



# Enrichment of organochlorine contaminants in the sea surface microlayer: An organic carbon-driven process

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## Abstract

Over 50 seawater samples from two different sites—Barcelona (Spain) and Banyuls-sur-Mer (France)—were analyzed in order to study the extent and postulate the processes driving the enrichment of hydrophobic organic pollutants in the sea surface microlayer (SML). A number of individual polychlorinated biphenyl (PCB) congeners (41) were measured to study their partitioning between the particulate (fraction  $>0.7 \mu\text{m}$ ) and the dissolved+colloidal phases (fraction  $<0.7 \mu\text{m}$ ), with the latter being differentiated into estimated dissolved and colloidal phases. In addition, several organochlorine pesticides were also measured, namely, HCB,  $\alpha$ -HCH,  $\gamma$ -HCH, 4,4'-DDE, 4,4'-DDD and 4,4'-DDT. The presence of PCB congener profiles found in the SML suggests a dynamic coupling with the atmosphere in Banyuls sampling site, whereas offshore Barcelona the presence of highly chlorinated congeners was due to persistent sediment resuspension. The average PCB concentration in the SML dissolved+colloidal phase were higher in Banyuls ( $7.8 \text{ ng L}^{-1}$ ) than in Barcelona ( $3.6 \text{ ng L}^{-1}$ ) samples, but in the particulate phase concentrations were higher in Barcelona ( $3.2 \text{ ng L}^{-1}$ ) to that of Banyuls ( $1.4 \text{ ng L}^{-1}$ ). However, PCB concentrations in the SML generally also showed large variability. Enrichment factors of PCBs and other organochlorine compounds in the SML with respect to the underlying water column ranged from 0.2 to 7.4. This may be explained for both the dissolved+colloidal and particulate phases by the enrichment in the SML of organic carbon (OC) as discerned from particle–water and colloid–water partitioning.

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*Keywords:* Sea surface microlayer; Polychlorinated biphenyls; Organochlorine pesticides; Enrichment factors; Phase partitioning

## 1. Introduction

The sea surface microlayer (SML) is defined as the interfacial film existing between the atmosphere and the ocean. The SML is a unique environmental com-

partment due to its enrichment with organic matter (OM), trace metals and organisms (Hardy, 1982; Zhou and Mopper, 1997), its higher exposure to solar radiation and its interaction with the atmosphere. Therefore, it may play a key role in the transfer processes of persistent organic pollutants (POPs) between the atmosphere and the hydrosphere (Booij and Van Drooge, 2000) and/or their persistence in the environ-

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ment. Despite being structurally and temporarily unstable, it has been estimated that a well-developed SML occurs when wind speed is below  $4 \text{ m s}^{-1}$  (Romano and Garabetian, 1996), which in the case of the Mediterranean accounts for ~40% of the time in summer (Dachs, unpublished data).

The presence of organic compounds in the SML results in a decrease in surface tension (Zuev et al., 2001) and a consequent increase in film stability that facilitates enrichments in particles, organisms and dissolved material. The thickness of the SML varies from ~30 to 300  $\mu\text{m}$  (Zuev et al., 2001) and is a function of the amount of OM, film elasticity (Frew and Nelson, 1992) and wind speed (Liu and Dickhut, 1998). In situ and laboratory experiments have estimated the SML operational sampling thickness to be ~40  $\mu\text{m}$  (Jun et al., 1998).

The elasticity of the film also relies on the chemical composition of the natural organic substances present, i.e., lower productivity waters show a decrease in the protein/lipid ratio in the SML, subsequently increasing its elasticity (Frew and Nelson, 1992). Based on interactions with the underlying

water mass, organic substances are considered either dry or wet surfactants (MacIntyre, 1974). Dry surfactants are amphiphilic molecules whose hydrophilic groups orient towards the water, while their hydrophobic tails stick out. The hydrophobic character of these films may enhance the surface enrichment of hydrophobic substances such as POPs. Conversely, wet surfactants are regarded as long heteropolymeric molecules, essentially hydrophilic in nature but attached to the surface by occasional hydrophobic groups. Enrichments in the SML may also result from hydrodynamic processes (Zuev et al., 2001). For example, Langmuir circulation causes the formation of water cells moving on helical paths in the wind direction (wind speed ca.  $3 \text{ m s}^{-1}$ ), giving rise to alternate parallel lines of divergence and convergence (Valiela, 1995), where accumulation patches of floating particles and plankton can be seen (Evans and Taylor, 1980). Other physical processes that enhance the enrichment involve the adsorption of organic compounds to small particles (0.2–1.2  $\mu\text{m}$ ), and their scavenging caused by rising bubbles (Zuev et al., 2001).

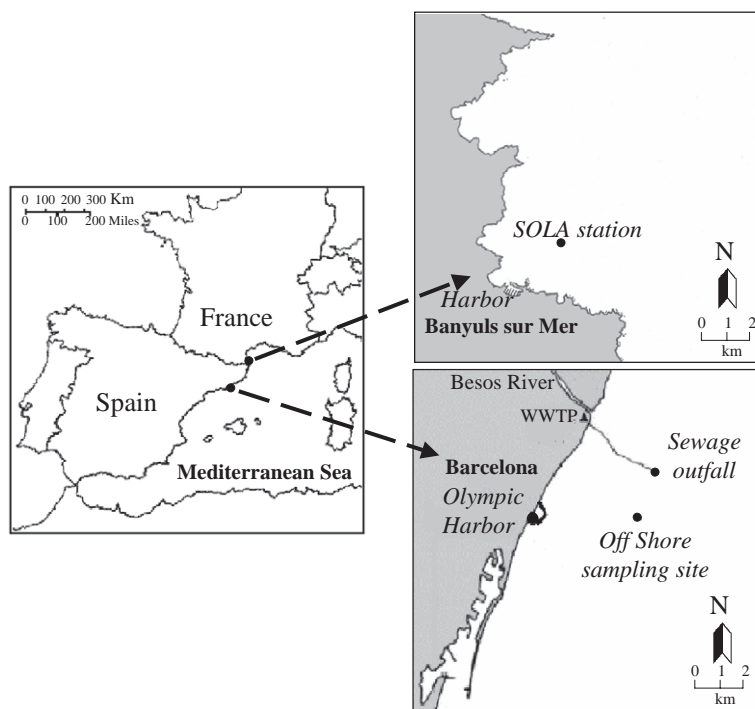


Fig. 1. Map showing the locations of the different sampling sites in this study.

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