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Modelling of mercury transport and transformations in the water compartment of the Mediterranean Sea

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Abstract

The Mediterranean Basin is highly heterogeneous with regard to its climatic and oceanographic properties. The appropriate approach for simulating the transport and transformations of Hg in the water compartment requires the use of a hydrodynamic model with additional modules for transport–dispersion and biogeochemistry. In this work, the PCFLOW3D model was upgraded with a biogeochemical module and used for simulation of mercury transport and transformation processes in the Mediterranean. The circulation for the four seasons due to wind, thermohaline forcing and inflow momentum of the main rivers and through the straits was calculated. The results were compared with measurements and the results of another model (POM — Princeton Ocean Model). An acceptable agreement was achieved. The seasonally averaged velocity fields obtained were used to simulate transport and dispersion of mercury.

A new biogeochemical module dealing with the different mercury species: gaseous elemental (Hg^0), divalent (Hg^{2+}), and monomethyl mercury (MMHg) in dissolved form and bound to particulate matter and plankton was introduced. Exchange of mercury at the boundaries (bottom sediment/water and water/atmosphere) and transformation processes such as methylation, demethylation, reduction and oxidation were taken into account. The transformation rates between the mercury species were described using simple equations, and thus the time and space variable reaction coefficients should be determined from in-situ measurements. Instead, machine-learning tools and classical statistical methods were used to connect the measured sets of geophysical/environmental parameters and concentrations of different Hg species. The provisional annual Hg mass balance established for the Mediterranean showed that exchange with the atmosphere is the most important source/sink of mercury for the water compartment. Therefore, the model was further upgraded with a gas exchange module for Hg^0. To improve the results of the simulations the PCFLOW3D aquatic model was further linked to the RAMS–Hg atmospheric model which provided real-time meteorological data, deposition and concentrations of mercury in the atmosphere.

Simulations with the integrated modelling tool were performed and the results were compared to the measurements. Acceptable agreement of the average concentrations down the water column for both total mercury (HgT) and elemental mercury (Hg^0) was achieved. Agreement of Hg^0 concentrations near the surface was good; thus exchange with the atmosphere can be simulated with relatively high reliability. Agreement of simulated MMHg concentrations with measurements was not satisfactory, which is probably due to poor understanding of the processes of MMHg formation and its dependence on environmental factors, which have, so far, not been taken into account in the modelling.

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In view of the satisfactory modelling results obtained for HgT and Hg^0, a simulation of management scenarios, particularly the policy target (PoT) scenarios for 2010 and 2020, was performed. The results of these simulations were further used to establish the mass balance of HgT in the Mediterranean Sea.

Keywords: Mercury; Modelling; Speciation; Three-dimensional model; Hydrodynamics; Transport; Transformations; Mediterranean Sea

1. Introduction

In the late 1970's elevated concentrations of mercury were found in Mediterranean fish (Bernhard and Renzoni, 1977), and concern about the possible effects on human health soon resulted in mercury oriented projects, studies and investigations in the Mediterranean area (Bernhard, 1988; Bacci, 1989; UNEP-MAP, 1986, 1998, 2001). Mercury, particularly in its elemental form, can be transported long distances through the air and water, and thus many studies were dedicated to global mercury cycling (Mason et al., 1994; Fitzgerald and Mason, 1996). Numerous studies have dealt with mercury cycling in the oceans (Cossa et al., 1996; Mason and Fitzgerald, 1996; Mason and Gill, 2005) and reduction processes in seawater (Amyot et al., 1997; Costa and Liss, 1999; Rolfhus and Fitzgerald, 2001, 2004; Gårdfeld et al., 2002). Mercury evasion at the ocean–atmosphere interface is also relatively well described and understood (Mason and Fitzgerald, 1996; Gårdfeldt et al., 2003). However, much less is known about mercury oxidation in the surface layer of the open ocean, and methylation and demethylation of mercury in the water column of the open sea and bottom sediment, as most of the studies deal with coastal areas (Hines et al., 2001; Mason and Gill, 2005; Monperrus et al., 2004). In the last decade mercury speciation in all environmental compartments of the Mediterranean Basin was performed during sampling cruises and coastal campaigns in the framework of the European mercury-oriented projects MAMCS and MERCYMS. Their aims were to determine the state of mercury pollution and provide qualitatively and quantitatively acceptable data for modelling purposes.

Mercury speciation in air (Sprovieri et al., 2003), measured and calculated mercury fluxes through the marine boundary layer (Gårdfeldt et al., 2003) and the established natural and anthropogenic mercury emission inventory to the atmosphere from the Mediterranean countries and the wider background area (Pirrone et al., 2001; Pacyna and Pacyna, 2002; Pacyna et al., 2003) enabled the use of models dealing with the air compartment and the marine boundary layer of the Mediterranean region (Pirrone and Hedgecock, 2001; Kallos et al., 2001; Pirrone et al., 2003). On the other hand, the data collected from water column measurements in Mediterranean deep-water (Cossa et al., 1997; Ferrara et al., 2003; Horvat et al., 2003) have never been used for modelling purposes. The main reason is that some of the processes in the water column and in the bottom sediment, particularly methylation and demethylation, are still not well understood. New methods and more measurements are needed to clarify relations and processes occurring in and between mercury species in the aquatic environment (Monperrus et al., 2004; Vidimova et al., 2004). Adequate measurements were available only in the coastal waters of the Mediterranean Sea, the Rhone estuary (Cossa and Martin, 1991) and the Gulf of Trieste, Northern Adriatic (Horvat et al., 1999; Faganeli et al., 2001; Hines et al., 2001). Consequently, there are only a few mathematical models capable of simulating simplified mercury transformation processes in the aquatic, mostly freshwater environment (Tetra-Tech Inc., 1999; Carroll et al., 2000; Carroll and Warwick, 2001; Harris et al., 2004; Žagar et al., 2006). Until this study, mathematical modelling of mercury transport and some basic transformations in the marine environment has only been performed in contaminated coastal areas, namely in the Gulf of Trieste (Rajar et al., 1997; Širca et al., 1999; Rajar et al., 2000) and Minamata Bay (Rajar et al., 2004c).

The Mediterranean Sea is very heterogeneous regarding its climate and oceanographic properties. Climatologically, there are two main and two transient seasons in the Mediterranean region. The cold season (November to February) is the rainy period, and the warm season (June to September) is the dry period with almost no rain. During spring and autumn the winter and summer-type weather patterns interchange. The circulation of Mediterranean Sea waters is also relatively complicated, as it is driven by the exchange of salinity and heat through the Strait of Gibraltar and net fresh water loss and heat loss to the atmosphere. The Mediterranean Sea water circulation has been the subject of numerous studies and is relatively well understood and modelled (Bethoux, 1979; Zavatarelli and Mellor, 1995; Boukthir and Barnier, 2000; Rajar et al., 2007-this issue). The exchange of water and pollutants between the Mediterranean and the Atlantic Ocean, as well as river and atmospheric inputs, were also

the subject of many studies (Bethoux, 1979; UNEP-MAP, 1986; Ferrara and Maserti, 1988; UNEP-MAP, 1996; Boukthir and Barnier, 2000; Lafuente et al., 2002; Rajar et al., 2007-this issue).

As the circulation/transport patterns and the patterns of mercury transformations significantly change during the seasons and along the water column, the modelling approach appropriate for the Mediterranean Sea requires the use of a hydrodynamic and transport model. The model should be capable of simulating the transport of different mercury species, as well as transformations between these species in the water column and the fluxes at the water–sediment and water–atmosphere interface. Rajar et al. (2004c) described the need for multidimensional modelling and methodologies applied in different cases, as well as the benefits and disadvantages of spatial and temporal averaging in the models. Taking into account the described spatial and temporal variability of the Mediterranean Sea, the use of a non-steady state three-dimensional model with as few annually averaged parameters as possible is necessary in order to properly simulate circulation, seawater properties and mercury processes in space and time.

The aim of the present study was to improve the modelling tool for simulation of mercury transport and transformations in seawater, to calibrate and validate the upgraded model using measurement data from the water column (from MERCYMS cruises, Fig. 1) and to simulate the present state of mercury pollution. Taking into account all currently available data on the sources and sinks of mercury, it was determined that a water model alone is not enough to give an appropriate description of mercury cycling in the water column. Due to the importance of evasion of mercury from water to the atmosphere, the water model was linked to an atmospheric one in order to improve the modelling results. The linked models (integrated modelling tool) exchanged data regarding concentrations near the water surface and fluxes through the water–air interface on a seasonal basis. With this integrated model it was possible to perform simulations of the mercury species distribution in space and time throughout the Mediterranean. The results were used to improve the previously established provisional annual mercury mass balance of the Mediterranean Sea and to simulate the mercury concentration distribution in the future, following policy-target scenario. This study complements the paper presented in the same special issue discussing the present and future mercury mass balance in the Mediterranean Sea (Rajar et al., 2007-this issue).

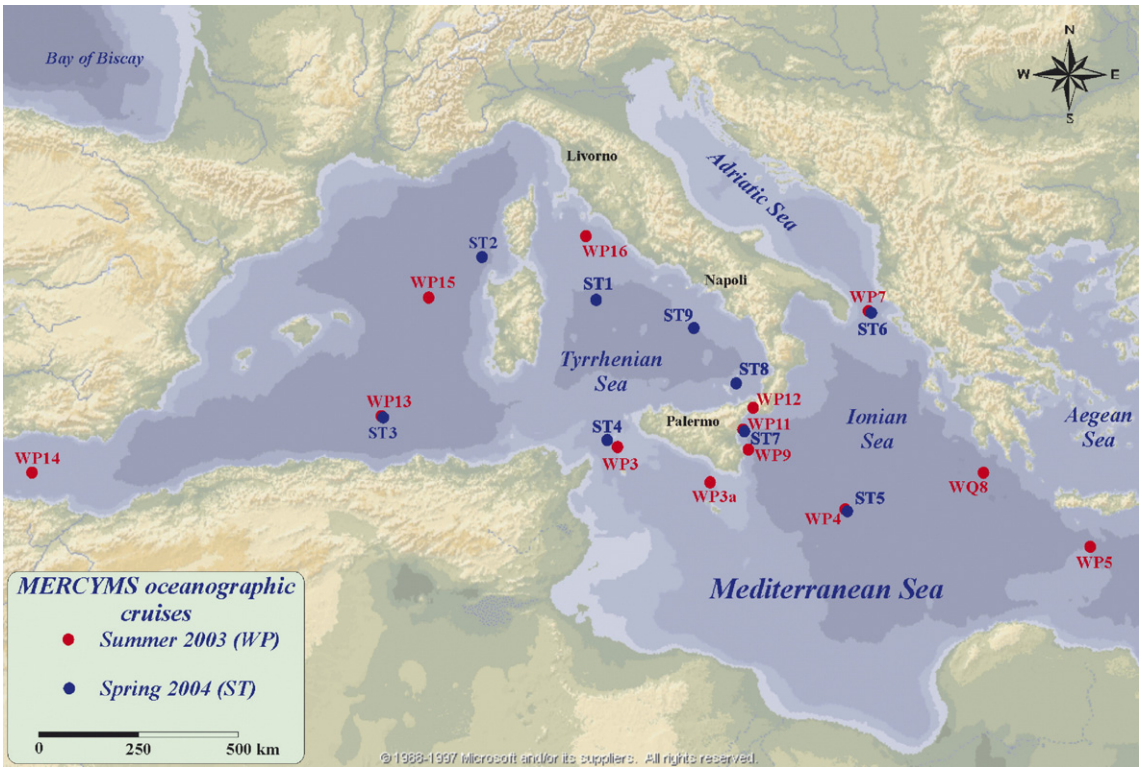

Fig. 1. The Mediterranean Sea with the sampling points of the two MERCYMS cruises. Based on MS Encarta World Atlas.

