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Mercury transport and fate in the Gulf of Trieste (Northern Adriatic)—a two-dimensional modelling approach

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Abstract

The Gulf of Trieste is subject to mercury pollution from the Soča River which drains polluted sediments from the region of a former mercury mine in Idrija, Slovenia. This has resulted in elevated mercury levels in some marine organisms. Due to a concern for human health, a study has been undertaken to predict mercury contamination trends through the use of a field program and a mathematical model. An annual mercury mass balance of the Gulf is presented first in the paper. This confirms the assumption of the importance of the particulate mercury loads and sedimentation in the mercury cycle. A two-dimensional (2D) advection-dispersion model for non-conservative pollutants which simulates mercury cycling in the Gulf, is then described. This model incorporates the results of a 2D steady-state, primarily wind-driven hydrodynamic model and a 2D sediment transport model. A coupling of the submodels and verification of the integral mercury cycling model are also presented.

Keywords: Mercury; Biogeochemical processes; Mathematical model; Mass balance; Hydrodynamics; Sediment transport; Gulf of Trieste; Northern Adriatic

Software Availability

Program title:	STATRIM
Developers:	Andrej Širca, Rudi Rajar, Matjaž Četina, Dušan Žagar
Address:	Faculty of Civil and Geodetic Engineering, Hydraulics Division, Hajdrihova 28, 1000 Ljubljana, Slovenia/EU. Tel.: + 386-61-1254-052, fax: + 386-61-219-897, e-mails: rrajar@fagg.uni-lj.si, andrej.sirca@ibe.si.
First available:	1996
Hardware:	PC compatible (at least Pentium 100 and 16 MB RAM)
Software:	any FORTRAN Compiler and AutoCAD or Surfer
Language:	FORTRAN
Size:	75 kB, the size of executables depends on grid density
Availability:	STATRIM is available for 150 USD with a simple list of instructions. No manual is currently available. STATRIM also requires a separate hydrodynamic model for velocity field and a sediment transport model for the field of suspended sediments. Any available 2D or 3D model can be used to obtain them. A 3D multi-purpose package PCFLOW3D is available for 5000 USD with documentation from the same group of authors who developed STATRIM. A user interface is in development for this package. Also in development is a 3D quasi unsteady state version of the STATRIM, called DYNTRIM.

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1. Introduction

The Gulf of Trieste is a semi-enclosed gulf in the north-eastern part of the Adriatic Sea. It has an approximate area of 600 km^2, an average depth of 16 m and a maximum depth of 25 m in the central part. The most important source of freshwater and inorganic suspended matter is the Soča River which discharges into the north-eastern part of the Gulf (Fig. 1).

Occasional measurements of dissolved total mercury in the Gulf (e.g. Ferrara and Maserti, 1992) have shown up to 100% higher concentrations than those recorded in the middle Adriatic (Ferrara and Maserti, 1992). The concentrations of mercury in marine organisms (Planinc et al., 1993) were some hundreds of percents higher than those in the central Mediterranean Sea (Bernhard and Buffoni, 1981); the mercury concentrations in the sediments (SEADATA, 1992) were two to three orders of magnitude higher than in the middle or southern Adriatic (Ferrara and Maserti, 1992). Based on the data from the latter source, the average geo-accumulation index (Müller, 1979) in the Gulf equals 5.6, and varies between 4.8 and 6.4, according to the distance from the Soča River mouth. The mercury concentrations in the Soča River bed sediments and its tributary, the Idrijca River, are an order of magnitude higher than those in the Gulf of Trieste (Gosar et al., 1995). This indicates that the main component of mercury contamination in the Gulf is the Idrija mining area, which was active for almost 500 years, but has been closed since 1995.

The deterioration in the water quality in the Gulf of Trieste in the last few decades has resulted in occasional anoxic conditions at the bottom of the Gulf. There is concern that such conditions could intensify the production of monomethylmercury (MeHg) in the sediments and in the water column, and its accumulation in fish. The latter is an important economic factor, as well as food source, for the population around the Gulf.

The processes of mercury cycling in freshwater environments are already being modelled by a number of zero-dimensional (Harris, 1991; Hudson et al., 1994; Driscoll et al., 1995; Leonard et al., 1995; Henry et al., 1995) and one-dimensional (AScI, 1991) models, but there are very few models applied to marine environments. In addition to the difference in the water chemistry, the effects of chloride, pH, dissolved organic carbon and sulphates, and a multi-dimensional description of the hydrodynamics must especially be applied for the modelling of a marine environment.

