Chemosphere 75 (2009) 1266–1272

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

# Modelling the influence of thermal stratification and complete mixing on the distribution and fluxes of polychlorinated biphenyls in the water column of Ispra Bay (Lake Maggiore)

Sibylle Dueri [a], Javier Castro-Jiménez [a], José-Manuel Zaldívar [b,*]

[a] European Commission, Joint Research Centre, Institute for Environment and Sustainability, Ispra (VA), Italy
[b] European Commission, Joint Research Centre, Institute for Health and Consumer Protection, Ispra (VA), Italy

ARTICLE INFO

*Article history:*
Received 22 August 2008
Received in revised form 31 December 2008
Accepted 24 January 2009
Available online 28 February 2009

*Keywords:*
PCBs
Vertical mixing
Fate model

ABSTRACT

A 1D coupled hydrodynamic and contaminant fate model was applied to simulate the distribution of polychlorinated biphenyls (PCBs) in the Ispra Bay located in the southern part of Lake Maggiore (Italy). The model succeeded in representing the hydrodynamic processes occurring in the lake such as thermal stratification during summer 2005 followed by the complete mixing of the water column in February 2006. The results of the PCB fate model highlighted that these processes play a key role for the settling of particles and consequently for the distribution of PCBs in the water column as well as for the contaminant flux at the sediment–water interface. On the air–water front, the simulations emphasised that the net atmospheric PCB input fluxes are generally more important during the cold season and show peaks during periods of high wet deposition. Finally, the seasonal variability of the distribution of PCB in the water column was assessed.



## 1. Introduction

The preservation of aquatic ecosystems and the enhancement of water quality has become a global priority at international level. In particular, persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) have to be carefully considered, since they show high persistence in ecosystems (Tanabe and Tatsukawa, 1986). Moreover they are present in different trophic levels of biota and they are generally magnified through food chains (Geyer et al., 1984).

PCBs comprise a large family of synthetic compounds (209 congeners) that differ in their physico-chemical and toxicological properties (Eisenreich, 1987; Tosola et al., 1997). They are of anthropogenic origin and were used in wide spectra of industrial applications, e.g. dielectric fluids in capacitors and transformers, lubricating oils, placticisers, additives to pesticides, inks and paints, etc. (Erickson, 1992). Originally PCBs were manufactured since 1929, however in the 1960s their usage increased dramatically until environmental and human health concerns resulted in some legislative regulation in 1970s aiming to restrict PCBs applications to closed circuits (Tosola et al., 1997). Some current sources of emissions to the environment are landfills, open burning of products containing PCBs, waste incinerations and accidental fires (Breivik et al., 2002).

The role of mathematical models in assessing the fate and effects of contaminants in aquatic ecosystems is continuously increasing (Koelmans et al., 2001). Mathematical models, once properly validated, allow simulating complex processes and interactions, calculating temporal variability of contaminant fluxes and distribution. They can be used to assess the effect of different scenarios and are a source of information for the driving processes and global dynamics of the studied systems. However, to develop and validate a model a considerable amount of experimental data is required. The modelling of the distribution of PCBs in the environment has been the subject of numerous publications. The majority of these models assume one or two boxes for the water column (Wania and Mackay, 1996; Scheringer et al., 2000; Dalla Valle et al., 2003; Meijer et al., 2006), whereas the number of models that consider spatial variability is still reduced (Carafa et al., 2006; Jurado et al., 2007; Marinov et al., submitted for publication) mainly due to the difficulties in their validation for the absence of enough experimental datasets. However, a recent overview on the global fate of POPs by Lohmann et al. (2007) stressed the need of a less simplistic characterization of the models and the need to consider spatial and temporal dynamics.

The distribution of PCBs in the water column depends on several factors such as the exchange fluxes at the air–water and sediment–water boundaries and the distribution of the suspended particulate matter (SPM). Several studies have documented a seasonal trend in deposition of PCBs from air caused by seasonality in meteorological conditions such as temperature and rainfall

* Corresponding author. Tel.: +39 0332 789202; fax: +39 0332 785807.
*E-mail address:* jose.zaldivar-comenges@jrc.it (J.-M. Zaldívar).

0045-6535/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2009.01.066

distribution as well as changing concentration in air (Dickhut and Gustafson, 1995; Agrell et al., 2002; Van Ry et al., 2002; Teil et al., 2004). Moreover the SPM is affected by biological productivity and turbulence, which may change during the year. Therefore, a seasonal pattern is expected in the distribution of PCBs in the water column and consequently in its potential to bioaccumulate. Recently, some experimental studies have addressed the question of seasonality in the water column distribution of PCBs (Smith and McLachlan, 2006; Cailleaud et al., 2007; Odabasi et al., 2008). Given the complexity of the biogeochemical interactions driving the distribution of PCBs in the water column, modelling is an appropriate and helpful tool to gain a better understanding of the system's dynamics.

An important hydrodynamic process that occurs in deep subalpine lakes is the vertical mixing of the water column that sometimes occurs at the end of the limnological winter (Ambrosetti and Barbanti, 2005). In Lake Maggiore, due to its great depth, this homogeneization is not always completed. In fact, according to Ambrosetti et al. (2003) due to the warming temperatures during the last 20 years the occurrence of this complete vertical homogenization of the water column has decreased considerably (Ambrosetti et al., 2006).

