_{OW} + b$	
Set of compounds	***a***	***b***
Alkylated and chlorinated benzenes, PCBs	0.74	0.15
PAHs	0.98 1.0	-0.32 -0.21
PBDEs	0.81	0.1
PCDDs	0.95	-0.19
PCDFs	0.88	0.53

Schwarzenbach *et al.* (2003) have pointed out that these correlations produce K_{OC} values between a factor of 2 to 3. In order to improve these results, several other correlations have been proposed that take into account not only the organic matter but also the inorganic matter. Xia and Ball (1999) analysing the sorption of PAHs (Polycyclic Aromatic Hydrocarbons) and CBs (Chlorinated Benzenes) concluded that for the planar compounds it should be necessary to add a new term that takes into account the fraction of black carbon (bc) in the sediment. They suggested that the equilibrium concentration should be obtained:

$$C_{part} = f_{OC} \cdot K_{OC} \cdot C_{diss} + f_{bc} \cdot K_{bc} \cdot C_{diss}^{0.7} \tag{9}$$

and that K_{bc} could be correlated with K_{OW} as:

$$\log K_{bc} = 1.6 \cdot \log K_{OW} - 1.4 \tag{10}$$

Along the same lines Shimazu *et al.* (2002) analysed data on 28 chemicals with $\log K_{OW}$ values between -1.37 and 6, and proposed the following correlation to obtain K_d and therefore C_{part}:

$$K_d = K_{OM} \cdot f_{OM} + K_{IM}(1 - f_{OM}) \tag{11}$$

where f_{OM} refers to the fraction of organic matter (OM) in the sediment and K_{IM} is the sediment inorganic matter-water partition coefficient. They also proposed the two following correlations based on K_{OW} to calculate the sediment-water partitioning coefficients:

$$\log K_{OM} = 0.824 \cdot \log K_{OW} - 0.0228 \tag{12}$$

$$\log K_{IM} = 0.212 \cdot \log K_{OW} + 1.32 \tag{13}$$

As already stated, the equilibrium partitioning approach will provide, in the case of sediments, the relationships between the concentration in the porewater and in the sediment, whereas the application to the water column will provide the relationships between the dissolved and particulate phases. However, they do not provide the correlation between the concentrations in porewater and surface water. These are regulated by mass transfer mechanisms that depend not only on the physico-chemical properties of the chemical but also on the hydrodynamic characteristics of the water body under consideration.

When the diffusive flow parameters are poorly known the mass transfer between surface water and sediments may be represented with a sediment-water exchange rate coefficient k_{ws} (Farley *et al.*, 1999):

$$F^{W/S} = k_{ws}(C_{pore} - C_{diss}) \tag{14}$$

Concerning the sediment-water diffusive transfer coefficient, Di Toro *et al.* (1981) concluded that the main resistance to mass transfer lies in the sediment and that it is possible to write:

$$k_{ws} = 2.2 \cdot 10^{-6} \phi \cdot MW^{-2/3} \tag{15}$$

for k_{ws} in m/s. A typical order of magnitude for k_{ws} is then about $1.2 \cdot 10^{-8}$ – $1.2 \cdot 10^{-7}$ m/s. Evidently this formulation does not take into account the settling and resuspension processes that are controlled by the hydrodynamics (see Modelling Section 4.1).

3. ANALYSIS OF EXPERIMENTAL DATA

Table 2 shows a list of 27 case studies providing information on concentration of different contaminants (PCDD/Fs, PCBs, PAHs and Pesticides) in the sediment, surface water and pore water. These data sets have been analysed to test if any correlation can be found between the concentrations in the different compartments.

Table 2. List of case studies reviewed in this work.

Case study	Contaminants	Type of data w=water,s=sediments, p=porewater	Reference
Houston Ship Channel, USA	PCDD/Fs	w,s	Suarez et al. 2006
Ya-er Lake, China	PCDD/Fs	w,s	Wu et al. 2001
La Plata Harbour, Argentina	PCBs	w,s	Colombo et al. 1990
Hudson River, USA	PCBs	Koc	Erickson et al 2005
Delfzijl Harbour, Netherlands	PCBs	p,s	Booij et al. 2003
Odra River, Poland	PCBs	w,s	Tomza et al. 2006
San Francisco Bay, USA	PAHs	p,s	Maruya et al 1996
Delaware coastal plain, USA	PAHs,CBs	Koc	Xia and Ball 1999
Japanese water bodies	PAHs+other chemicals	w,s	Shimazu et al. 2002
Izmit Bay, Turkey	PAHs	w,s	Telli-Karakoc et al. 2002
Sacca di Goro, Italy	Pesticides	w,s	Carafa et al. 2007
Lake Volvi, Greece	Pesticides	w,s	Fytianos et al. 2006
Coastline of Singapore	Pesticides	w,s	Wurl and Obbard 2006
Mar Menor, SE Spain	Pesticides	w,s	Perez-Ruzafa et al. 2000
Meric Delta, Turkey	Pesticides	w,s	Erkmen and Kolankaya 2006
Coastline of Mumbai, India	Pesticides	w,s	Pandit et al. 2006
Chinandega Lagoon, Nicaragua	Pesticides	w,s	Carvalho et al. 2002
Beijing Guanting reservoir, China	Pesticides	w,s,p	Xue et al. 2005
Western Xiamen Sea, China	Pesticides	w,s,p	Maskaoui et al. 2005
Venice Lagoon, Italy	PCDD/Fs, PCBs	w,s	Micheletti et al. 2007
Venice Lagoon, Italy	PCDD/Fs, PCBs	w,s	Dalla Valle et al. 2005
Koster Fjord, Sweden	PCBs, PAHs	w,s	Palm et al. 2004
Qiantang River, East China	PCBs, PAHs, Pesticides	w,s	Zhou et al. 2006
Xiamen Harbour, China	PCBs, PAHs, Pesticides	w,s,p	Zhou et al 2000
Ulsan Bay, Korea	PCBs, PAHs, Pesticides	w,s,p	Khim et al. 2001
Minjiang River Estuary, China	PCBs, Pesticides	w,s,p	Zhang et al. 2003
Ebro river, Spain	PCBs, Pesticides	w,s	Fernandez et al. 1999

3.1. Sediments-surface water concentrations

3.1.1. PCDD/Fs

The concentration of PCDD/F in the Venice lagoon (Dalla Valle *et al.* 2005) and in the Ya-er Lake in China (Wu *et al.* 2001) show a correlation between the sediment concentration and concentration in the water column (see Figs. 1-2). This correlation might be linked to the low solubility and high K_{OW} of these compounds, which means that they tend to be bound to the particulate fraction also in the water column. Thus, in closed or almost closed systems, the distribution of different dioxins has a similar pattern in the water column and in the sediment.