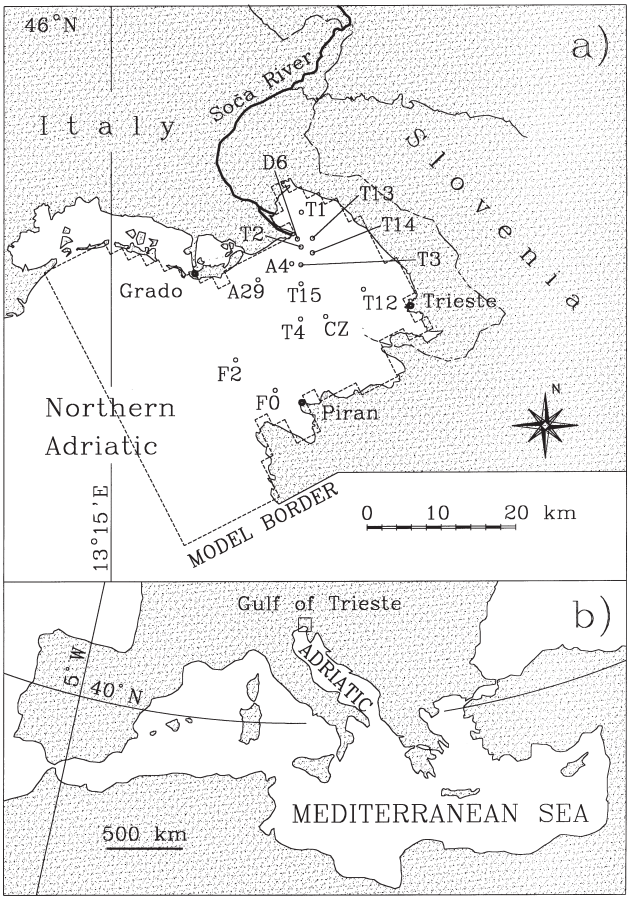

Fig. 1. A schematical map of the Gulf of Trieste and the lower Soča River, an extent of the computational domain and locations of the verification points (a). Location of the considered area in the Mediterranean (b).

2. Mercury mass balance

The total mercury mass balance of the Gulf of Trieste consists of five main items: inputs from the Soča River, the open sea of the Northern Adriatic, the atmosphere, and outputs due to sedimentation in the Gulf and the outflow to the Northern Adriatic (Fig. 2). A loss of mercury from the water body due to inorganic mercury (HgII) reduction/volatilisation was also considered but was assumed to be negligible in the mass balance in comparison with other system losses, and, partly, due to low elemental mercury concentrations in the water. The Soča River averages a discharge of 150 m^3/s, a sus-

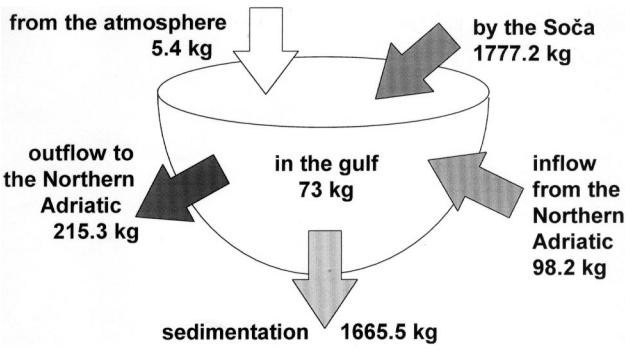

Fig. 2. Annual mercury mass balance for the Gulf of Trieste.

pended matter concentration of 50 mg/l dry weight and a mercury content of 7.5 μg/g dry weight in suspended matter (SEADATA, 1992). This results in a load of 1773.9 kg of mercury per year. According to the measurements of SEADATA (1992), the load of dissolved mercury from the Soča River is only 3.3 kg/year. A residual current of 1557 m^3/s along the southern coast (Širca and Rajar, 1997a) adds 98.2 kg/year to the mass balance, while deposition from the atmosphere contributes 5.4 kg/year, considering the 1500 mm of annual precipitation with a mean mercury concentration of 6 ng/l. The westbound residual current of 1707 m^3/s (Širca and Rajar, 1997a) along the northern coast reduces the amount of mercury in the Gulf by 215.3 kg/year, while, in the absence of other sinks, the remainder is deposited at a rate of 1665.5 kg/year. Although the last value was obtained as a difference between the inputs and the output due to the residual current, its magnitude has been confirmed by other authors. For example, the downward fluxes of mercury as reported by Planinc and Faganeli (1993) for the southern part of the Gulf would result in 1860 kg/year at a depth of 20 m and 774 kg/year at 10 m if the same rates were to apply to the entire Gulf. Further, considering the sedimentation rate of 1 mm/year in the central part of the Gulf, and its low terrigenous portion (Ogorelec et al., 1991) originating from the Soča River, the amount of deposited mercury would equal, on an average, 1687 kg/year. Finally, the relatively high values of the mass balance items seem to be reasonable, bearing in mind that 130 tons of mercury are deposited over or flushed into the Mediterranean Sea every year (SEADATA, 1992).

3. The model

The water quality in lakes is often treated by zero-dimensional (box) models or so-called well-mixed reactor models. In rivers, at least a one-dimensional (linear) hydrodynamic sub-model is required to accommodate the direction of flow. A further extension to 2D hydrodynamics is necessary for coastal seas. In some cases, such as the occurrence of temperature and density stratification and the presence of river plumes, or in the case of the water quality modelling of the open seas, even a three-dimensional description of water motion can be required. For the purpose of mercury modelling in the Gulf of Trieste, a 2D hydrodynamic model, **PCFLOW2D-HD**, was applied. This 2D model offered a satisfactory description of water circulation and enabled model verification by using a reasonable amount of measured data.

Since the mercury mass balance of the Gulf revealed the importance of suspended matter, a sediment transport component was included in the mercury model by a preceding application of another 2D model, **MIKE 21 MT** (Mud Transport).