2. The PCFLOW3D model

2.1. Description of the basic PCFLOW3D model

The PCFLOW3D is a non-steady state three-dimensional non-linear baroclinic *z*-coordinate model with a hydrostatic approximation. The model was developed at the Faculty of Civil and Geodetic Engineering of the University of Ljubljana and consists of four modules: a hydrodynamic (HD) module, a transport–dispersion (TD) module, a sediment-transport (ST) module and a biogeochemical (BGC) module, developed in the framework of the MERCYMS project in order to simulate the transport and transformations of mercury. Within the BGC module Hg speciation and exchange with the bottom and the atmosphere are taken into account. The model in its original form, without the recently developed BGC module, has been applied to many practical pollutant dispersion problems in Slovenia and abroad (Rajar and Širca, 1996; Rajar et al., 1997; Rajar and Širca, 1998; Rajar et al., 2000, 2004a,b,c). A short description of the basic modules is given below.

The HD and TD modules are based on the finite difference (finite volume) method. The following water motion forcing factors can be accounted for: wind forcing, tidal forcing, inflow momentum of rivers and through the straits, as well as thermohaline forcing due to non-uniform distribution of temperature and salinity and consequently non-uniform distribution of water density. The transport equation in the model can be solved either by an Eulerian finite difference method (FDM) or a Lagrangean particle tracking method (PTM). The FDM was used for mercury transport simulations. The ST (Sediment Transport) module solves the advection dispersion equation where the empirical equation for the sedimentation velocity (van Rijn, 1993) of the particles is accounted for. The module is similar to the 3D sediment-transport model described in Lin and Falconer (1996). The transport of non-cohesive material can be simulated. The sedimentation and resuspension of sediments from the bottom, and the thickness of eroded or deposited material are calculated as a result of the shear stress produced by the combined impact of currents and waves. A detailed description of the three basic modules of the PCFLOW3D model (Fig. 2) was given in Rajar et al. (1997), Četina et al. (2000) and Rajar et al. (2004c).

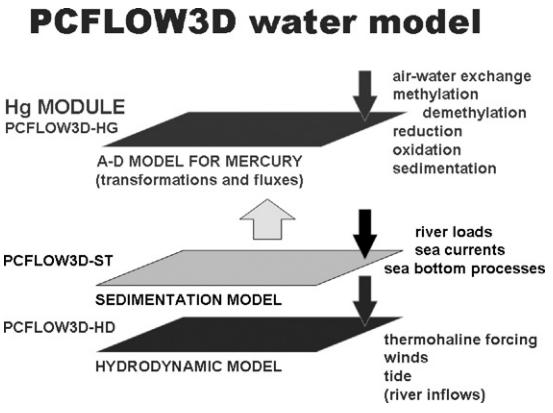

Fig. 2. Basic structure of the PCFLOW3D model without the biogeochemical module.

2.2. Upgrades of the hydrodynamic and transport–dispersion modules

Our aim was to perform long-term simulations of transport and biogeochemical transformations of mercury in the Mediterranean. Therefore, numerical diffusion, which is a known problem with numerical schemes of the first order of accuracy (Žagar et al., 2001), had to be reduced as much as possible. In order to solve this problem the existing hybrid (central-upwind) implicit scheme (Patankar, 1980) was replaced by the QUICK numerical scheme with the second-order of accuracy (Leonard, 1979; Hayase et al., 1992). The model was also upgraded with two multi-parameter turbulence models, i.e. the Smagorinski model in the horizontal direction and the Mellor–Yamada turbulence closure scheme in the vertical direction (Mellor and Yamada, 1982). In this way a significant improvement of the results was achieved.

2.3. Upgrade of the biogeochemical module

The biogeochemical module of the PCFLOW3D model was developed from the two-dimensional STATRIM advection–dispersion module (Širca et al., 1999), created at the University of Ljubljana, which simulated the transport of non-methylated and methylated mercury. Concentrations of both species in each control volume were represented by single values that included dissolved, particulate and plankton fractions, calculated by partitioning coefficients. Mercury processes included the input of atmospheric mercury, sedimentation, reduction, methylation and demethylation. The module itself and the simulations performed in the Gulf of Trieste are described in Rajar et al. (1997), Širca et al. (1999) and Rajar et al. (2000).

The new biogeochemical module of the PCFLOW3D model accounts for three different mercury species: gaseous elemental mercury (Hg^0), and divalent (Hg^{2+})

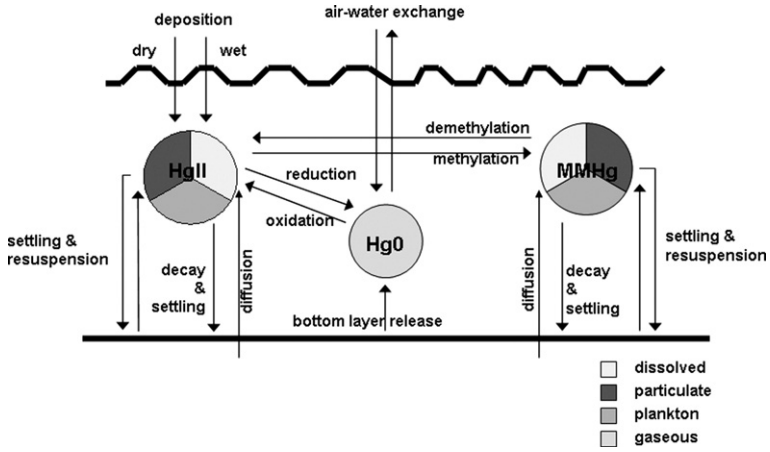

Fig. 3. Biogeochemical module of the PCFLOW3D model.

and mono-methyl (MMHg) mercury in dissolved form and bound to particles and plankton (Fig. 3). On the basis of velocity fields calculated in the HD module, the transport of each Hg species due to advection and dispersion is determined. Thereafter, the transformation processes in each cell of the three-dimensional computational domain are simulated. The module takes into account exchange with the bottom sediment (diffusive fluxes from sediment to the bottom layer) and exchange with the atmosphere (evasion from the surface layer as well as wet and dry deposition). Some transformation processes (methylation, demethylation, reduction and oxidation) were also simulated.

The main benefit of a 3D non-steady state biogeochemical module is that such a model can account for temporally and spatially variable transformation coefficients. However, the transformation processes in the water column and their dependence on different oceanographic and ecological parameters are still poorly understood. Therefore, it was not possible to use a set of algebraic or differential equations to determine the reaction coefficients with satisfactory accuracy. We decided to use relatively simple first-order transformation equations: in each control volume the source/sink term in the advection–dispersion equation for each of the Hg species was calculated as

$$\Delta M_i = K_r{}^* M_r{}^* \Delta t,$$

where ΔM_i represents a change in the mass of the reaction product (Hg^0, Hg^{2+} or MMHg, respectively) in the observed time-step Δt, K_r are reaction coefficients of either methylation, demethylation, oxidation and reduction and M_r is the mass of the reactant. In the future, for better accuracy of modelling work, the time and space variable reaction coefficients (K_r) need to be determined from in-situ measurements, due to the complexity of mercury transformation processes and the necessity to simulate a large part of mercury biogeochemical cycling within such a large and heterogeneous domain.

2.4. Transformation parameters of the BGC module

During the coastal campaigns and particularly during the deep-sea measurements in the framework of mercury oriented projects in the Mediterranean (MAMCS and MERCYMS) many data on concentrations of Hg species in all the considered compartments were collected, as well as geophysical and environmental parameters (Horvat et al., 2003; Ferrara et al., 2003, Gårdfeldt et al., 2003; Andersson et al., 2007-this issue; Kotnik et al., 2007-this issue). As basic knowledge about the transformation rates is still not very precise

Table 1
Measured parameters and mercury species

Geophysical/ Environmental parameters	Mercury species
Date (season)	HgT (total)
Time of day	HgT (d) (total dissolved)
Location	MMHg (T) (total mono-methyl)
Depth	MMHg (d) (dissolved mono-methyl)
Water temperature	DMHg (dimethyl)
Air temperature	DGM (dissolved gaseous)
Wind speed and direction	
Salinity	
Transmissivity	
Conductivity	
Fluorescence	
Dissolved oxygen	
Chlorophyll-A	

and the reaction rates are given in the literature over relatively wide ranges (e.g. Carroll et al., 2000; Rolfhus and Fitzgerald, 2004), the basic idea was to connect the mercury concentrations with the measured geophysical and environmental parameters, (i.e. both sets of data collected within the same campaign), and to determine the time and space distribution of the transformation rates. Due to the quantity of possible relations between the mercury species and the other measured parameters, conventional statistical methods were difficult to use. On the other hand, artificial intelligence methods (machine-learning tools) are known to be a suitable instrument for dealing with such problems, as they result in transparent models, appropriate for further use with similar problems and are easy-to-upgrade when new data-sets become available (Kompare, 1998; Džeroski et al., 1999, 2004).

It is hard to expect that machine-learning tools would be capable of replacing experimental methods in determination of reaction coefficients. Thus, the main aim of the use of these tools was rather to improve the approximation of transformation coefficients, and, consequently, the modelling results. The data from two deep-sea measurement campaigns (MERCYMS project, summer 2003 and spring 2004, Fig. 1) were used. The measured parameters and the mercury species are presented in Table 1. From a wide variety of machine-learning tools the technique called "model-tree", developed by Quinlan (1992) and further improved by Wang and Witten (1997) was adopted. The method is incorporated in the WEKA package of machine-learning algorithms, available at http://www.cs.waikato.ac.nz/ml/weka/. This method was previously compared to some other machine-learning tools and has been found to be capable of working without measured time-series of data (Bratko et al., 2003a,b; Sirnik, 2004). The method uses data to build piece-wise linear equations, i.e. relations between the concentration of a chosen independent parameter and other dependent parameters in the form of a set of linear equations. The reaction coefficients in the form of functions f_i, (where par_i represents measured parameters and Hg_{xi} represents the chosen mercury species concentration) in linear equations of type

$$\mathrm{par}_x < y_1 : \; Hg_{x1} = f_1(\mathrm{par}_1, \mathrm{par}_2, \mathrm{par}_3 \ldots . \mathrm{par}_n, \mathrm{Hg}_{x2}, \mathrm{Hg}_{x3} \ldots \mathrm{Hg}_{xn})$$
$$y_1 < \mathrm{par}_x < y_2 : Hg_{x1} = f_2(\mathrm{par}_1, \mathrm{par}_2, \mathrm{par}_3 \ldots . \mathrm{par}_n, \mathrm{Hg}_{x2}, \mathrm{Hg}_{x3} \ldots \mathrm{Hg}_{xn})$$
etc.

were gathered by the use of the machine-learning tools.

2.5. Air–water exchange sub-module

On the basis of previous measurements and modellingresults (Cossa et al., 1997; Horvat et al., 2003; Gårdfeldt et al., 2003; Sprovieri et al., 2003; Kallos et al., 2001) a provisional annual mercury mass balance for the Mediterranean Basin was calculated (Žagar et al., 2005). Despite large discrepancies between values from several older sources, it has become evident that the atmosphere is the most significant source and sink of mercury for the Mediterranean Sea. Moreover, even preliminary simulations with the PCFLOW3D model for typical winter conditions, with and without the use of a (very simplified) gas exchange sub-module, showed a significant difference in dissolved gaseous mercury concentrations in the surface layer (Žagar et al., 2005).

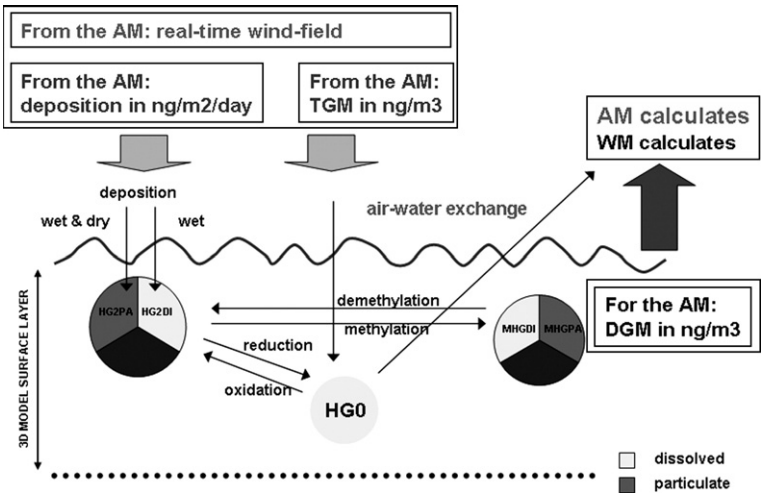

Fig. 4. The principle of coupling of the water and the atmospheric model.