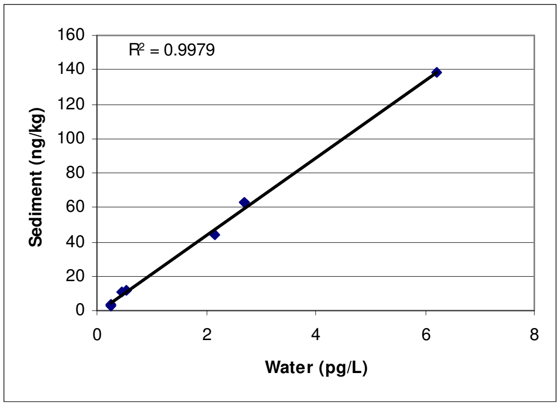

Figure 1. Relationship between PCDD/F concentrations in the water column and in the sediments from Venice Lagoon (Italy). Data from Dalla Valle *et al.* (2005).

Interestingly, in another work performed also in Venice lagoon recently published (Micheletti et al., 2007) the correlation found for PCDD/Fs was not as good as the one observed by Dalla Valle et al. (2005), see Fig.3. A less evident correlation ($R^2 = 0.68$) was also found in the data of the Houston Ship Channel, USA (Suarez et al. 2006) (result not shown).

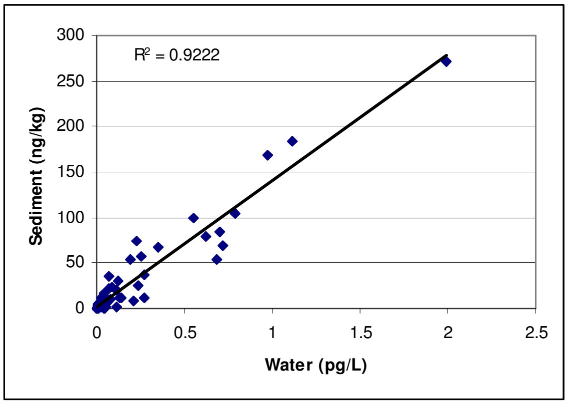

Figure 2. Relationship between PCDD/F concentrations in the water column and in the sediments from Ya-er Lake (China). Data from Wu et al. (2001).

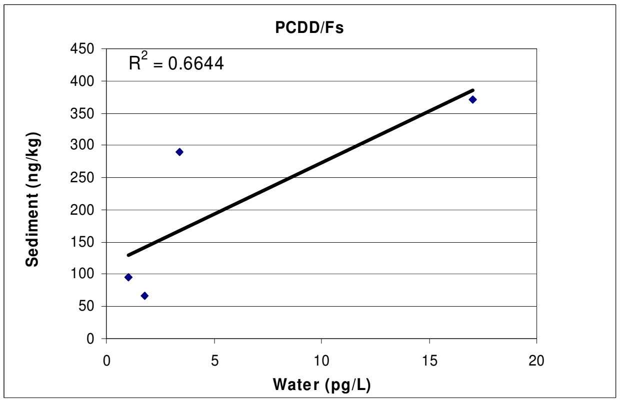

Figure 3. Relationship between PCDD/F concentrations in the water column and in the sediments from Venice Lagoon (Italy): Data from Micheletti et al (2007).

Another example in the literature that illustrates the fact that the correlation between the PCDD/Fs concentrations in water and sediments have to be considered carefully when using pollution status monitoring purposes comes from a survey performed in river systems throughout the UK territory in which water and sediments were sampled at the same places. Results from this study showed that the analysis of 40 water samples from both potentially polluted and background areas indistinctly exhibited very low PCDD/Fs concentrations, whereas the sediment results from industrial areas were in general higher that the background areas reproducing better the situation (Rose et at., 1994). The authors of this work concluded that the bottom sediments constituted a reservoir for PCDD/Fs and therefore would more usefully provide a means for monitoring PCDD/Fs levels in the aquatic environment.

3.1.2. PAHs

Low correlation was found in a study performed in the Izmit Bay (Marmara Sea) between concentration of ∑PAHs (16 congeners) in coastal sediments and sea water (Telli-Karakoç et al., 2002), while no correlation was found in the distribution of ∑PAH measured at 9 station of the Xiamen Harbour (China) (Zhou et al. 2000) nor in the distribution of 6 PAH congeners detected at the Koster Fjord (Sweden) (Palm et al. 2004). Also the data on the sediment and water concentration of ∑PAH measured in the Ulsan Bay (Korea) showed no correlation (Khim et al. 2001).

3.1.3. PCBs

A correlation was found for dioxin-like PCBs in a study carried out in Venice Lagoon by Micheletti et al (2007), see Figure 4. Furthermore, the distribution of ∑PCBs at 7 stations located in the Ulsan Bay (Korea) (Khim et al. 2001) shows a correlation between sediment and water concentrations (Fig.5). However, no correlation was found between ∑PCB concentrations in water and sediments reported in a study performed in La Plata harbour (Argentina), where concentrations of PCBs in water and sediments at 17 sampling sites were measured (Colombo et al., 1990). Still, examining some single congeners a better correlation was found for some of them such as PCB52 (R^2 =0.6695). Also, the data collected at 5 sampling stations of the Lower Odra River (Poland) shows a weak correlation between the ∑PCB in water and sediment (R^2=0.6603) but the correlation becomes better if we consider only the single congener PCB101 (R^2=0.8533). No correlation was found in the data of the Koster Fjord, Sweden (Palm et al. 2004), of the Minjiang River Estuary, China (Zhang et al. 2003) and of the Ebro river, Spain (Fernandez et al. 1999).

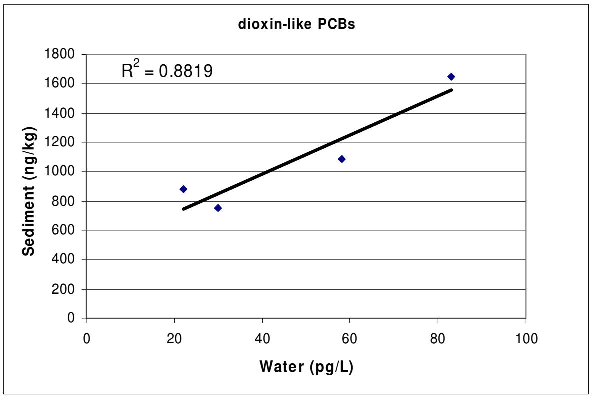

Figure 4. Relationship between dioxin-like PCB concentrations in the water column and in the sediments from Venice Lagoon (Italy): Data from Micheletti et al (2007).