Finally, the results of both sub-models were used as inputs for the 2D **STATRIM** (STAtionary TRIeste gulf Mercury) model (Fig. 3). All three models were based on solving the corresponding 2D equations by the finite difference method, which divided a water body into *control volumes*. For all models, the control volumes were defined by a numerical grid with a uniform spacing of 1800 m along both co-ordinate axes which resulted in a computational field of $26 \times 26 = 676$ grid cells.

3.1. Hydrodynamic sub-model

The PCFLOW2D-HD is a stationary, two-dimensional, depth-averaged hydrodynamic model for rivers, lakes and coastal seas (Rajar and Četina, 1986; Četina and Rajar, 1993; Rajar and Četina, 1994; Rajar and Širca, 1996). It simulates water level changes and currents caused by wind, tide and different sources and sinks. In this model, two momentum equations and a continuity equation are solved by the finite differences method of Patankar (1980). A hybrid solution scheme is used along with the SIMPLE solution algorithm to link the momentum equations with the continuity equation. Since our aim was to determine the average (residual) circulation in the Gulf, the stationary version of the PCFLOW2D-HD model was used.

Based on previous experience, a turbulence model with a constant eddy viscosity coefficient of $\nu = 5$ m^2/s, was used. This value, as well as Manning's bottom friction coefficient $n_g = 0.03$ $sm^{-1/3}$, were obtained from previous simulations of circulation in the same area (Rajar and Četina, 1992; Rajar et al., 1992, 1995). These authors concluded that wind was the main forcing factor in the Gulf. Therefore, special attention was paid to the development of new methods for evaluating the effect of the wind on long-term hydrodynamic and advection-dispersion simulations (Širca and Rajar, 1997b). The VECTRA method was finally applied. It gives a single average (representative) wind on the basis of an available wind rose (Širca and Rajar, 1997b). The average wind was defined by an average velocity of 1.61 m/s and an average direction of 73° (from the North, clockwise).

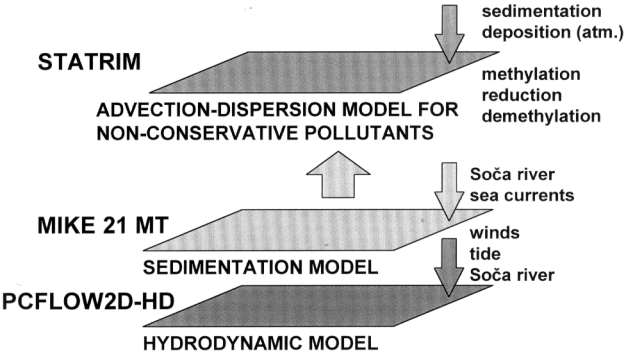

Fig. 3. Setup and submodels of the STATRIM model.

The residual tidal circulation in the Gulf of Trieste is almost an order of magnitude weaker than the residual circulation due to the wind (Širca, 1996), and was not included. Although small, the influence of the Soča River plume was taken into account by using an average discharge of 150 m^3/s and a direction of 105° (from the North, clockwise). At the open boundary, a constant-level boundary condition was applied. Since such a boundary condition might affect the velocity field in the Gulf, it was applied distant enough (9 grid cells) from the Gulf to minimise its influence.

The computed average velocity field (Fig. 4) is similar to the fields obtained by other models which have applied the *burja* wind forcing (Rajar et al., 1992; Longo et al., 1990). Although the velocity magnitudes, in this case, are lower than those of the previous authors due to applied wind averaging, the dominant influence of the burja is evident from a well-developed westbound flow over the shallow area along the northern coast and from a cyclonic (anti-clockwise) circulation in the northern and central parts of the Gulf. A deviation from the overall cyclonic circulation in the south eastern part of the Gulf and along the southern coast was very probably due to the applied rough numerical grid. This is confirmed by the preceding 3D model (Rajar et al., 1992) where anti-cyclonic anomalies were limited to both bays on the southern side of the Gulf only. Since the main focus of the present research was in the northern part of the Gulf, where mercury transport was not affected by the currents from the southern part, the latter were not elaborated in detail.

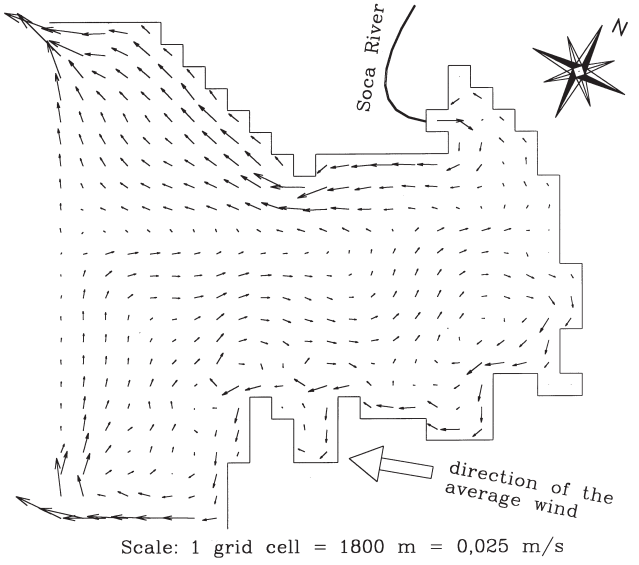

Fig. 4. Computed velocity field in the Gulf of Trieste as an input for the STATRIM model.