Therefore, the next step was to develop and include the air–water exchange sub-module into the biogeochemical module of the PCFLOW3D model.

In this module, the exchange between water and the atmosphere consists of the evasion of elemental gaseous mercury, and the deposition of different airborne mercury species. The upward flux (mercury evasion), represents the most important part of the exchange between water and the air, and can be calculated by different gas exchange models. The relationship between wind-speed and gas exchange described by Wanninkhof (1992), also used by Gårdfeldt et al. (2003), was adopted for the PCFLOW3D model. As deposition is relatively difficult to determine from measurements, the data should be the result of an atmospheric model and should take into account both wet and dry deposition. Wet deposition relates to soluble chemical species (Hg^{2+} and some Hg^{0}) and scavenging of particulate (Hg^{P}) mercury, while dry deposition accounts for deposition of divalent and particulate mercury. Deposition is highly important for the water model, as the majority of mercury is deposited in divalent form, and, as such it can immediately enter transformation processes (methylation, reduction) in the surface layer.

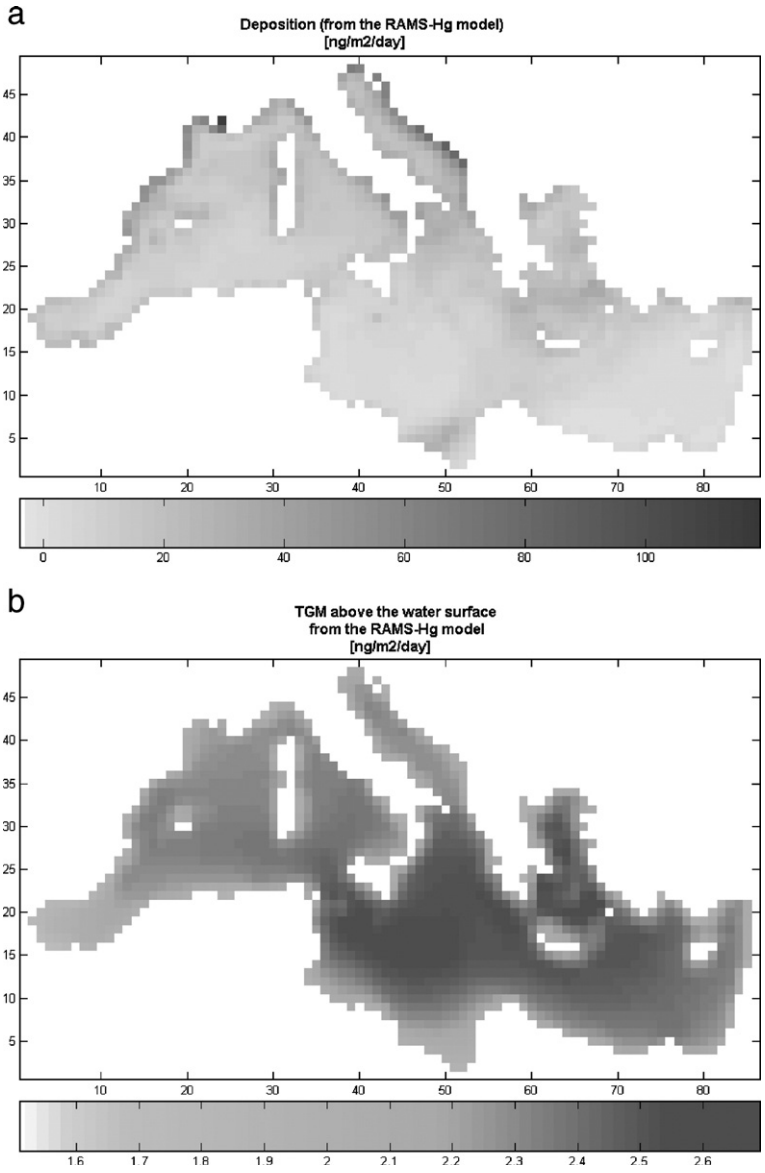

Fig. 5. Deposition field in [ng m^{-2} day^{-1}], above and total gaseous mercury (TGM) in [ng m^{-3}], below — spring, weekly averaged (result of the RAMS–Hg model used as input for the PCFLOW3D).

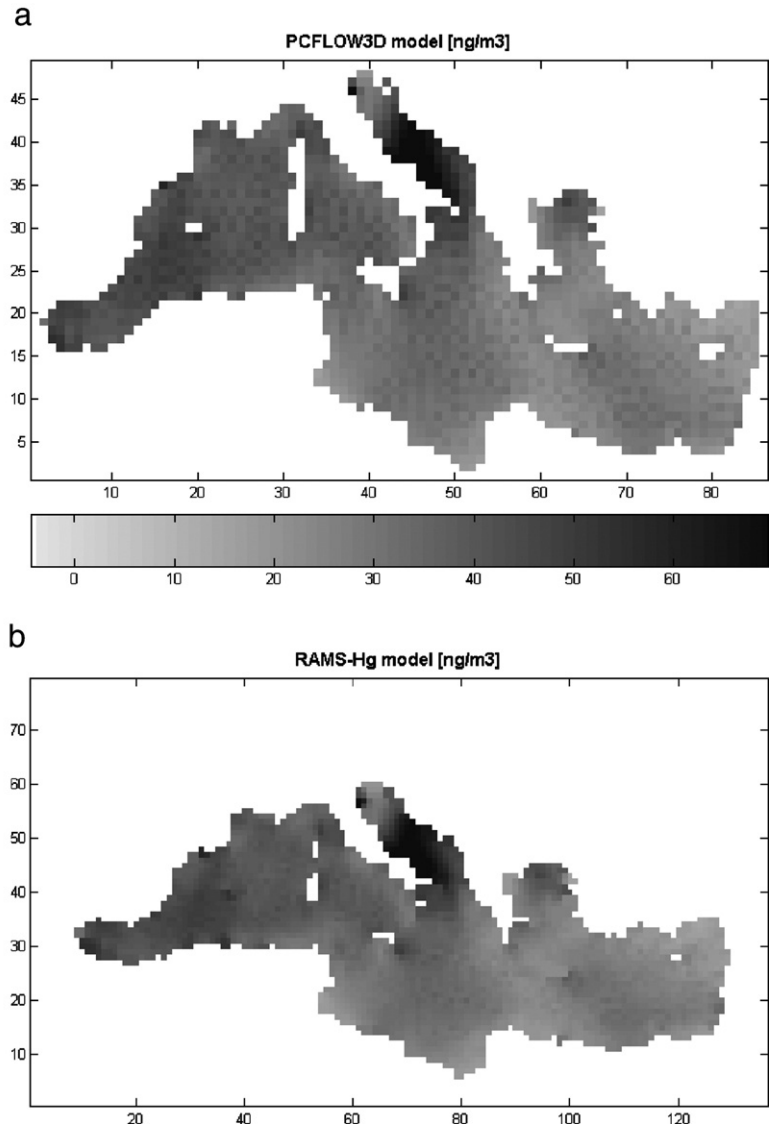

Fig. 6. Dissolved gaseous mercury (DGM) in [ng m^{-3}] — spring, weekly averaged. Result of the PCFLOW3D model (above) transformed and used as input of the RAMS–Hg model (below). 1 pM = 200 ng/m^3.

As already mentioned, the adopted method requires data from the air and the water compartment. Thus, the best approach in solving the evasion equation would be an integrated air–water model, which would be capable of exchanging the water and the air data in each computational time step. As such coupled models do not exist at present, we decided to link the PCFLOW3D model and the RAMS–Hg model (Kallos et al., 2001; Voudouri and Kallos, 2004, in press; Voudouri et al., 2004), as further described in Chapter 2.6 of this paper. In this way, all the required parameters for the computation are exchanged between the models in any chosen time interval. In this way, the water model provides elemental gaseous mercury (DGM) concentrations in the surface layer and the water temperature, while the atmospheric model gives the deposition, the concentrations of total gaseous mercury in air (TGM), and wind speed fields above the computational domain (u_{10}). According to Wanninkhof's model, the evasion fluxes in ng/(m^2 h) can be calculated using the following equation:

$$\text{Evasion} = k_w(\text{DGM} - \text{TGM}/H'(T_w))$$

where H' is Henry's Law constant for elemental mercury and depends on the properties of water. Sanemasa

(1975) proposed the following formula

$$H' = \frac{M_w(10^{-1078/T+6.250})}{R\rho_w T}$$

where M_w is the molar weight of water, R is the gas constant, ρ_w is water density and T is temperature in degrees Kelvin. Sanemasa (1975) also proposed that the H' in seawater should be about 13% higher than in pure water. However, an investigation by Andersson et al. (2004) showed that the correct formula for Henry's Law constant in seawater is as follows:

$$H' = \frac{M_w \cdot \exp^{-2708.4/T+15.151)}}{R\rho_w T}$$

Wanninkhof (1992) and Gårdfeldt et al. (2003) proposed the following form of the gas transfer velocity (k_w):

$$k_w = \frac{A \cdot u_{10}^2}{(Sc_{Hg}/B)^{0.5}}$$

where A equals either 0.31 or 0.39 for measured data and averaged values, respectively; Sc_{Hg} is the Schmidt number for elemental mercury (the ratio between the kinematic viscosity of water and the aqueous diffusivity of Hg^0), B is the Schmidt number for CO_2 and u_{10} is the wind speed at the height of 10 m above the water.

2.6. Linking of the water model and the atmospheric model

As shown, the water model cannot reliably simulate mercury transport and transformation processes in the water compartment without being coupled or linked to an atmospheric model. The two models, PCLOW3D and RAMS–Hg, were linked in order to improve the quality of the modelling results (Fig. 4).

The two models cover different areas and use different grids, which are also based on different cartographic projections. The RAMS–Hg model has a space resolution of 32 × 32 km in the domain covering most of Europe and North Africa, as the impact of mercury emissions from a much wider area has to be accounted for. On the other hand, the PCFLOW model covers only the area of the Mediterranean Sea itself and has a resolution of 1/2 and 1/3 degrees in the longitudinal and lateral directions, respectively, refined in the vicinity of the Gibraltar strait. A data conversion tool for transforming the data from one grid into the other had to be applied; weight coefficients were calculated for each grid–cell in both grids, and the concentrations were transformed from one grid to the other and vice versa. Mass conservation of any scalar field was assured during the transformation.

Both models also have quite different response times to forcing factors. For the water model, the response time is of the order of magnitude of about a week, while different processes in the air occur in a timeframe of a few hours. This represents a difference of two orders of magnitude. Taking into account uncertainty in the input data about the other mercury sources and the transformation parameters, we opted for a weekly exchange of data between the models. The atmospheric model provided real-time wind fields, deposition data and TGM concentrations (6 h, 12 h and 12 h, respectively). The deposition and TGM data were transformed to the water model grid and further averaged over the period of each week and over the four seasons. As wind is a very important parameter in the calculation of mercury evasion, the original 6-hour wind fields were used. The results of the PCFLOW3D model were transformed back to the air model grid and used for computations with the atmospheric model.

Some of the data-fields exchanged between the models are presented in Figs. 5 and 6. The partially wet grid–cells of the RAMS–Hg model in Fig. 6 are shown as wet; therefore the coastline shape of the Mediterranean Sea is partially distorted.