As this process has important effects on the lake ecosystem (Salmaso et al., 2003), the objective of this study is to analyze, after the characterization of the seasonal variability of PCB distribution and fluxes at Ispra Bay, its importance. In particular, we were interested in elucidating the importance of vertical mixing affecting not only the SPM distribution in the water column but also the distribution of contaminants and how the dynamics of the contaminants is affected by this sudden event. For this purpose, it is necessary to apply a dynamic model that represents all important processes in the water column and interactions with the boundaries (air and sediment) as a function of the physico-chemical and biological characteristics of the system.

## 2. Material and methods

### 2.1. Case study: Ispra Bay, Lake Maggiore

Lake Maggiore is the second largest (212 $km^2$) and deepest (370 m) Italian subalpine lake (Fig. 1). It is located in the foothills of the Alps, just north of the most industrialized part of Italy, which includes cities such as Milan and Turin. The lake is situated at 194 m above sea level (a.s.l.), in a fluvial valley reshaped by glacier activity in the Alpine area of Northern Italy. This region forms one of the largest basins in Italy, and is connected with river Po, the most important watercourse in Italy, through its effluent the Ticino. The catchment lays half in Italy (Piedmont and Lombardy) and half in Switzerland (Canton Ticino). The northernmost part of the area is occupied by the Alps, with the highest peak (Monte Rosa) at 4633 m a.s.l.; most of population (634 000) lives in the subalpine area in the southern part of the catchment where the main industrial activities are also located. Lake Maggiore is a well studied and monitored ecosystem and since 1978 yearly reports are produced regarding all relevant limnological aspects (temperature, phytoplankton productivity and the main chemical parameters) by the Commissione Internazionale per la Protezione delle Acque Italo-Svizzere (CIPAIS).

In this study we present the application of a 1D hydrodynamic and contaminant fate model to a station located in the Ispra Bay, in the southern part of the Lake Maggiore, at a water depth of 33 m (Fig. 1). The choice of the location is motivated by the availability of PCBs concentration data concerning all relevant compartments necessary to provide the forcing values to run the fate model. In fact, the dataset contains weekly values of air concentration (gas and aerosol-bound) of PCBs and information on sediment concentrations. Due to the absence of concentration data in the water column, data regarding the settling of particulate-bound PCBs from the deployment of a sediment trap (Vives et al., 2007; Castro-Jiménez et al., 2008) has been used to assess model's performances.

### 2.2. Model description

A fully coupled 1D hydrodynamic and contaminant fate model was applied to simulate the concentrations in the water column of Lake Maggiore considering the exchange of contaminant with the atmosphere and the sediments. The model was originally implemented for plant protection products (Carafa et al., 2006) and successively adapted for simulation of PCBs (Jurado et al., 2007), and other POPs families (PAHs, PBDEs and PCDD/Fs) (Marinov et al., 2007). The model coupling is achieved by incorporating the contaminant fate module into the program structure of 3D COHERENS model (COupled Hydrodynamical Ecological model for REgioNal Shelf seas), a 1D/3D finite-difference multi-purpose model (Luyten et al., 1999, 2003), which is freely available for scientific purposes.

COHERENS was originally dedicated to coastal and shelf seas but can be adapted to lake conditions; in our runs tides were not considered and the reference salinity was set to 0.5. The appropriate description of vertical exchange processes and light attenuation is crucial for the output of the hydrodynamic model. Turbulence and optical parameters were defined following the parameterisation of a previous hydrodynamics modelling study carried out at the Ispra Bay (Stips et al., 2002). The $k$–$\varepsilon$ turbulence scheme was used with a stability function evaluated as a function of the Richardson number and the Xing formulation for the mixing length. Limiting conditions were enabled. For the light attenuation following parameters were used: light attenuation coefficient = 2.5 $m^{-1}$, attenuation coefficient for PAR = 0.125 $m^{-1}$, infrared fraction of solar irradiance = 0.75.

The contaminant fate module represents the concentration of contaminant in the water column and in the surface mixed layer of the sediment as three different phases: freely dissolved, bound to dissolved organic carbon (DOC) and particulate-bound (Fig. 2). The boundary is represented by the atmospheric concentration and the concentration in deep sediment. In addition, all relevant processes (partitioning, atmospheric exchange, settling, degradation, resuspension, burial and diffuse interaction with sediments) have been parameterized and included. The SPM of both, physical and biological origin is represented as a separate compartment in the model due to its important effect on the partitioning of the PCBs. A detailed description of the model is provided in the Supplementary material section.

### 2.3. Model forcing

The model is forced with hourly values of meteorological parameters such as wind direction and speed, air temperature, cloud coverage and rainfall and values of Chlorophyll a. The meteorological data were obtained by the Meteorological Station in Ranco, about 5 km from the Ispra Bay (Fig. 1). The air temperature shows a variation between a maximum value of 33.7 °C at the end of June 2005 and −4.9 °C at the end of January 2006, with a yearly average of 13.2 °C, while precipitation was high in April (152 mm), August (119 mm) and September 2005 (130 mm), and low in November 2005 (13 mm).

The Chlorophyll a concentrations were calculated from the monthly values of the phytoplankton biovolume measured in the top 20 m at a station located in the central part of Lake Maggiore (CIPAIS, 2005, 2006) using the correlation given by Felip and Catalan (2000). The yearly average concentration of Chlorophyll a is