3.2. Sediment transport sub-model

MIKE 21 MT is a module of the MIKE 21 Modelling System for Estuaries, Coastal Waters and Seas developed by the Danish Hydraulic Institute (Abbot et al., 1973; Warren and Bach, 1992). The MIKE 21 system modules are based on the same two-dimensional depth-averaged approach as the PCFLOW2D model but apply different solution algorithms (Abbot et al., 1973; DHI, 1993) and have a dynamic (non-stationary) character. Since MIKE 21 MT describes the transport (motion, deposit and re-suspension) of mud particles ($\Phi < 60$ μm) in the water body due to hydrodynamic circulation, it can only run simultaneously with the MIKE 21 HD module.

Using MIKE 21 MT, it is possible to account for different suspended sediment fractions. Due to the relatively uniform grain distribution of the suspended matter in the Gulf of Trieste, however, it was decided to simulate only the representative 20 μm fraction. The parameters of the simulation were determined from the literature (DHI, 1993; Choudhry et al., 1984), measurements and experience, as follows: critical deposition velocity $V_{cd} = 0.007$ m/s, critical erosion velocity $V_{ce} = 0.29$ m/s, average settling velocity $w = 1$ m/day, erosion coefficient 0.005 and relative height of the centroid 0.3. The average concentration of suspended matter at the source (in the Soča River), 50 mg/l dry weight, was estimated through an extensive study of the measured suspended sediment concentrations in the Soča and the Idrijca Rivers, and the sediment deposit rates in the Gulf of Trieste (Širca, 1996).

The open boundary condition was defined as follows: where outflow from the domain occurred, the concentrations in the cells beyond the boundary were computed according to the concentrations in the neighbouring cells inside the computational domain. In the case of inflow, the inflowing sediment flux in every such grid cell was zero. A constant dispersion coefficient of 5 m^2/s was applied over the entire domain.

With these data, a one-year simulation with actual suspended loads (measured discharge times average suspended load) from the Soča River and the measured winds was performed, as described by Širca and Rajar (1997a). Since MIKE 21 is a dynamic model, the result of the simulation was a time-series of 1464 two-dimensional matrices which represented the conditions in the Gulf with a time step of 6 hours. Finally, an average field of suspended matter was created, using the MIKE 21 PP (Pre- and Post-Processing)module, which performed a statistical elaboration of the time series. The final result of the sediment transport simulation is given in Fig. 5. It is evident that most of the Soča's suspended load is retained in the northern part of the Gulf, while only a small amount (10%) is carried out of the Gulf by the residual current.

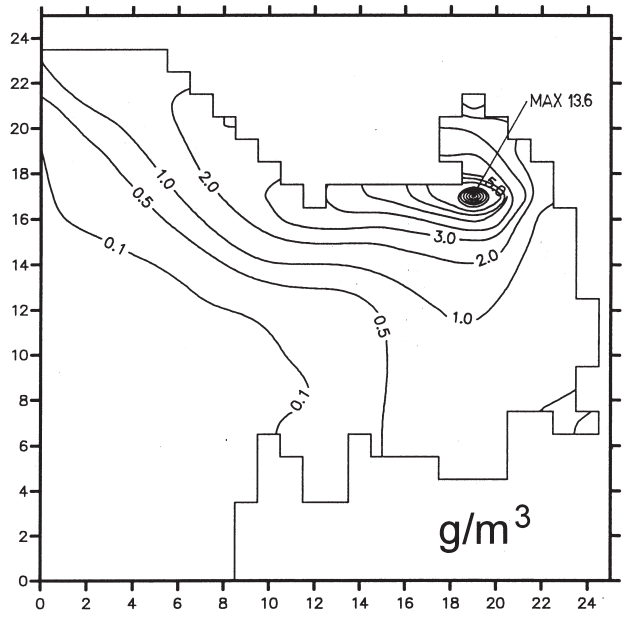

Fig. 5. Computed average suspended sediment concentrations as an input for the STATRIM model.

3.3. Mercury cycling model

A steady-state two-dimensional depth-averaged approach was adopted as a platform for the STATRIM model. The stationary description was justified by the typical cyclonic circulation which was evident in the Gulf during all the seasons (Širca, 1996). At the same time, this was necessary due to a limited amount of measured mercury data, insufficient to form a time-series. The depth-averaged description was acceptable due to the preceeding 3D simulations (Rajar et al., 1992) which had shown the cyclonic circulation in the majority of the Gulf layers. Another reason for this simplification was the shelf-like character of the northern part of the Gulf, where most of the mercury transformations take place. The theoretical basis of the STATRIM model was, thus, a 2D steady-state advection-dispersion equation:

$$\frac{\partial(huC)}{\partial x} + \frac{\partial(hvC)}{\partial y} = K_{x2}\frac{\partial}{\partial x}\left(h\frac{\partial C}{\partial x}\right) + K_{y2}\frac{\partial}{\partial y}\left(h\frac{\partial C}{\partial y}\right) + \mathrm{SRC} \quad (1)$$

where x and y represent the Cartesian co-ordinate axes, u and v are velocities along them, h is depth, K_{x2} and K_{y2} are dispersion coefficients and SRC is a source term. This equation is used to describe the transport and fate of inorganic mercury (HgII) and monomethylmercury (MeHg) in the water column. It is important to note that HgII refers to all mercury which is neither MeHg nor elemental mercury.