Table 2
Sensitivity analysis of the PCFLOW3D model. The input parameters are ordered by importance from top to bottom for the surface and subsurface layers

Surface	Subsurface
Wind (evasion)	Reactions
Deposition	Advection/dispersion
Advection/dispersion	Bottom release
TGM (evasion)	Deposition
Reactions	Wind (evasion)
Bottom release	TGM (evasion)

3. Boundary conditions: mercury inputs to the Mediterranean

Data about mercury contamination from rivers, point and diffuse sources to the Mediterranean Sea as well as the output of mercury via fish-harvesting, sedimentation to the bottom and exchange with the Atlantic Ocean and the Black Sea, used as input data for the PCFLOW3D model, were collected from available measurements, the MERCYMS database (http://www.cs.iia.cnr.it/MERCYMS/project.htm) and the literature (Bacci, 1989; Cossa et al., 1997; Cossa and Coquery, 2005). All considered sources and sinks are described in detail

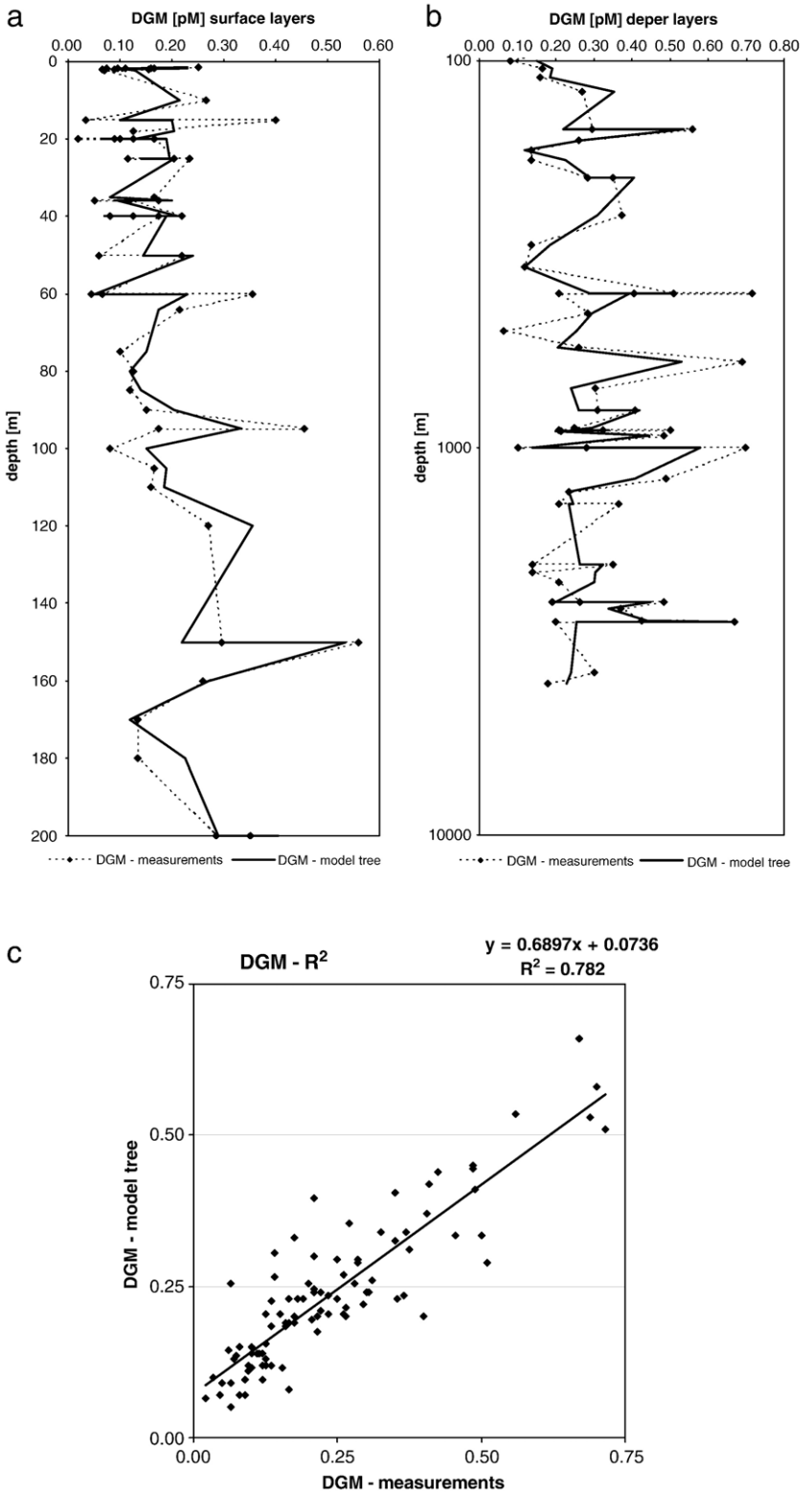

Fig. 7. Connecting the environmental parameters and the DGM concentrations. Results of the WEKA artificial intelligence tool.

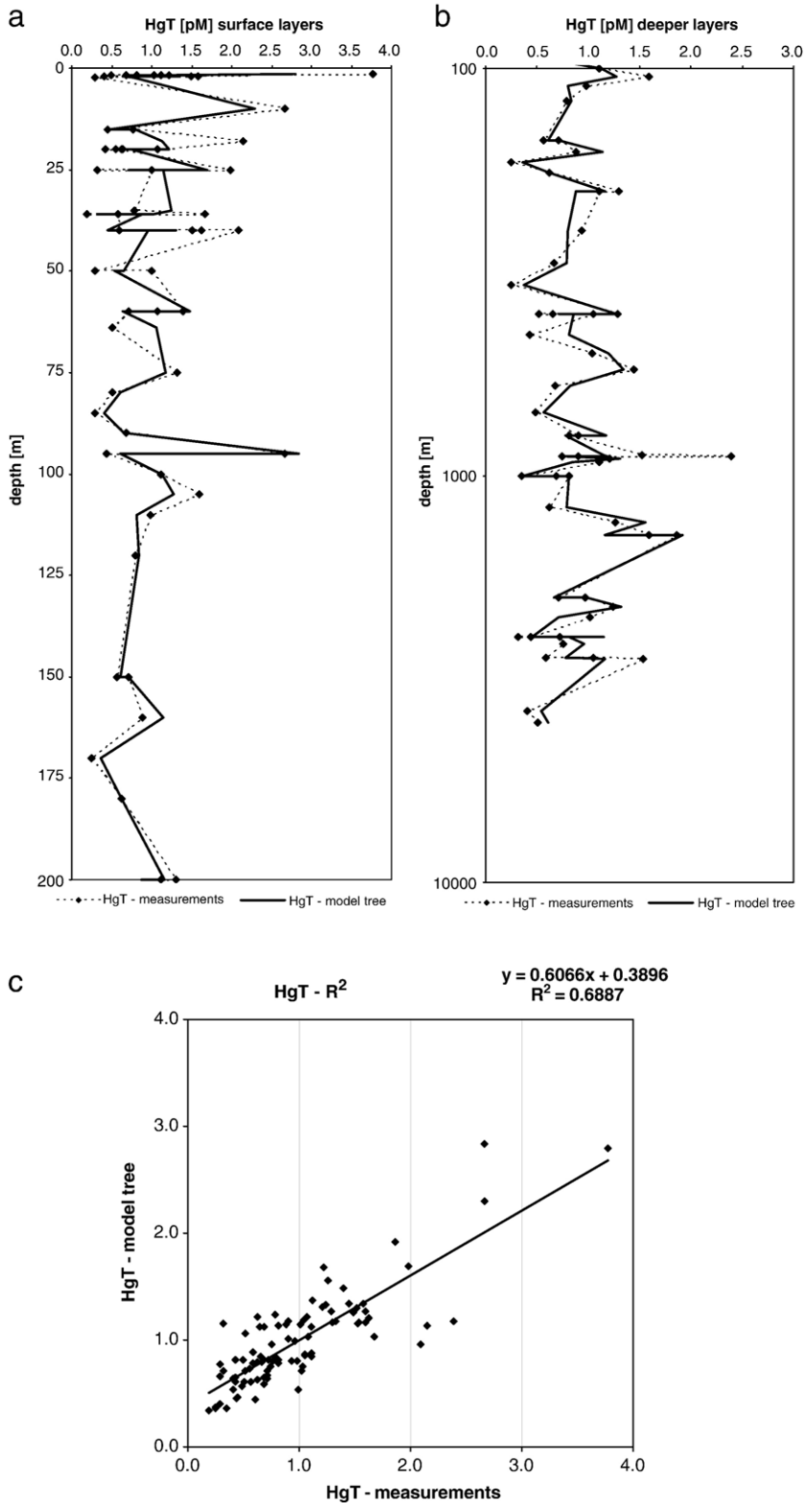

Fig. 8. Connecting the environmental parameters and the HgT concentrations. Results of the WEKA artificial intelligence tool.

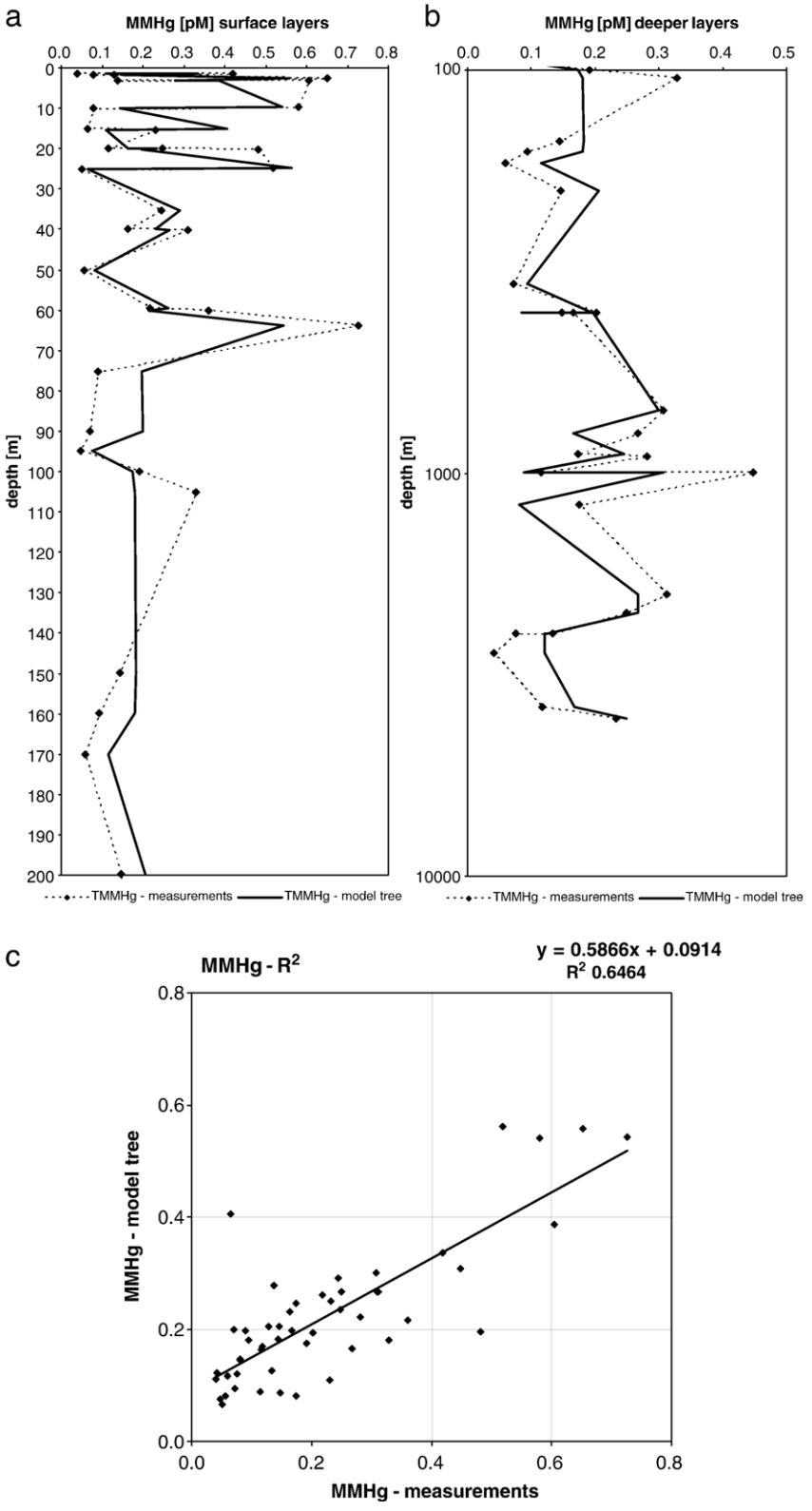

Fig. 9. Connecting the environmental parameters and the mono-methyl Hg concentrations. Results of the WEKA artificial intelligence tool.