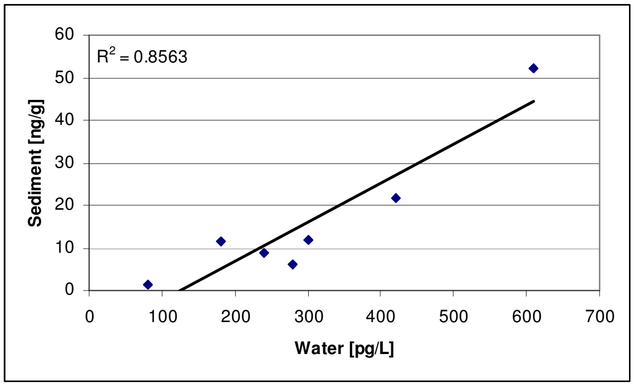

Figure 5. Relationship between ΣPCB concentrations in the water column and in the sediments from Ulsan Bay (Korea): Data from Khim et al (2001).

3.1.4. Pesticides

A correlation (R^2=0.8203) was found in the distribution of 18 insecticides in the Jiulong River Estuary and the Western Xiamen Sea (China) (Maskaoui *et al.* 2005). Furthermore, the concentrations in the sediment and in the water column measured at 14 stations of the Chinandega coastal lagoon (Nicaragua) (Carvalho et al 2002) show a correlation of R^2=0.8637 (Fig.6). The correlation becomes even better if we consider only the distribution of Toxaphene (R^2=0.9849). In all the other datasets found in the literature no significant correlation could be found.

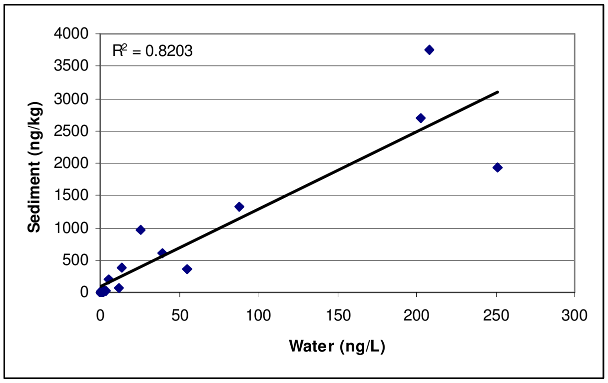

Figure 6. Relationship between OCP concentrations in the water column and in the sediements. Data from Maskaoui *et al* 2005.

Even though in some cases it is possible to find a correlation between concentrations in the water column and in the sediments, these correlations can not be approximated using the partitioning approach (results not shown) and therefore cannot be regarded as general. In some specific cases, it could be possible to develop these correlations and then use the measurement in one media to infer concentrations in the other media, but the validity of the correlation will be limited to each specific site.

3.2. Sediments-porewater concentrations

3.2.1. PAHs

For PAHs we have found literature data concerning the concentrations in pore water and in the sediment in Maruya *et al.* (1996), Xia and Ball (1999), Zhou *et al.* (2000) and Shimazu *et al.* (2002). Table 3 and Fig. 7 summarize the calculations of log K_{OC} with the experimental data sets. As it can be seen even though there is a linear correlation between log K_{OC} and log K_{OW}, the results differ in several orders of magnitude.

Table 3. Calculated log K_{OC} as a function of experimental data and literature values.

Compound	log K_{OC}[6] Xia and Ball (1999)	log K_{OC}[7] Shimazu et al. (2002)	log K_{OC}[8] Zhou et al. (2000)	log K_{OC}[9] Maruya et al. (1999)	log K_{OW}
Acenaphtene				4.81	3.90
Anthracene			4.07	5.26	4.54
Benzo[b]fluoranthene			3.94	6.59	6.00
Benzo[k]fluoranthene		6.16		6.41	6.00
Benzo[e]pyrene				6.19	6.44
Benzo[g,h,i]perylene				6.67	6.90
Chrysene				5.98	5.84
Fluoranthene		5.74	4.93	6.15	5.10
Fluorene	4.37	4.16	4.05	4.69	4.20
Indeno [1,2,3-cd]pyrene			4.42	6.93	6.58
Naphthalene	3.30				3.30
Phenanthrene	4.92	4.68	4.98	4.99	4.57
Pyrene	5.61	6.65	4.96	5.75	5.61

These results are one extreme case since it is well known that the planar PAHs need a correction factor to take into account black carbon (Schwarzenbach et al., 2003). As stated before, for these compounds it has been suggested to use Eq (9). Unfortunately, the fraction of black carbon was not available in all the analysed data sets.

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[6] f_{OC}=0.0149

[7] f_{OC}=0.01 (assumed, not indicated in the paper)

[8] f_{OC}=0.01.

[9] only K_{OC} , no experimental data in the original paper

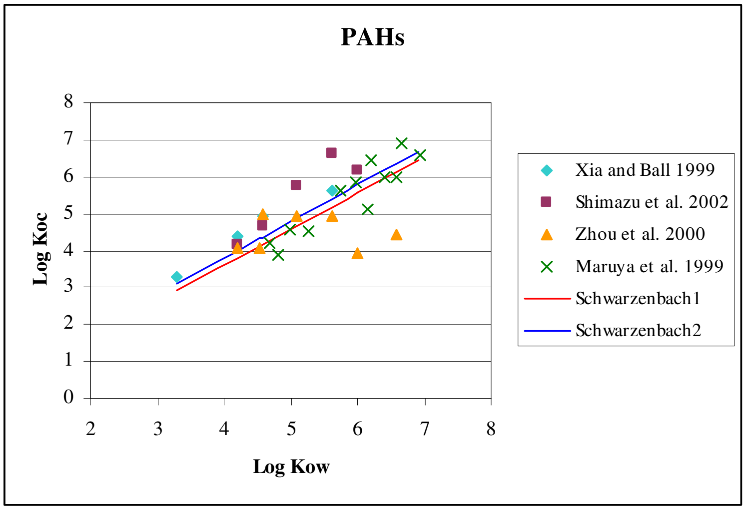

Figure 7. Relationship between octanol-water and organic carbon partition coefficients. Points, experimental data from Table 3 and correlations from Table 1

3.2.1. PCBs

Table 4 and Figure 8 illustrate the log K_{OC} calculated using the PCBs distribution in sediment and pore water presented in Zhang *et al.* (2003), Erickson *et al.* (2005) and Booij *et al.* (2003). Once again, even though the relationship between log K_{OC} and log K_{OW} seem to follow a linear trend, the values are spread over several orders of magnitude.

Table 4. Calculated log K_{OC} as a function of experimental data and literature values.