The transport modelling itself is a rather common task described elsewhere (e.g. Rajar and Četina, 1994); thus, only the source term details are described herein. Mercury processes in the model include the atmospheric deposition of HgII and MeHg, the transport and burial of the particulate HgII and MeHg, the HgII reduction to elemental mercury, the methylation of HgII to MeHg, and the demethylation of MeHg to elemental mercury. The partitioning of HgII and MeHg onto non-living particles and into plankton was determined assuming instantaneous equilibrium. It is recognized that, in the case of plankton, the kinetics of uptake, losses and growth very likely determine mercury concentrations. However, for the purposes of these simulations, it is assumed that a pseudo-steady state is established for the plankton mercury dynamics and that the equilibrium partitioning is a reasonable approximation. The equilibrium partitioning of HgII is assumed to occur between non-living particles, plankton and the total dissolved HgII pool in solution. The same assumption applies to MeHg.

Only the transport of total HgII and total MeHg were modelled in the STATRIM model. Computation of their interactions and the mercury fate processes was allowed in the source term by their division into dissolved, particulate and plankton fractions. Partitioning constants were estimated empirically on the basis of concentrations measured in the field in different phases of research. The expressions for the spatially variable fractions (F) of HgII and MeHg in the dissolved, particulate, and plankton phases are as follows:

$$F_{\mathrm{diss}}(i) = \frac{1}{1 + K_{\mathrm{part}}(i)\cdot C_{\mathrm{part}} + K_{\mathrm{plan}}(i)\cdot C_{\mathrm{plan}}} \quad (2)$$

$$F_{\mathrm{part}}(i) = \frac{K_{\mathrm{part}}(i)\cdot C_{\mathrm{part}}}{1 + K_{\mathrm{part}}(i)\cdot C_{\mathrm{part}} + K_{\mathrm{plan}}(i)\cdot C_{\mathrm{plan}}} \quad (3)$$

$$F_{\mathrm{plan}}(i) = \frac{K_{\mathrm{plan}}(i)\cdot C_{\mathrm{plan}}}{1 + K_{\mathrm{part}}(i)\cdot C_{\mathrm{part}} + K_{\mathrm{plan}}(i)\cdot C_{\mathrm{plan}}} \quad (4)$$

which were linked by the equation

$$F_{\mathrm{diss}}(i) + F_{\mathrm{part}}(i) + F_{\mathrm{plan}}(i) = 1 \quad (5)$$

where i represented either HgII or MeHg in all equations. The K_{part} was a quotient between the average concentration of a mercury compound in particulate matter [μg/g dry weight], and the average concentration of a dissolved compound [μg/m^3], thus having the dimension of m^{3}kg^{-1}. Similarly, the K_{plan} was a quotient between the average concentration of a mercury compound in plankton and the average concentration of a dissolved compound. Both parameters were determined from the measurements (Ferrara and Maserti, 1992; SEADATA, 1992; Horvat et al., 1996; Širca, 1996), and were taken to be constant over the entire 2D area. Their values were:

$$K_{\text{part}}(\text{HgII}) = \frac{\text{HgII}_{part}}{\text{HgII}_{diss}} = \frac{(1\cdot\mu\text{g/g})}{(1\cdot\mu\text{g/m}^3)} = 1.0\,\frac{\text{m}^3}{\text{g}} \quad (6)$$

$$K_{\text{part}}(\text{MeHg}) = \frac{\text{MeHg}_{part}}{\text{MeHg}_{diss}} = \frac{(0.017\cdot\mu\text{g/g})}{(0.1\cdot\mu\text{g/m}^3)} \quad (7)$$

$$= 0.17\,\frac{\text{m}^3}{\text{g}}$$

$$K_{\text{plan}}(\text{HgII}) = \frac{\text{HgII}_{plan}}{\text{HgII}_{diss}} = \frac{(0.335\cdot\mu\text{g/g})}{(1.0\cdot\mu\text{g/m}^3)} \quad (8)$$

$$= 0.335\,\frac{\text{m}^3}{\text{g}}$$

$$K_{\text{plan}}(\text{MeHg}) = \frac{\text{MeHg}_{plan}}{\text{MeHg}_{diss}} = \frac{(0.03\cdot\mu\text{g/g})}{(0.1\cdot\mu\text{g/m}^3)} \quad (9)$$

$$= 0.3\,\frac{\text{m}^3}{\text{g}}$$

C_{part} [μg/m^3] was a spatially-dependent concentration of inorganic suspended matter which was computed by the sediment transport model (Fig. 5). For the spatially constant plankton concentration C_{plan}, an average estimation of 0.02 g/m^3 was adopted, according to Fonda Umani et al. (1992). In this amount, about 75% was considered as zooplankton and the rest as phytoplankton.