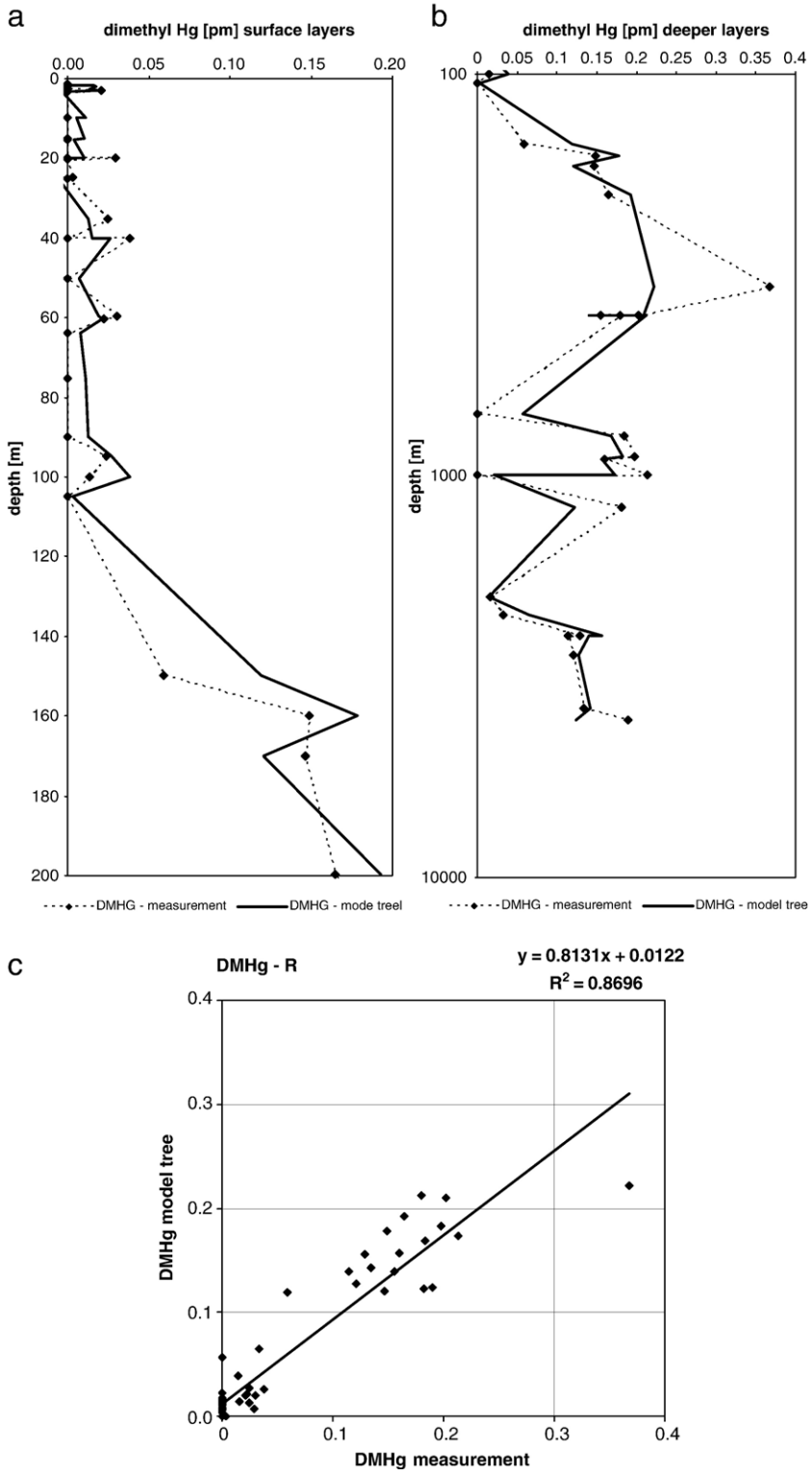

Fig. 10. Connecting the environmental parameters and the dimethyl Hg concentrations. Results of the WEKA artificial intelligence tool.

Table 3
Statistical analysis of the results of the WEKA model

Hg species	DGM	HgT	MMHg	DMHg
r^2 (excel)	0.782	0.689	0.646	0.870
Correlation coefficient	0.723	0.616	0.376	0.817
Mean absolute error [pM]	0.081	0.347	0.117	0.033
Root mean squared error [pM]	0.110	0.483	0.163	0.049
Relative absolute error	64.31 %	76.51 %	85.63 %	43.75 %
Root relative squared error	68.34 %	79.12 %	93.53 %	56.27 %

and discussed in Rajar et al. (2007-this issue). According to measurements made in the coastal area (Cossa and Martin, 1991; Horvat et al., 1999; Cossa and Coquery, 2005), only about 10 % of mercury washed into the marine environment is in the dissolved form. Mercury is mostly bound to suspended sediment that usually settles close to the river mouths. Although some of the incoming mercury is further remobilised, only a minor part of the mercury brought to the sea is directly available for transformation processes. Therefore, only the inflow concentrations of dissolved Hg were used in the deep-water column simulations. On the other hand, the total mercury input (in dissolved and particulate form) was taken into account in calculations of the mercury mass balance of the Mediterranean Basin (Rajar et al., 2007-this issue).

4. Hydrodynamic simulations

Transport of any pollutant either dissolved or bound to suspended sediment particles largely depends on the velocity field. However, simultaneous non-steady state (real-time) simulations of circulation, transport and mercury biogeochemical transformations for the whole Mediterranean Sea were not feasible. Beside the lack of input data, such simulations over the period of a decade or more would demand an extremely long computational time. As the main goal of the study was to simulate long-term processes, we decided to use the so-called quasi-steady state approach, which has previously been used with the PCFLOW3D model in similar cases (Rajar et al., 2000; Četina et al., 2000; Žagar et al., 2001). Considering the many uncertainties in the mercury input data and lack of knowledge about the mercury transformation processes, this methodology was estimated to be accurate enough. In this way, non-steady state computation of hydrodynamics is performed for the typical seasons. Such seasonally averaged velocity fields are further applied to the transport and transformation processes of pollutants, which are, again, calculated with time and space variable parameters.

The grid used for the simulations was non-uniform in the horizontal plane, the area from 6° W to 36° E and from 30° N to 46° N being divided into 84×47 cells, with the dimension of 30′ by 20′, in the longitudinal and lateral directions, respectively, and further refined in the lateral direction near the Strait of Gibraltar (minimum cell width 12′) in order to properly simulate the discharge, as well as the inflow and outflow momentum through the Strait. In the vertical direction, the Mediterranean Sea was divided into 19 layers, with thicknesses from the surface to the bottom (in metres) of 10, 15, 22, 33, 50, 70, 80, 120, 150, 200, 300, 350, and then seven 400-m thick layers.

Geophysical data on bathymetry, temperature and salinity were collected from the Mediterranean Oceanic Database (MODB, http://modb.oce.ulg.ac.be/) and wind forcing data from the Comprehensive Ocean – Atmosphere Data Set (COADS, http://www.ncdc.noaa.gov). Hydrological and hydraulic data on the main river inflows and exchange through the straits (Gibraltar, Bosporus/Dardanelles, Strait of Sicily) and data on evaporation/precipitation were collected from the UNEP–MAP reports (1996, 2001), Boukthir and Barnier (2000) and Zavatarelli and Mellor (1995). These data are described in detail in Rajar et al. (2007-this issue).

To obtain the seasonally averaged hydrodynamic circulation for the four seasons, the following methodology was used. The measured 3D fields of temperature and salinity (at each computational control volume) were given as input data (initial conditions) to the PCFLOW3D model, together with the data on seasonally averaged wind fields, river inflow and velocity distribution in the Gibraltar and Dardanelle Straits. During the model run these input parameters caused forcing of the hydrodynamic circulation, which mostly approached a steady state after 30 days of simulation. In this way we obtained four velocity fields, one for each season, which were further used as steady state fields, over which the unsteady simulations of transport/dispersion and biogeochemical processes of mercury were computed. The seasonal velocity fields were exchanged at the end of each season and further used for the simulations of transport and transformations of mercury compounds.

Table 4
Ranges of the transformation coefficients used with the PCFLOW3D model

Reaction	Coefficient	Range [day^{-1}]
Methylation	K_M	$5\ 10^{-5}$–10^4
Demethylation	K_D	$8\ 10^{-5}$–$4\ 10^4$
Net reduction	K_{Rnet}	$8\ 10^{-5}$–$2.5\ 10^2$

The results of the hydrodynamic simulations were validated in two ways (Žagar et al., 2005). They were compared to available measurement results (MODB) and to the results of modelling by another model. A comparison of the PCFLOW3D results to measurements (MODB) showed an acceptable agreement between the calculated and measured velocity fields. The velocity fields calculated with the PCFLOW3D model were also in good agreement with simulation results of the POM model (Princeton Ocean Model), which were performed and described by Zavatarelli and Mellor (1995).

5. Simulations of transport, dispersion and transformations of mercury

The next step was the sensitivity analysis of the upgraded PCFLOW3D model with all the transformation and exchange processes included. The input data that should be provided by the atmospheric model were held constant at this phase of the work. Input parameters were changed in order to evaluate their significance and the results are presented in Table 2, separately for the surface layers (top 100 m) and for the layers below. Again, the importance of water–air exchange was confirmed, as the results for the near-surface layers were highly dependent on the data provided by the atmospheric model.

As the results of the hydrodynamic module were encouraging and a reliable turbulence closure scheme was used, further calibration of transport parameters was not performed. The calibration of the PCFLOW3D model consisted of determination of transformation parameters and a comparison of the simulation results with the measured data.