PCB	logKoc[10] Zhang et al. (2003)	logKoc[11] Erickson et al. (2005)	logKoc[12] Booij et al. (2003)				log Kow
1	4.59	4.40					4.46
5	4.23	5.68					4.97
28	3.39	6.17	6.21	6.08	6.38	6.31	5.67
29	3.32						5.60
47	4.35						5.85
49	4.14						5.85
52	4.14	5.72	6.17	6.75	6.54	6.40	5.84
77	4.42						6.36
97	3.94						6.29
101	4.19	5.54	6.54	6.39	6.90	6.43	6.38
105	3.81						6.65
118	3.87		6.81	6.67	7.08	6.76	6.74
138	4.39						6.83
153	3.97		7.15	7.04	7.02	6.85	6.92
154	3.73						6.76
169	4.13						7.42
171	4.57						7.11
180	3.87		7.70	7.29	7.22	7.19	7.36
187	4.42						7.17
195			8.05	7.54	8.15	7.67	7.56
200	3.99						7.27
204	4.35						7.30

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[10] f_{OC}=0.0005 (assumed, not indicated in the paper)
[11] only K_{OC} , no experimental data in the original paper
[12] f_{OC}=0.001

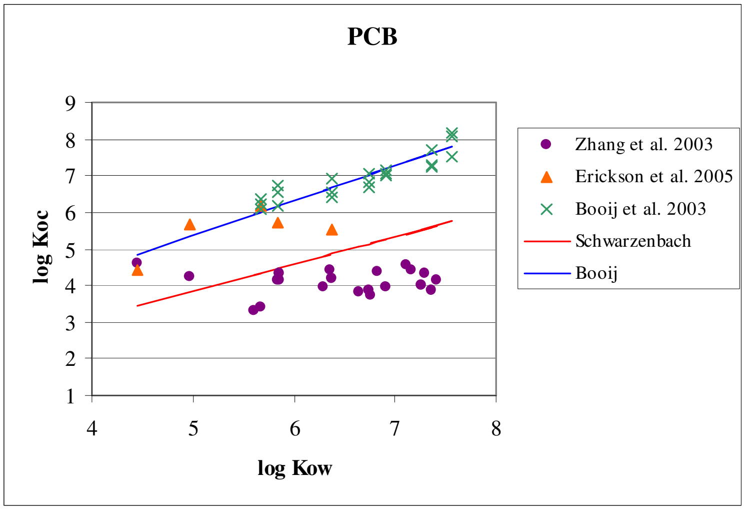

Figure 8. Relationship between octanol-water and organic carbon partition coefficients.

3.2.3 Pesticides

The data presented in Zhou *et al.* (2000), Maskaoui *et al.* (2005), Xue *et al.* (2005) aand Zhang *et al.* (2003) on partitioning of pesticides in sediments and pore water were used to calculate the log K_{OC} (Table 5).

Table 5. Calculated log K_{OC} as a function of experimental data and literature values.

	log Koc[13] Xue et al. (2005)	log Koc[14] Maskaoui et al. (2005)	log Koc[15] Zhou et al. (2000)	log Koc[16] Zhang et al. (2003)	log Kow
Trifluralin	3.46				5.10
HCB	3.89				5.18
Heptachlor	3.35	2.95	3.04	3.29	4.95
Alachlor	3.98				2.92
Aldrin	3.51	3.40	3.70	3.99	6.28
Metolachlor	3.21				3.13
Chlorpyriphos	4.30				3.81
γ-Chlordane	4.61				6.00
α-Chlordane	3.41				6.00
Dieldrin	3.76	3.17	3.19	3.53	4.55
Endrin	4.13	3.52		3.55	4.28
Endosulfan II	4.64	3.55	3.92	3.71	3.62
Endosulfan	3.52				4.50
Endosulfan I	3.37	3.26		3.66	3.55
Methoxychlor	3.22	3.76		3.78	5.08
p,p'-DDT	4.41	3.04	2.66	3.99	6.19
o,p'-DDT	4.91				6.19
p,p'-DDE	4.30	3.58	2.56	3.87	5.70
p,p'-DDD	4.12	3.46		3.48	5.50
α-HCH	3.78	2.43	2.89	3.53	3.77
β-HCH	4.58	2.56	2.87	3.43	4.04
γ-HCH	4.90	3.24	3.28	3.66	3.64
δ-HCH	4.37	3.42		3.38	3.85

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[13] f_{OC}=0.001 (assumed, not indicated in the paper)
[14] f_{OC}=0.001 (assumed, not indicated in the paper)
[15] f_{OC}=0.01
[16] f_{OC}=0.001 (assumed, not indicated in the paper)

The relationship between the calculated log K_{OC} vs log K_{OW} are compared to the correlation curve for pesticides proposed by Lyman et al. 1990 (log K_{OC} = 0.544 log K_{OW}+1.377) in Figure 9. Also in this case the results differ in several orders of magnitude.

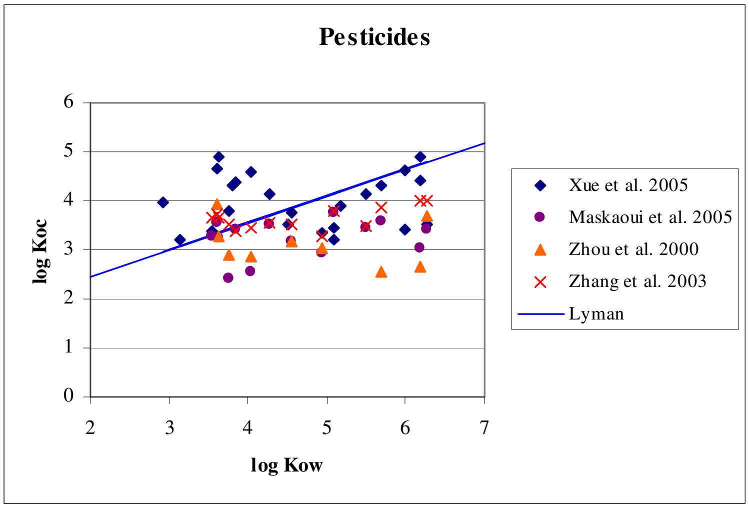

Figure 9. Relationship between octanol-water and organic carbon partition coefficients.

Several studies (Kraaij et al 2003, Lu et al.2004, Lu et al. 2006). have pointed out the important difference between the measured pore-water concentration of hydrophobic organic compounds and the concentration predicted by the traditional equilibrium partitioning method, and the reason is that a large fraction of the contaminants is released only very slowly. Measured partition coefficient K_{OC} were generally higher than predicted from K_{OW} thus, it is recommended to measure pore-water concentration rather than to derive it indirectly using partitioning coefficients.

3.3. Porewater-surface water concentrations

Zhou *et al.* (2000) analyzed 16 PAHs,18 PCBs and 18 organochlorine insecticides in Xiamen harbour (China) and found that PAHs levels in porewater were an order of magnitude higher than in seawater except in two stations[17] (over nine).The PCBs levels in porewater were from one to two orders of magnitude higher than in surface water. Concerning organochlorine insecticides in six stations porewater concentrations were higher than those of seawater, in four they were one order of magnitude higher and in two were approximately similar. However, the authors pointed out to waste discharges as a major source of inputs in this area. In a similar

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[17] In these two cases no PAHs were detected in the sediment samples.

study by Zhang *et al.* (2003) in the Minjiang River Estuary, they found that organochloride pesticides and PCBs levels in porewater were one to two orders of magnitude higher than in surface waters. The same results were obtaining by comparing porewater and surface water in the Jiulong River Estuary for 12 PCBs and 18 insecticides. Xue *et al.* (2005) analyzed 31 pesticides in water, porewater and sediments at the Beijing Guanting reservoir (between them the PS alachlor, chloropyrifos, endosulfan and trifluralin) and found that mean porewater concentrations were higher in 27 of them in certain cases by one to two orders of magnitude. Specifically, for the PS substances the mean values are summarized in Table 6.