The processes of deposition from the atmosphere, sedimentation, methylation and reduction, which change the amount of HgII in the water column, were included in the SRC term (Eq. (1)) and described by the respective equations:

$$\Delta\text{HgII}_{atin} = +\,k_{\text{HgII—atin}}\cdot A_{\text{cell}} \quad (10)$$

$$\Delta\text{HgII}_{sedi} = -\,v_{\text{settling}}\cdot\text{HgII}_{tot}\cdot F_{\text{part}}(\text{HgII})\cdot A_{\text{cell}} \quad (11)$$

$$\Delta\text{HgII}_{meth} = \quad (12)$$

$$-\,k_{\text{methylation}}\cdot\text{HgII}_{tot}\cdot F_{\text{diss}}(\text{HgII})\cdot A_{\text{cell}}\cdot h_{\text{cell}}$$

$$\Delta\text{HgII}_{redu} = \quad (13)$$

$$-\,k_{\text{reduction}}\cdot\text{HgII}_{tot}\cdot F_{\text{diss}}(\text{HgII})\cdot A_{\text{cell}}\cdot h_{\text{cell}}$$

In these equations, ΔHgII_x represented the temporal mass variations of HgII in a control volume with the dimension kgs^{-1}, due to the process x. HgII_{tot} stood for the total amount of HgII in the water column, while A_{cell} and h_{cell} were the surface area in plain view and the height of the control volume, respectively. The processes were governed by the respective rate constants $k_{\text{HgII—atin}}$ = 0.0274 μg/m^2/day, estimated by comparison with some mercury deposition rates from Scandinavia (e.g. Iverfeldt et al., 1995; Mukherjee et al., 1995), and v_{settling} = 1.0 m/day, determined by the calibration of the ST model and by literature (Choudhry et al., 1984; Ogorelec et al., 1991). This velocity was considered as an effective settling rate which meant overall settling minus resuspension; it was, in fact, the burial rate. The value of $k_{\text{methylation}}$ = 0.00021 day^{-1} assumed a methylation rate of 5 ng/m^2/day, an average water depth of 16 m and an average dissolved HgII concentration of 1.5 ng/l (SEADATA, 1992; Širca, 1996). Analogously, the $k_{\text{reduction}}$ = 0.00031 day^{-1} assumed a reduction rate of 7.5 ng/m^2/day and the same average water depth and dissolved HgII concentration as for the determination of the methylation constant. Such a value was in accordance with some previously reported seawater (e.g. E_{ocean} by Hudson et al., 1995) and freshwater emission rates. The amount of reduced HgII (Eq. (13)) was considered to be a loss from the system.

Four additional model equations described the changes of MeHg in the water column due to deposition from the atmosphere, sedimentation, methylation and demethylation, respectively:

$$\Delta\text{MeHg}_{atin} = +\,k_{\text{MeHg—atin}}\cdot A_{\text{cell}} \quad (14)$$

$$\Delta\text{MeHg}_{sedi} = -\,v_{\text{settling}}\cdot\text{MeHg}_{tot}\cdot F_{\text{part}}(\text{MeHg})\cdot A_{\text{cell}} \quad (15)$$

$$\Delta\text{MeHg}_{meth} = -\,\Delta\text{HgII}_{meth} \quad (16)$$

$$\Delta\text{MeHg}_{deme} = \quad (17)$$

$$-\,k_{\text{demethylation}}\cdot\text{MeHg}_{tot}\cdot F_{\text{diss}}(\text{MeHg})\cdot A_{\text{cell}}\cdot h_{\text{cell}}$$

where MeHg_{tot} was the total amount of MeHg in the water column. The rate of atmospheric input of MeHg $k_{\text{MeHg—atin}}$ equaled 0.0003 μg/m^2/day, while the $k_{\text{demethylation}}$ = 0.00125 day^{-1} assumed a demethylation rate of 3 ng/m^2/day and an average MeHg concentration in the Gulf of 0.15 ng/l. The demethylated amount of MeHg was lost from the system (Eq. (17)). In lieu of any available on-site data, the above methylation and demethylation rates were assumed to be of similar orders of magnitude as those modelled for freshwater systems.

4. Simulations and verification

Case G5 was the main verification simulation which also attempted to reproduce the present state of mercury pollution in the Gulf. The Soča River was assumed to be the only source, bringing in 4874 g of mercury per day, while input from the open sea was assumed to be zero. It was also assumed that the total amount of inflowing mercury consisted of 99.6% HgII and 0.4% MeHg. Since there were only available measurements of the total Hg in the Soča River, this division was based on the facts that 99.8% of the mercury from the river is in particulate form (see mass balance above) and that

Table 1
Results of the G5 case (simulation of the present state of pollution)

	Hg_{tot} [g/day]	Hg_{tot} [ng/m^2/day]	HgII [g/day]	HgII [ng/m^2/day]	MeHg [g/day]	MeHg [ng/m^2/day]
from the Soča River	+ 4874	+ 8123	+ 4855	+ 8091	+ 19	+ 32
from the atmosphere	+ 16.2	+ 27	+ 16.0	+ 26.7	+ 0.2	+ 0.3
sedimentation	− 4559	− 7598	− 4542	− 7570	− 17	− 28
methylation	± 5.5	± 9.2	− 5.5	− 9.2	+ 5.5	+ 9.2
demethylation	− 0.8	− 1.3	–	–	− 0.8	− 1.3
reduction	− 8.2	− 13.7	− 8.2	− 13.7	–	–
net outflow	− 322	− 537	− 315	− 525	− 7.0	− 12.0

the proportion of MeHg in the total Hg of the bottom sediments around the river mouth averaged 0.30% (SEADATA, 1992). All relevant mercury fate processes were included in the G5 case (Table 1). During calibration, with the dispersion coefficient as the only parameter, the best fit was obtained for $D = 20$ m^2/s (Širca and Rajar, 1997a). Although, in comparison with the preliminary annual mass balance, the model predicted that a larger portion of the total input will leave the Gulf via the residual current, and a smaller amount of mercury in the whole water body (compare Fig. 2 and Table 1). A satisfactory agreement was reached with the annual mass balance as a whole, which is shown later.