In order to determine the transformation parameters, the next step was to use measured data on mercury

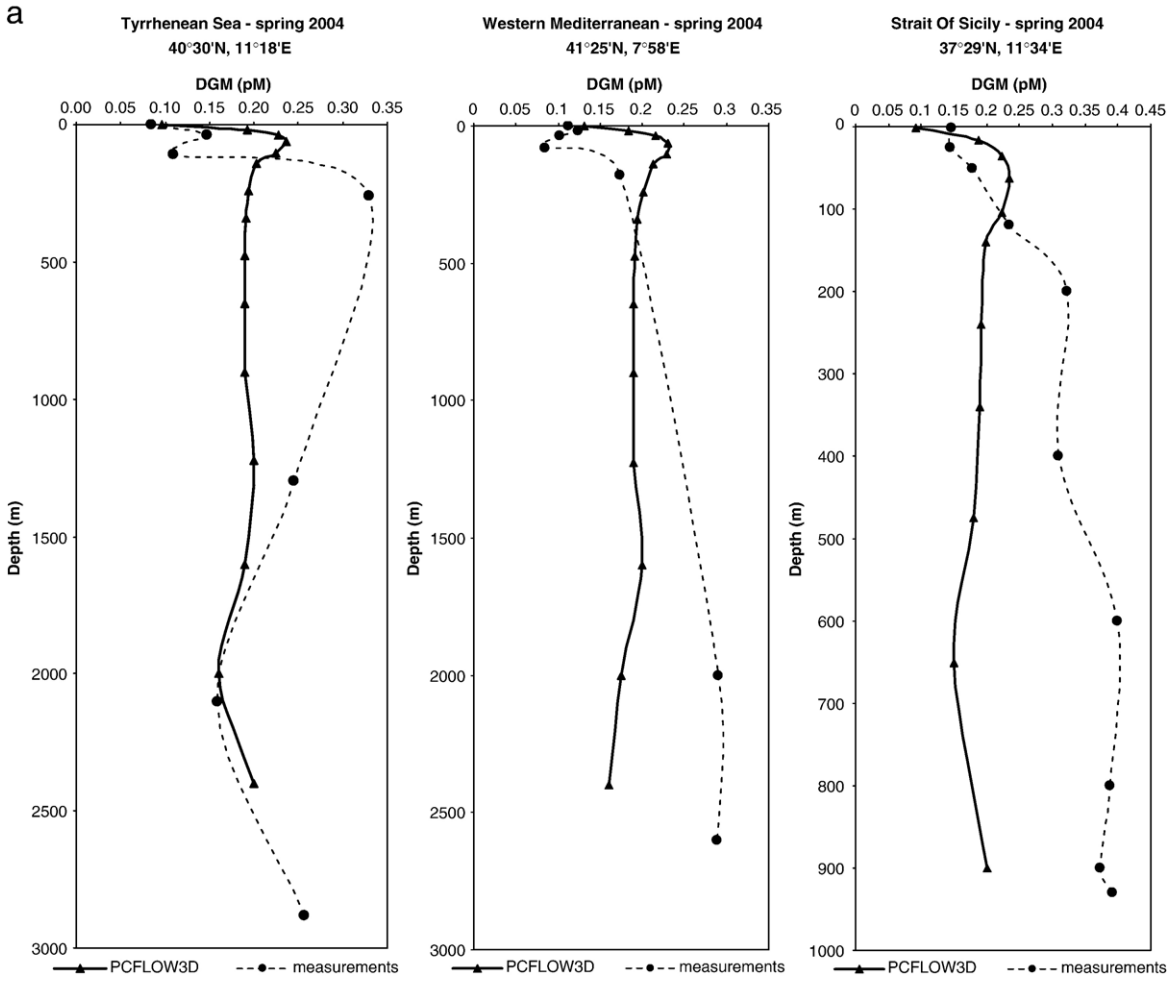

Fig. 11. Comparison of modelled and measured DGM profiles. Spring (above) and summer (below).

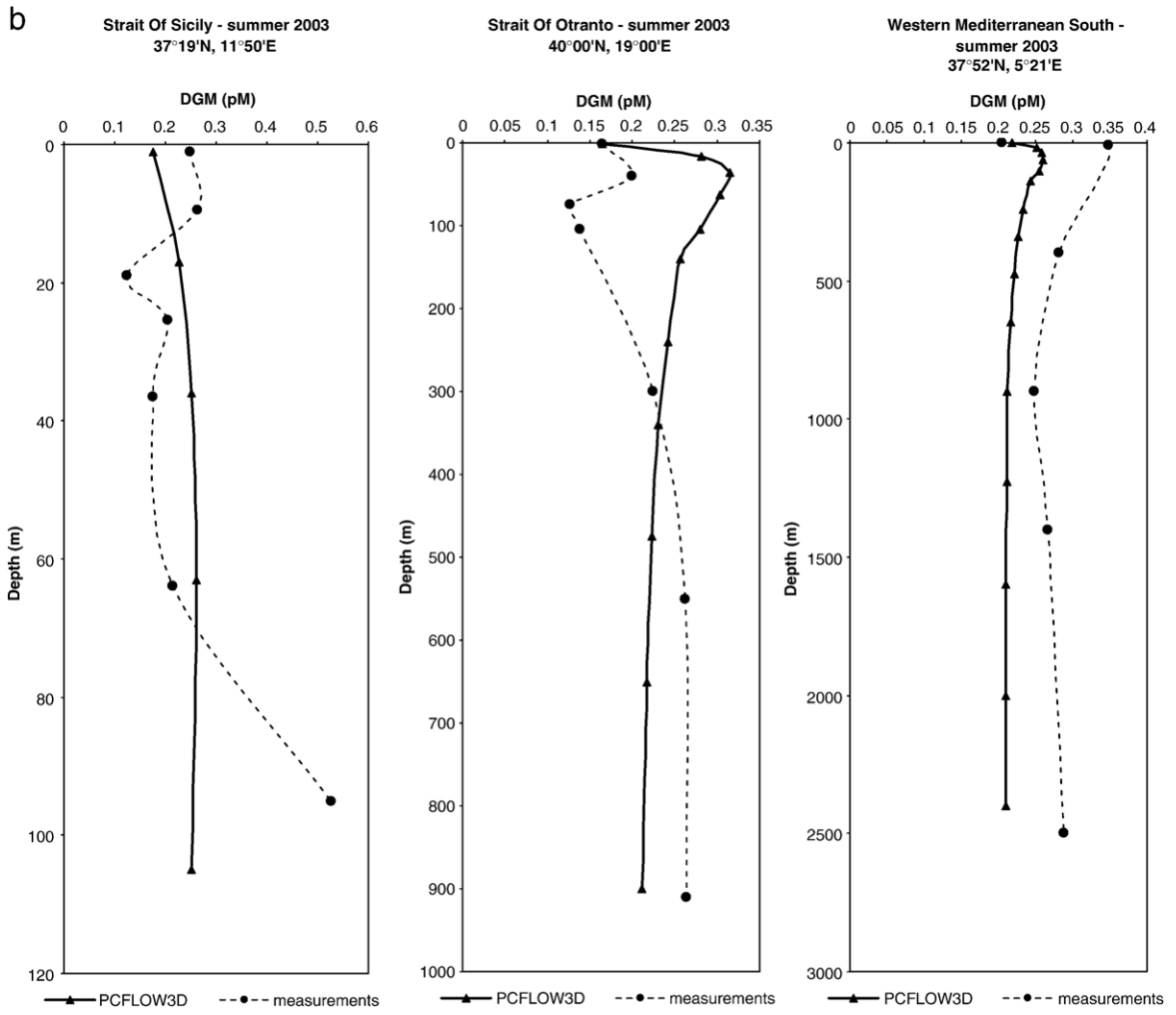

Fig. 11 (*continued*).

species concentrations and geophysical/environmental parameters from the cruises to build several model trees for the dissolved Hg species. Some of the results are presented in Figs. 7–10. It can be seen that the r^2 values are lower than 0.85, except for dimethyl–mercury. Moreover, for the HgT and MMHg species even visual agreement between the modelled and measured results is questionable and insufficient sensitivity of the model can clearly be seen. Some statistical parameters of the results gathered by the WEKA modelling tool are shown in Table 3. On the basis of both visual and statistical agreement of the results, we can conclude that the relationships between the environmental parameters and mercury concentrations are not clear. One of the possible reasons may be that not all important environmental parameters were measured (e.g. pH, eH, nutrients). Also, some of the measured parameters (dissolved oxygen, chlorophyll) are not yet included in the PCFLOW model, as they would demand modelling of at least the lower part of the food chain. Therefore, at present, it was not possible to simulate the relationship between the reaction coefficients and the environmental parameters within the PCFLOW3D model, which can be considered its main drawback at present, and should be the focus in future model development.

Some test simulations were performed with the reaction coefficients gathered by the machine-learning tools, but the modelling results were not acceptable. Although at least some of the figures (e.g. for DGM and for DMHg) show reasonable agreement of measured and modelled Hg concentrations, the computations with the PCFLOW3D model using these transformation rates gave rather poor results. Therefore, these coefficients were only used as a first approximation in further work.

To determine more reliable transformation coefficients than the ones gathered from the machine-learning tools the so-called back-modelling approach was used, and the reaction coefficients were determined from concentration patterns in different time intervals. The results of such a calibration were seasonally averaged matrices of spatially variable transformation coefficients. These upgraded coefficients were used in all following simulations of mercury transport and transformations. As the oxidation processes are relatively poorly understood, net reduction coefficients were used. The ranges of methylation, demethylation and net reduction coefficients are given in Table 4.

Further simulations were performed for those periods when the deep-sea campaigns were held. All the processes (advection and dispersion, transformations and exchange with the bottom and the atmosphere) were taken into account. The results of the model were compared to the measurements of Hg species in water, obtained during the two deep-sea campaigns in summer 2003 and spring 2004 (Kotnik et al., 2007-this issue). The measured concentration profiles were compared to the results of the model down the water column.

Fig. 11 shows the measured and simulated DGM concentrations down the water column at some sampling points. It is evident that the agreement of the DGM concentrations simulated by the PCFLOW3D model with depth is reasonable (mostly within a factor of two), while in the upper layers they are relatively close to the measured ones. Thus, accounting for realistic wind conditions (6 h wind-fields) and the TGM concentrations (both being the result of the RAMS–Hg atmospheric model), evasion was also calculated with relatively good accuracy.

Due to wind variation, which is the main forcing factor of evasion, the DGM concentrations in surface layer can vary considerably during each season. For the comparison of simulated and measured results, modelled

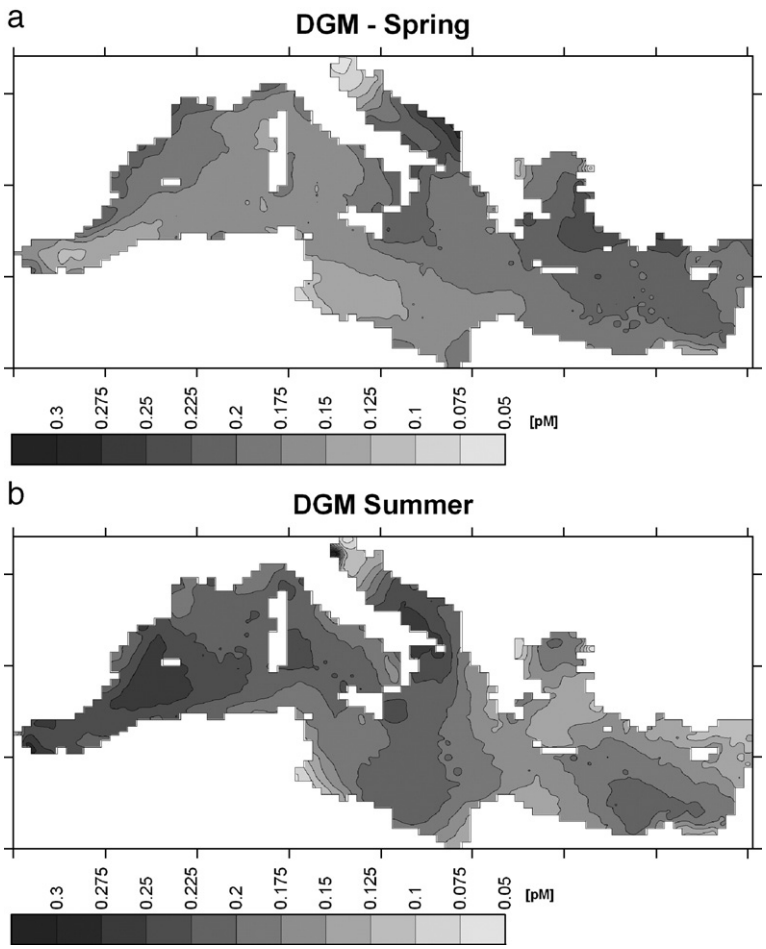

Fig. 12. Seasonally averaged DGM fields in [pM]. PCFLOW3D model. Spring (above) and summer (below).

DGM concentrations at the time of the measurements were used. However, to obtain a representative DGM field for the whole season, the simulated concentrations in the surface layer were further averaged throughout each season (Fig. 12).

The comparison of measured and simulated total mercury concentrations is shown in Fig. 13. In contrast to DGM concentrations, the agreement in the upper layers is worse than down the water column, where the model shows a satisfactory agreement mostly within a factor of two. The disagreement is particularly high in the Western Mediterranean Sea. One of the reasons could be very low mixing due to exceptionally stable weather conditions in the summer of 2003, which was difficult to simulate with the available data.