Table 6. Mean pesticides concentrations (PS) in water and porewater. Data from Xue *et al.* (2005).

Compound	**Water (ng L^{-1})**			**Porewater (ng L^{-1})**		
	Range	**Mean**	**SD**	**Range**	**Mean**	**SD**
Alachlor	ND-5.68	1.72	2.08	ND-41.2	9.1	13
Chloropyfos	0.30-1.89	1.5	0.44	1.90-8.77	3.3	2.81
Endosulfan	0.07-13.8	1.48	11.9	5.05-38.3	16.6	7.03
Trifluralin	3.41-5.15	4.5	1.32	ND-83.6	44.0	27.2

In a recent study by Persson *et al.* (2005) it was found for The Grenlandsfjords (Norway) that the deep water concentrations were factors 800-6000 lower than the observed porewater concentrations for PCDDs and factors 1100-43000 lower than those for PCDFs. The deep water concentrations were always below the 95% limit of the observed porewater concentrations.

These differences in values between porewater and surface water clearly indicate that there is a net flux of contaminants from the sediment to the water column. This net flux is probably the normal behaviour for historic POPs that had accumulated in the sediments over the last decades. Probably, this is not the case for emergent POPs such as PBDEs that still have to build up the sediment reserves.

4. ANALYSIS OF SIMULATED DATA

Models developed for environmental studies have to take into account that for certain contaminants atmospheric inputs are known to be the main entry route to the aquatic environment and therefore, as atmospheric inputs are very dynamic and variable in time (Dachs et al., 1999, 2002), they can induce temporally high concentrations in the water column. In a similar way more soluble contaminants that will reach the aquatic environment through the watershed will also have a high temporal variability depending on several factors. For example, herbicides will show a peak after the application period, normally in spring, and decrease during the winter, also peaks may occur after heavy rainfalls. Therefore, the models needed for studying these interactions should be dynamic (not at equilibrium or steady state) in order to be able to predict the high observed environmental variability, and thus able to predict episodes were EQS limit values are crossed.

4.1. 3D and 1D fate model for Contaminants

To study the dynamics of several families of contaminants a general fate model was developed. The model considers the dynamics in the water column as well as in the sediments. The model has been used as a 0D to simulate the fate of DDT and its isomers in Lake Maggiore (Dueri *et al*., 2005); the spatio-temporal variability of atrazine, simazine and terbuthylazine (s-triazines) in Sacca di Goro (Carafa *et al*, 2006) coupled with a 3D hydrodynamic model (COHERENS); and to study POPs fluxes and the role of turbulence in a standard 1D water column for PCBs (Jurado *et al*., 2007), PAHs, PBDEs and PCDD/Fs (Marinov *et al*., 2007).

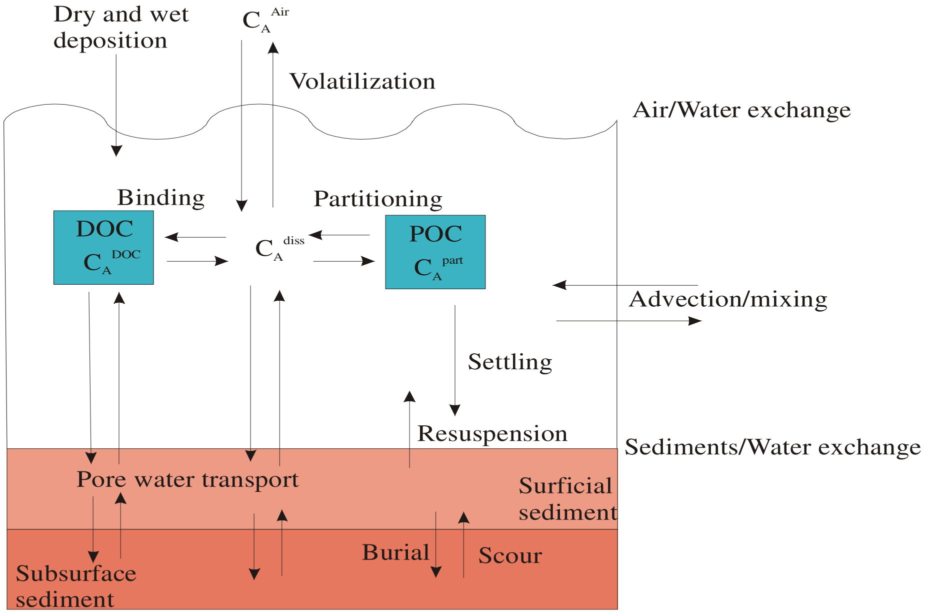

Figure 10. Fate and transport model processes and environmental compartments.

The model is state of the art environmental dynamic models and considers atmospheric inputs (dry and wet deposition and volatilization) and exchanges with subsurface sediments as boundaries where it simulates the concentrations in the water column (dissolved, bounded to DOC and particulate) as well as in the sediments (Fig. 10). The equations of the model have been described *in extenso* at the above mentioned papers, therefore, we will only summarize here some results. The 3D version of s-triazines was validated using experimental data from one year campaign at Sacca di Goro (Italy), see figs. 11 and 12, whereas the 1D version is being validate in the frame of the Thresholds of Environmental Sustainability Integrated Project following two Mediterranean campaigns (2006 and 2007), see figs.13 and 14.

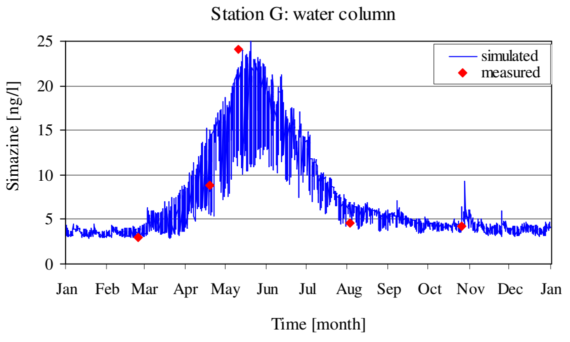

Figure 11. Temporal evolution of Simazine concentrations in the water column and in the sediments (Carafa *et al*., 2006). Dots correspond to measured values.