Because of the 2D and stationary character of the STATRIM model, the averages of the measurements which were performed at different depths and in different seasons were used for the verification (Table 2, Fig. 6). This averaging resulted in very high standard deviations of the total inorganic mercury at locations T1–T4 (SEADATA, 1992) and of the dissolved inorganic mercury at D6 and A4 (Širca, 1996) (Table 2), which could not be avoided. The best agreement between the computed and the measured results was reached for the dissolved HgII, where 11 out of 12 results were of the same order of magnitude. Less favourable were the comparisons of the concentrations of the particulate HgII, where only 5 out of 12 pairs agreed within the same order of magnitude. Consequently, the agreement was also not so good for the total HgII (6 out of 14 values). As to the plankton HgII, there were too few measured values available to give a final judgement about the accuracy of the model. Since only two measurements of MeHg were available, the following comparisons are performed for HgII only.

The gap between the computed and the measured results may seem less acceptable to somebody who is used to agreements within some tens of percents, as is the case in freshwater lakes. However, one must take into account some specific features of the Gulf of Trieste case, and of the modelling of marine environments in general:

Table 2
Verification of the STATRIM model. Comparison of measured and computed HgII concentrations

Location	Total HgII [μg/m^3]		Particulate HgII [μg/m^3]		Dissolved HgII [μg/m^3]		Plankton HgII [ng/m^3]	
	meas.	comp.	meas.	comp.	meas.	comp.	meas.	comp.
a	b	c	d	e	f	g	h	i
T1	22.2 ± 27.9	109.2	20.8	56.0	1.5	27.1	–	–
T2	52.6 ± 56.9	30.3	–	–	–	–	–	–
T3	42.2 ± 62.8	7.7	40.9	2.5	1.3	2.9	–	–
T4	9.9 ± 8.6	2.7	–	–	–	–	–	–
T12	6.4	4.9	3.6	2.2	2.8	2.7	–	–
T13	7.7	28.0	3.5	23.1	4.1	4.8	–	–
T14	7.1	30.3	3.2	25.6	4.0	4.7	–	–
T15	12.6	14.9	7.6	10.9	5.0	4.0	–	–
D6	10.3 ± 3.4	57.8	7.3	53.8	3.0 ± 1.9	4.0	–	–
A4	8.5 ± 3.6	21.2	6.7	17.0	1.8 ± 1.3	4.1	12 ± 7	27.1
A29	3.8 ± 0.3	15.6	2.4	12.1	1.4 ± 0.1	3.5	6 ± 2	23.3
CZ	1.56 ± 0.47	3.25	0.59	1.56	0.97 ± 0.33	1.68	5 ± 0.3	11.1
F0	1.54 ± 0.70	1.59	0.86	0.14	0.68 ± 0.32	1.44	4 ± 3	9.5
F2	1.65 ± 0.60	1.14	1.00	0.09	0.65 ± 0.43	1.04	8 ± 4	6.9
Average	13.4	23.5	8.2	17.1	2.3	5.2	7.0	15.6

Measured data in T1–T4 from SEADATA (1992) (b: *num* = 4; f: *num* = 2; d = b − f); in T12–T15 from Ferrara and Maserti (1992); in D6–F2 from Širca (1996) (b: *num* = 4, f: *num* = 4; d = b − f).