In Figs. 14 and 15, the simulated concentration of HgT in two layers during spring and summer is shown. HgT concentrations vary mainly between 1.0 and 1.5 pM. No direct verification of the simulated results is possible, except at the sampling points. However, as indicated in Rajar et al. (2007-this issue), the average HgT concentration in the Mediterranean Sea is about 1.5 pM. Thus at least the average value of the simulated results is relatively close to measured values.

The simulations of MMHg showed poorer results than for DGM and HgT. Concentration profiles obtained by the model and measurements were not in agreement. At least in the Ionian Sea obviously some important processes are missing, as even the average concentration with depth is relatively far from the measured values. Obviously, the methylation and demethylation rates from the literature and the rates calculated by the use of artificial intelligence and backmodelling did not provide satisfactory results, most probably due to missing information and poor

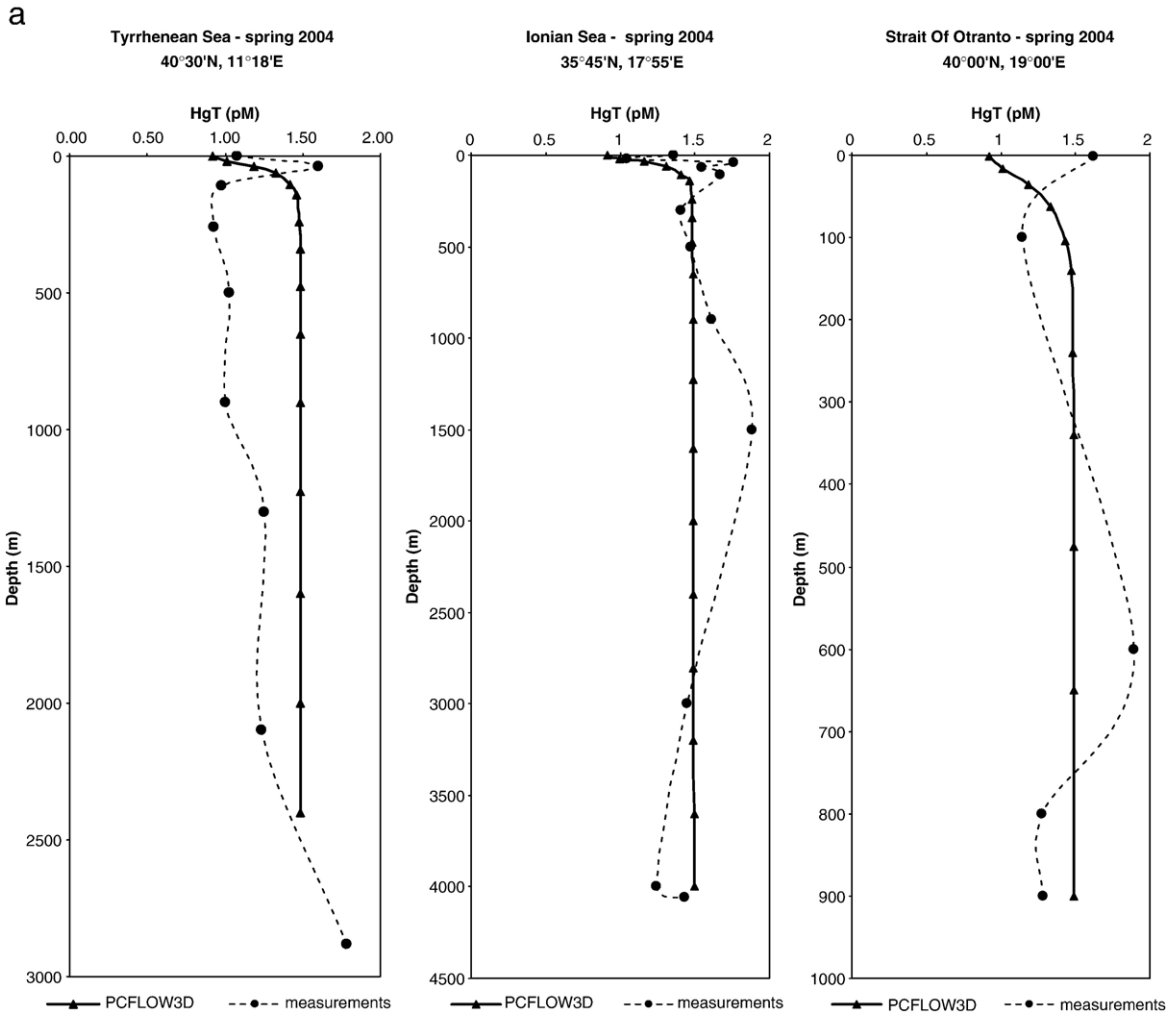

Fig. 13. Comparison of modelled and measured HgT profiles. Spring (above) and summer (below).

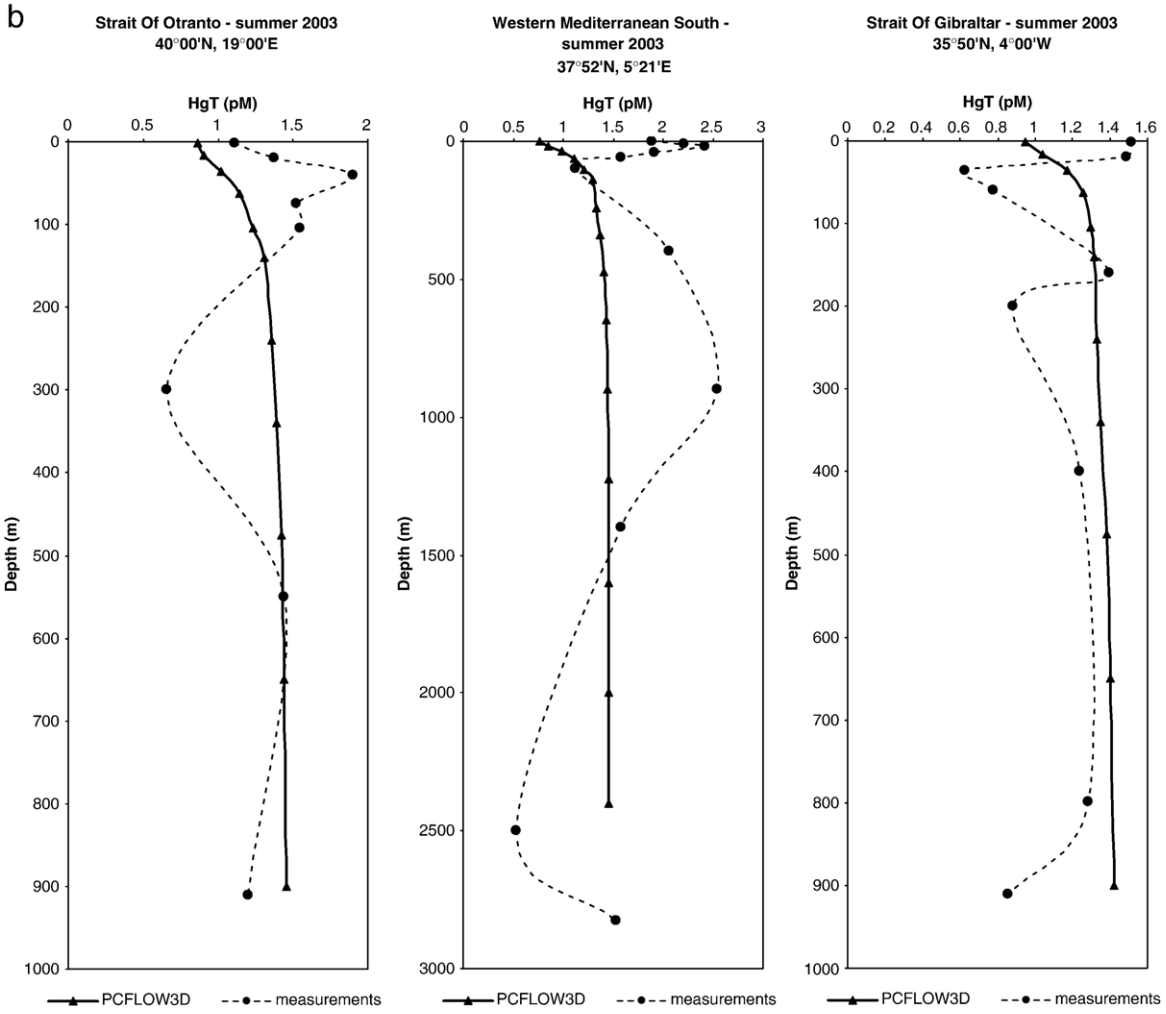

Fig. 13 (*continued*).

understanding of these processes which should also take into account environmental parameters. Consequently the PCFLOW3D model did not show sufficient sensitivity to the distribution of the transformation coefficients in space and time. Further studies should focus on better understanding of environmental and microbial processes affecting transformation of mercury species in the oceanic environment. Furthermore, well designed and focused measurements should be planned to achieve this goal. This would allow for improvements in the mathematical modelling of mercury transformation processes. Fig. 16 shows a comparison of some of the profiles for the MMHg concentrations.

6. Simulations of exchange with the atmosphere

With the model calibrated in such a way, it was possible to implement the policy-target socio-economic scenario for the future and perform simulations of transport and transformation processes for the years 2010 and 2020. The emission scenario was applied to sources that are important for input to the water compartment. The changes in mercury sources and sinks are discussed in Rajar et al. (2007-this issue), thus only the changes in deposition are given in this paper. Results of the RAMS–Hg model (statistically averaged over each season and summed over the computational domain) are shown in Table 5.

Exchange with the atmosphere for the years 2004, 2010 and 2020 (Table 6) shows the expected decrease of evasion in the future. Compared to recent results by other authors (about 500 kmol/year, Pirrone et al., 2001; Gårdfeldt et al., 2003) the evasion simulated by the PCFLOW3D model is about one half lower. Taking into account the evasion predicted by Pirrone et al. (2001) and Gårdfeldt et al. (2003) together with other known

mercury sources and sinks leads to the conclusion that the Mediterranean Sea should be recovering relatively fast, as the mercury sinks exceed the sources by about 125 kmol/year, which is rather hard to believe. The Mediterranean Sea should be recovering even if we take into account additional underwater natural mercury sources (80 kmol/year, Rajar et al., 2007-this issue), which were not considered in previous mass balance calculations (Cossa et al., 1997; Cossa and Coquery, 2005), and the evasion calculated by the PCFLOW3D model. Therefore, either the additional (probably mostly natural) sources of mercury in the Mediterranean Basin are largely underestimated or the evasion calculated by other authors is somewhat overestimated.