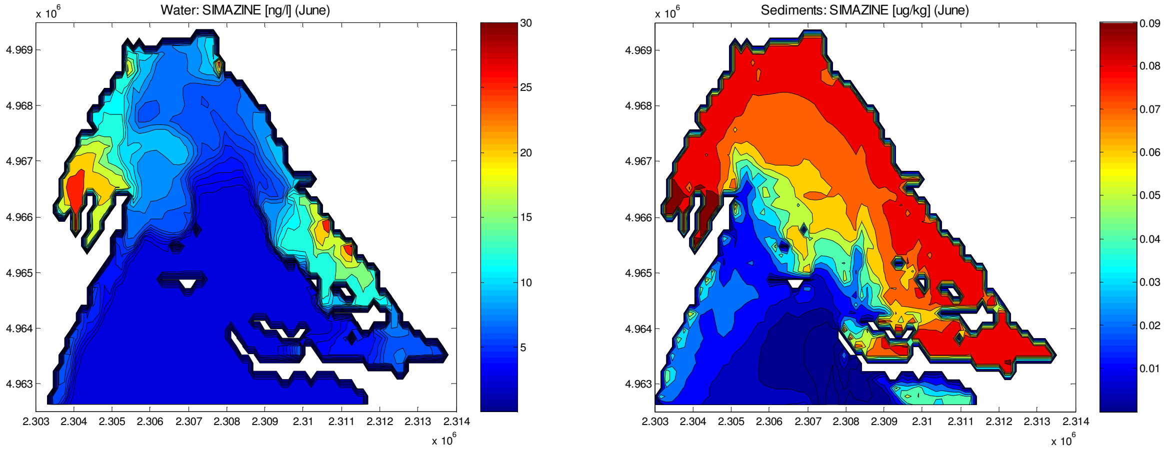

Figure 12. Spatial distribution of Simazine concentrations in the water column and in the sediments (Carafa *et al*., 2006).

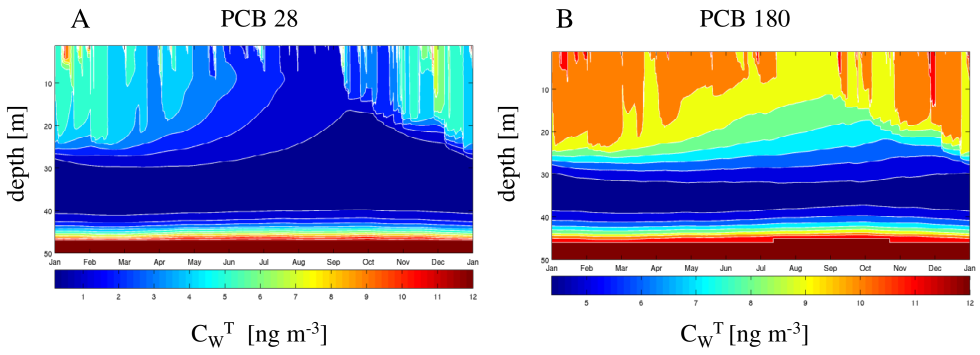

Figure 13. Depth-time distribution of total concentration in the water column for PCB 28 and PCB 180 (Jurado *et al*., 2007).

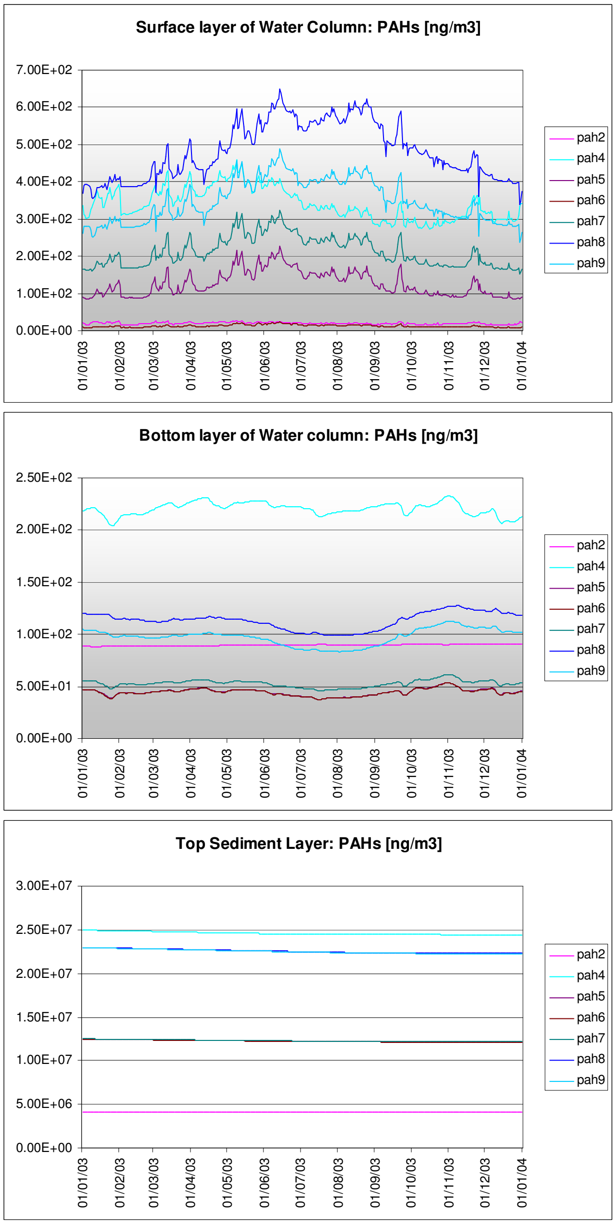

Figure 14. Total concentrations of seven PAHs (Anthracene-PAH2, Pyrene-PAH4, Benzo[b] fluoranthene-PAH5, Benzo[k]fluoranthene-PAH6, Benzo[a]pyrene-PAH7, Benzo[ghi]perylene-PAH8 and Indeno[1,2,3-cd]pyrene-PAH9) in: a/ surface layer of water column; b/ in bottom layer of water column; and c/ in active top sediment surface layer during one year (Marinov *et al*., 2007).

4.2. Sediments-surface water concentrations

Figure 15 shows the simulated values for simazine concentrations in the water column and in the sediments for Sacca di Goro (Italy). Also in this case there is no evident correlation between both concentrations. Even though Sacca di Goro is a shallow water body (mean depth 1.5 m), it has a water residence time in average of 1-2 days (Marinov et al., 2006) and therefore there is an intense water exchange with the Adriatic as can be observed from the simulated oscillations in the water concentration (see fig. 11) which correspond to the tidal oscillations (similar results have been found experimentally, see Carafa et al., 2007). Similar results are obtained for the other polar pesticides simulated, i.e. atrazine, terbuthylazine, alachlor.

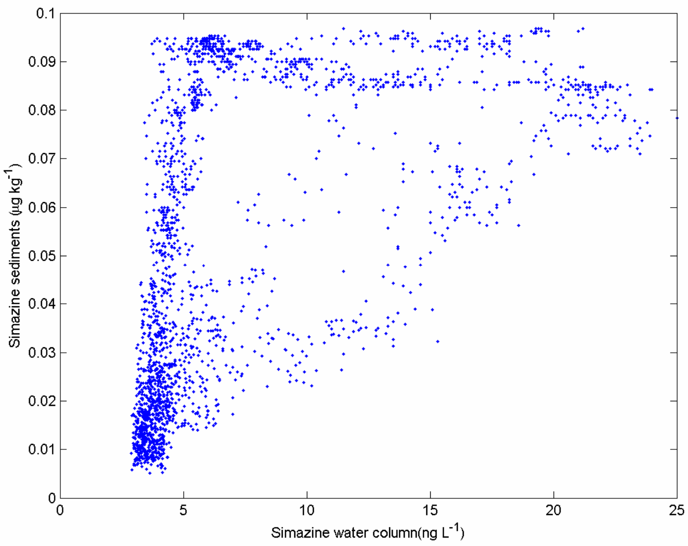

Figure 15. Simulated concentrations in the water column and in the sediments at Giralda Station in Sacca di Goro coastal lagoon (see Carafa et al., 2006).

The shape of this figure seems to correspond to some short of cyclic dynamic behaviour. Assuming that the process of exchange between the water column and the sediments has a certain delay, we have plotted 40 days delayed concentrations in fig. 16. As can be seen the variability between the water column and the sediments has decreased. Shorter (eg. 1, 2, 4, 10, 16 days) and longer time delays (eg. 80 days) does not modify appreciably Fig. 15. In any case, as it can be observed, it is not possible given a certain concentration value in the water column or in the sediment, to predict the other media concentration since high and low concentrations may be possible. This is probably due to the strong influence of the watershed (see fig. 12) that supply the plant protection products stored in its agricultural soils following a typical seasonal pattern (see fig.11).

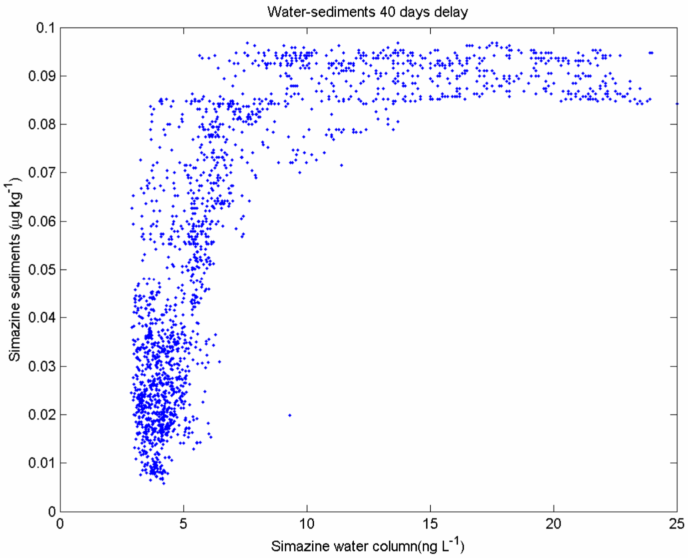

Figure 16. The same as fig.15 but simulated concentrations in the sediments have been delayed by 10 days.

Sacca di Goro is a very shallow water body; therefore it is a system where water column and sediments are in close contact. If we consider marine environment as in the 1D model of the water column with a 50 m depth, it is possible to see that the concentrations in the water column are not homogeneous. For example, fig. 17 shows the total water concentrations of pyrene in the first layer (1 m depth) and in the bottom layer (50 m depth). As it can be seen there are already differences in the water column. This is more evident for contaminants that reach the water through the atmosphere. In a previous study (Jurado et al., 2007) concerning PCBs, it was observed that top and bottom concentrations in the water column will have the higher values were lower concentrations will be found in the middle of the water column. This has been confirmed by concentration profiles measured in several experimental campaigns (Wurl and Obbard, 2006). The same effects have been obtained simulating PBDEs, PAHs and PCDD/Fs. In this case, it is already difficult to assess which are the relations between concentrations in the water column.

However, an important aspect, from the monitoring point of view, is that POPs should be sampled at the surface and/or close to the sediment and that there is a high temporal and spatial variability.

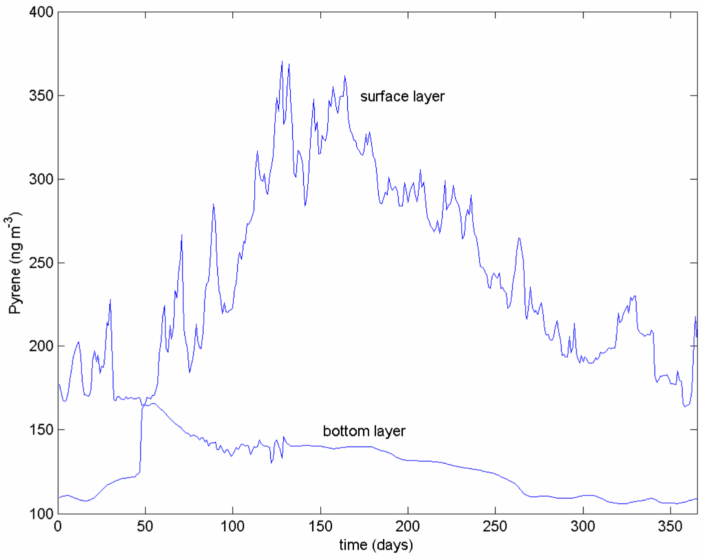

Figure 17. Simulated Pyrene concentrations over one year at the surface layer and at the bottom layer using a 1D water column model.

4.2. Sediments-porewater concentrations

The developed model considers the contaminant in dissolved phase, bounded to dissolved organic carbon (DOC) and bounded to particulate phase. The partitioning approach is applied and therefore a correlation between both phases should occur. This is observed in fig. 18 but in addition the seasonality (due to temperature changes in the water column) is also observed by the oscillations around equilibrium.

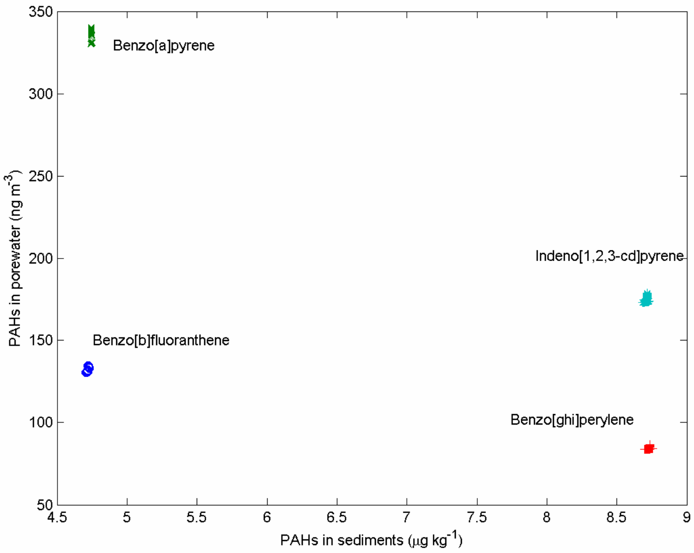

Figure 18. Simulated PAHs concentrations: Benzo[b]fluoranthene (blue), Benzo[a]pyrene (green), Benzo[ghi]perylene (red) and Indeno[1,2,3-cd]pyrene (magenta), over one year at the porewater and at the sediments using a 1D water column model.