7. Conclusions and further work

Although the modelling results show relatively high discrepancies compared to the measured mercury concentrations in the water compartment of the

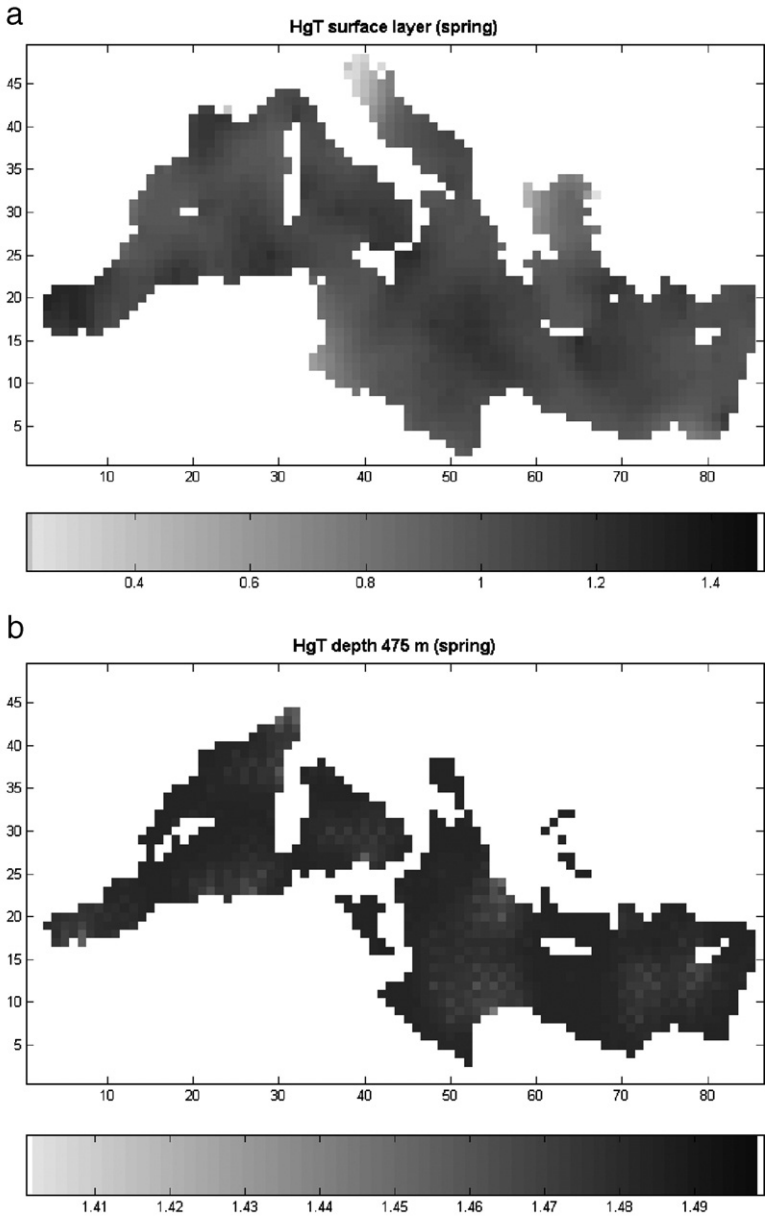

Fig. 14. PCFLOW3D HgT concentrations, surface layer (above) and depth 475 m (below) in [pM]. Winter simulation — end of March.

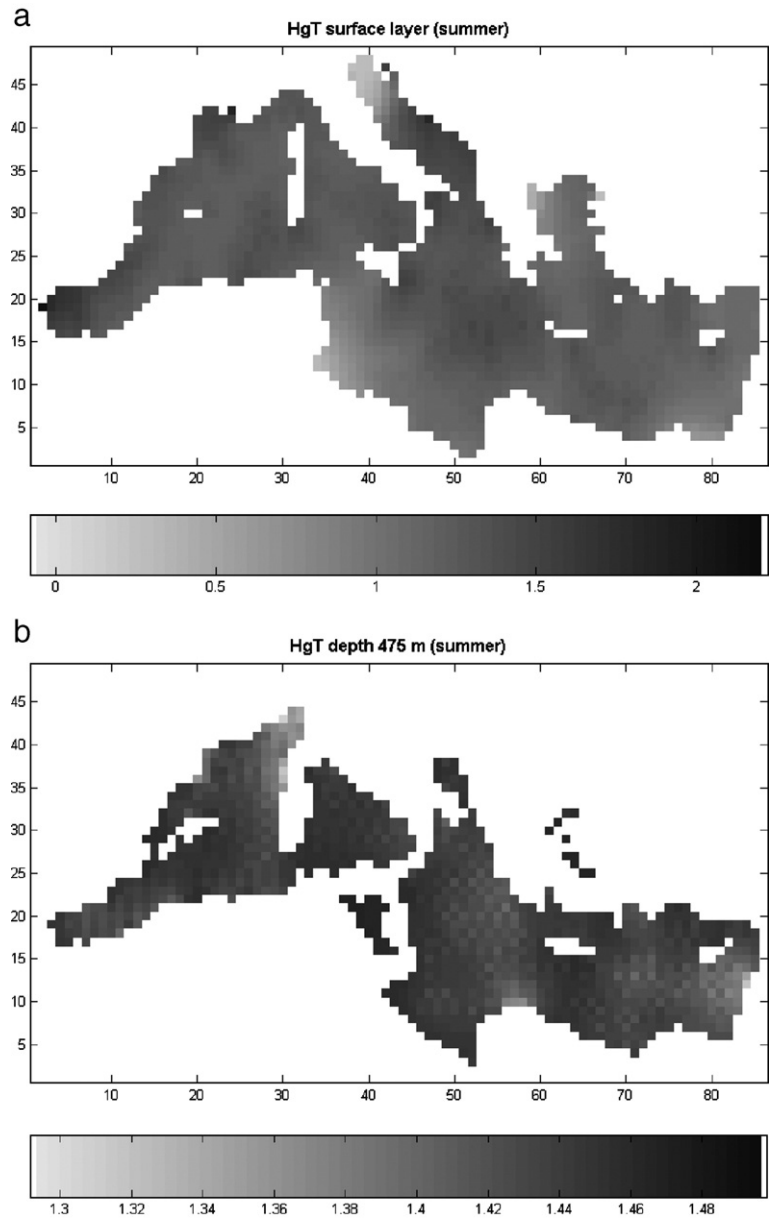

Fig. 15. PCFLOW3D HgT concentrations, surface layer (above) and depth 475 m (below) in [pM]. Spring simulation — end of June.

Mediterranean Sea, some important improvements in mercury transport and transformation modelling were achieved:

- The existing PCFLOW3D water model has been upgraded by a biogeochemical module, where most of the characteristic transport and transformation processes and fluxes in seawater can be simulated, although some considerable improvements and better understanding of abiotic and particularly microbially-mediated transformation processes in the marine environment are still needed.
- Seasonal simulations of water circulation in the Mediterranean Sea were performed and compared to measurements and other modelling results. These velocity fields were further used to simulate transport and also helped the team of experimentalists to decide on the optimum locations and sampling depths.
- A new approach, i.e. the use of machine-learning tools, was applied in order to connect the measured

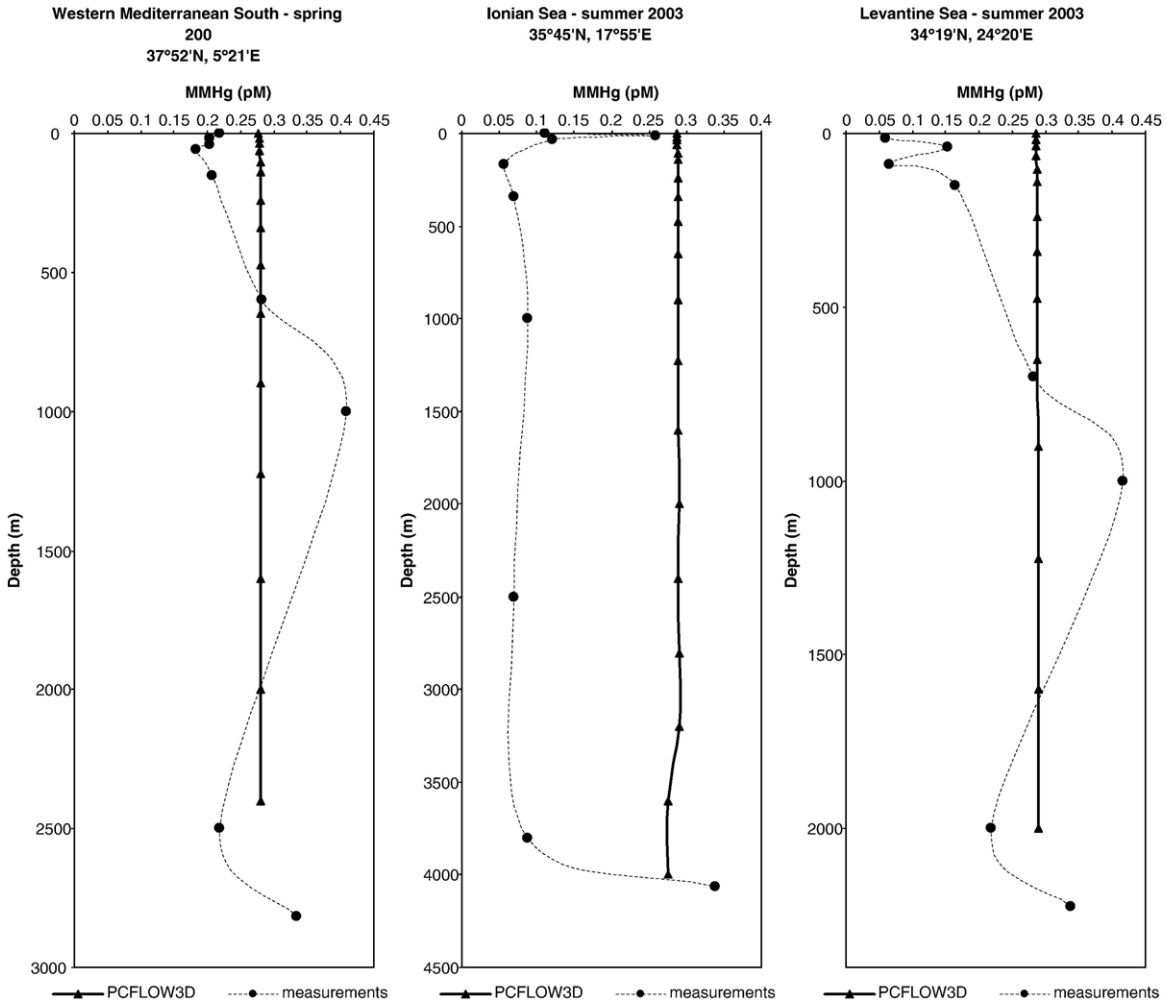

Fig. 16. Comparison of modelled and measured MMHg profiles.

geophysical and environmental parameters to the measured mercury concentrations in water. The method as a tool is promising; but some important parameters were not measured and the results of the model tree simulations were not directly applicable to the PCFLOW3D model.

- For the first time, an aquatic model and an atmospheric model have been linked together in order to improve the modelling results. The integrated modelling tool has significantly improved the accuracy of computation of one of the most important processes in the Mediterranean Sea, that is, the exchange of mercury between air and water. The integrated model is ready to use for further regional and local simulations and studies.

Table 5
Total deposition in [kmol Hg/year], statistically averaged values from the RAMS–Hg simulations

Season/year	2004	2010	2020
Spring	39.26	34.32	31.22
Summer	11.54	11.53	10.16
Autumn	34.28	31.58	30.79
Winter	30.14	30.11	28.40
Total	115.22	107.54	100.57

Table 6
Total evasion in [kmol Hg/year], PCFLOW3D simulations

Season/year	2004	2010	2020
Spring	62.25	57.00	54.25
Summer	53.30	47.45	44.10
Autumn	61.30	59.80	57.35
Winter	70.50	70.25	65.75
Total	248.85	234.50	221.50

- Simulations of mercury transport and transformation processes in water showed some encouraging results. We can conclude that the model is better at simulating the chemically-driven processes than the ones where biological and/or biochemical drivers are of high significance. Taking into account the low concentrations of chlorophyll-A in the surface layers of the Mediterranean Sea, particularly during summer, photochemical processes are assumed to be the main forcing factor of reduction. It can be seen that the modelled DGM concentrations, at least near the surface, are relatively close to the measured ones. On the other hand, the results of modelling of methylation and demethylation processes, which are mostly biologically driven, are in much worse agreement with the measured concentrations. Although photochemical processes can represent an important part of demethylation, particularly in typical Mediterranean summer conditions, it was not possible to quantify the importance of these processes and to include them into the simulations at the time.

On the other hand, the obtained modelling results indicate that some further improvements of the PCFLOW3D model and the modelling approach are necessary:

- The PCFLOW3D model needs to be further upgraded with additional biogeochemical transformation processes in order to improve the accuracy of mercury simulations. At least modelling of the lower part of the food-web (nutrients, oxygen) should be included in the model.
- Further investigation and the use of machine-learning tools (e.g. fuzzy logic) should be encouraged, provided that more systematic data-sets are collected.
- The atmospheric and water model should be coupled in so-called real-time coupling, where both models run on the same computer(s) and results/input data are exchanged between the models in each time step.

Acknowledgement

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