4.3. Porewater-surface water concentrations

As discussed above, when analysing dynamic processes one has to consider the temporal scales involved. Let us consider a contaminant dissolved in sediment, assume that the water column has initially zero concentration and that diffusion between porewater and the water column is the only process taking place.

Using Eq. (14) and a simple mass balance, it is possible to write:

$$V\frac{dC_{diss}}{dt} = A_s \cdot k_{ws}(C_{pore} - C_{diss}) \tag{17}$$

where V and A_s are the volume and the exchange area of the system into consideration. This differential equation can be solved explicitly, and assuming initial conditions C_{diss}=0 at t=0, we obtain:

$$C_{diss} = C_{pore}\left\{1 - \exp\left(\frac{-A_s \cdot k_{ws} \cdot t}{V}\right)\right\} \tag{18}$$

The half-lime time of this system then is given by:

$$t_{1/2} = \frac{\ln 2}{\left(\frac{A_s \cdot k_{ws}}{V}\right)} \tag{19}$$

Considering an average value for k_{ws} and a relationship between exchange area and volume of 0.1 (e.g. a water column of 10 m depth) one could obtain that it will take approximately 3.3 years for the dissolved phase to reach half the value of porewater concentration. Of course, if we consider resuspension the process will be faster. However, this is only to illustrate that there is a dynamic involved between the water column and the porewater and this dynamics depends, in addition to diffusional processes that are very slow, on the hydrodynamics of the system, which makes difficult to develop correlations for predict one as a function of the other.

Figure 19 shows the simulated concentrations of porewater as a function of the bottom layer in the water column. As can be seen simulated results are in agreement with experimental findings (see Section 3.3.) in which concentrations in porewater were around one to two orders of magnitude higher than in the water column. In this case, there is also a good relation between dissolved concentrations in the water column and in porewater (notice the axis scale). However, it is possible to see the dynamic effects and one should consider that this is the last layer of the model (50 m depth).

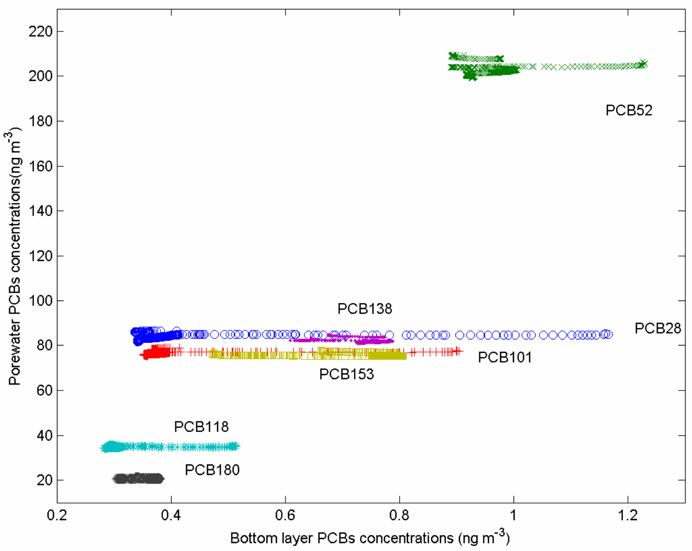

Figure 19. Simulated PCB180 concentrations in bottom layer versus porewater concentrations.

5. CONCLUSIONS

From the above analysis of experimental and simulated data, it is clear that even though there is a coupling between water column and sediments, it is not possible to assess the chemical quality status of sediments based on water column data and *viceversa.* At the moment EQS have been defined for the water column and therefore these EQS will assess only the compliance with good chemical status of surface waters. If EQS were to be defined for sediments, these EQS will not reflect systematically the surface water quality and therefore they could not be used for this purpose. However, it is clear that the good chemical quality of a water body will depend on both good chemical quality, i.e. the surface water and the sediments, and that to assess both it is necessary to measure in both media.

The same EQS developed for water could, in principle, be applied to porewater, hence, there is no need of another set of EQS. If porewater could not be measured, then the partitioning approach to pass to sediment concentrations could be applied. However, in this case an additional uncertainty is added to the procedure and therefore it is necessary to develop new techniques and better databases since at the moment the predictions are between several orders of magnitude, which is not adequate for setting EQS. Additionally, the use of this approach would certainly require the characterization of the sediments in terms of its physical (grain size, material, temperature), chemical (organic matter content, black carbon, pH, redox, etc.) and biological (e.g. bioturbation), which at the moment are not obtained from standard environmental monitoring. However, this approach may be difficult and therefore another option could be to develop “soft” extraction technologies to measure (simulate) bioavailability; this would also help in developing techniques to characterize sediments in terms of bioavailability (Dr. Umlauf, personal communication).

In any case, in highly variable systems as transitional and coastal waters, dynamics has to be taken into account. Environmental concentrations does not reflect the steady state approach

A more promising approach would be the development of EQS in biota, being mussels a promising species since it has been extensively studied and, due to their feeding behaviour, they are filtering the water column and hence it could be possible to develop a correlation between water column EQS and biota EQS. However in this case literature is even more scarce than for sediments and there has not been systematic approach developed yet.

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Abstract

An analysis of experimental and simulated data has been performed to study the relationships between EQS defined for surface waters in the Daughter Directive (COM (2006) 397) and possible EQS defined for sediments.

From the above analysis of experimental and simulated data, it is clear that even though there is a coupling between water column and sediments, it is not possible to assess the chemical quality status of sediments based on water column data and *viceversa*. At the moment EQS have been defined for the water column and therefore these EQS will assess only the compliance with good chemical status of surface waters. If EQS were to be defined for sediments, these EQS will not reflect systematically the surface water quality and therefore they could not be used for this purpose, being the contrary is also true, i.e. compliance with EQS values for water column does not reflect sediment chemical status. However, it is clear that the good chemical quality of a water body will depend on having good chemical quality of surface water and sediments and that to assess both it is necessary to measure in both media.

The same EQS developed for water could, in principle, be applied to porewater, hence, there is no need of developing another set of EQS. If porewater could not be measured, then the partitioning approach to pass to sediment concentrations should be applied. However, in this case an additional uncertainty is added to the procedure and therefore it is necessary to develop to develop new techniques and better databases since at the moment the predictions are between several orders of magnitude, which are not adequate for setting EQS. Additionally, the use of this approach would certainly require the characterization of the sediments in terms of its physical (grain size, material, temperature), chemical (organic matter content, black carbon, pH, redox, etc.) and biological (e.g. bioturbation), which at the moment are not obtained from standard environmental monitoring.

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