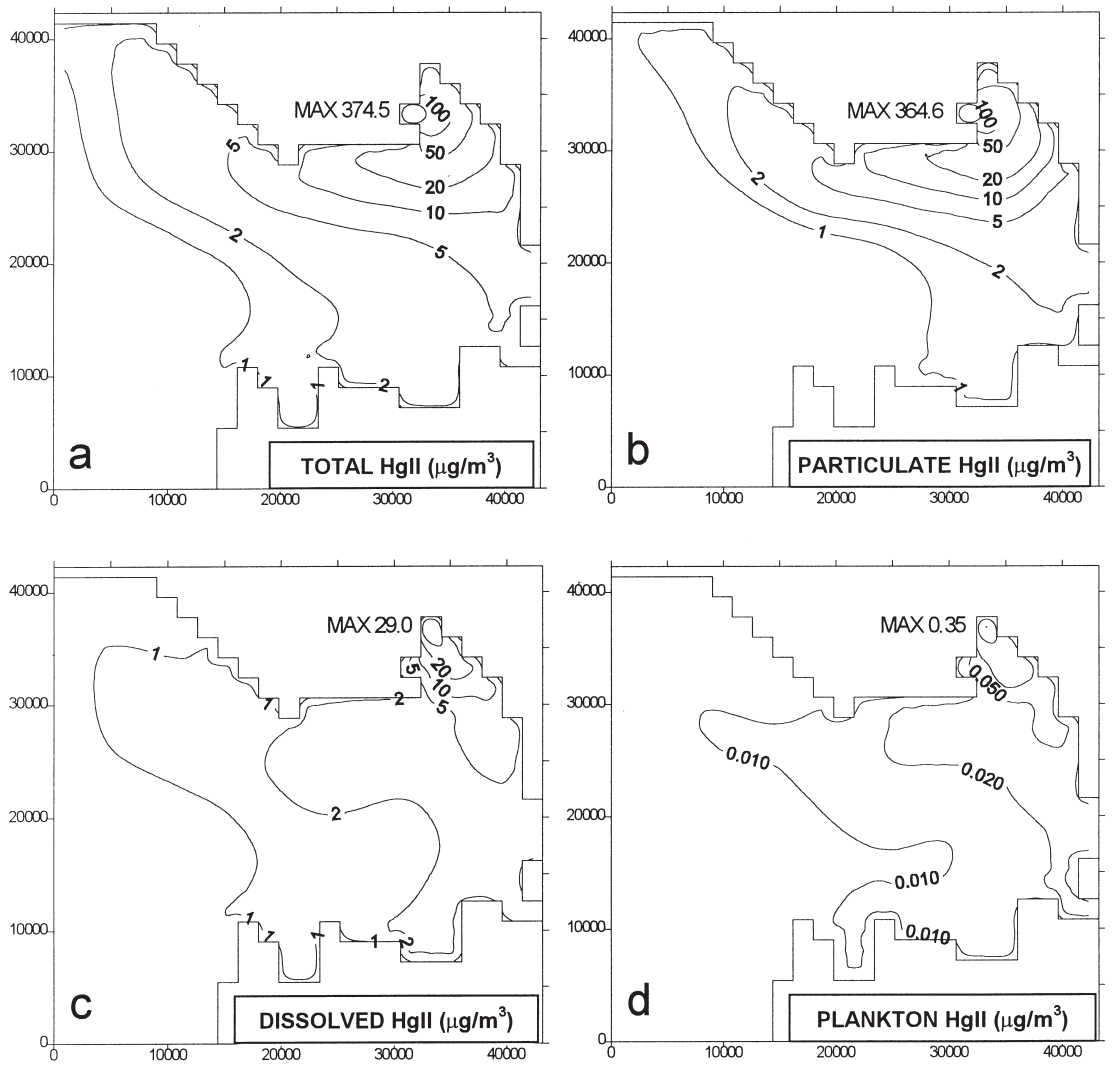

Fig. 6. Concentrations of total (a), particulate (b), dissolved (c) and plankton (d) HgII in $\mu g/m^3$ for the G5 case (present state of pollution).

1. The measurements at points T1, T3, T12, T13, T14 and T15 were performed in a single day; thus, they cannot be representative of the whole year, as the model tends to be. This unrepresentativeness originates mainly from the fact that most of the sediment and the Hg bound to it are transported during exceptional events, such as high river stages or storms. These events considerably increase the average concentrations of suspended matter and Hg but cannot be monitored by only occasional measurements. To overcome this deficiency, additional measurements are planned which were not yet available for this stage of the model.
2. The rough computational grid results and a rather weak residual circulation in the Panzano Bay (the northeasternmost part of the Gulf monitored by the T1 location from Fig. 1) which causes a retardation of the polluted Soča River water in the northern part of the Gulf of Trieste. This deficiency could be ameliorated by the application of a denser grid, which was not feasible at the time of the model development, due to insufficient computer power.
3. The excessive retardation of the pollution in the Gulf of Trieste is partly a result of the simplified description of the average wind by the VECTRA method. It applies only one average (representative) wind which has a direction similar to the direction of the burja, the predominant wind above the Gulf. In reality, there are also some less frequent and less intense winds from the south-east (*jugo*) and the north-west (*maestral*) which can cause some pollutant transport to the southern part of the Gulf. However, their influence on pollutant spreading from the Soča River could only be properly described by an unsteady state simulation which was, again, not yet possible, because of hardware limitations.
4. A simplified 2D description of the Gulf has also contributed to the noted differences because the hydrodynamic, sediment transport and mercury fate processes in this area are, in fact, of a three-dimensional charac-

ter (e.g. the effects of the thermal and salinity stratifications). An example of this is the resuspension of sediments, which was the main cause of the large standard deviations of the total HgII (Table 2, column b).

5. The last, but not the least, important reason for these differences could be that many of the processes of mercury transformation (e.g. methylation and demethylation) are not yet well understood, as their dependence on environmental parameters (e.g. pH, dissolved oxygen, sulphate, total organic carbon) is very complex.

To minimise the influence of the described simplifications, the averages of the computed and the measured results were compared (Table 2, last row). Except for plankton HgII, all average computed values agreed within the same order of magnitude with the measured results. However, the obvious difference of about 100% confirms the remarks listed above with an emphasis on the very low measured values of the particulate and, consequently, the total HgII.

A favourable verification result has been obtained by comparing the computed average total Hg bottom deposition rate of 2.77 mg/m^2/year (extracted from Table 1) with the measured values of 1.29 mg/m^2/year at a depth of 10 m and 3.10 mg/m^2/year at a depth of 20 m, according to Planinc and Faganeli (1993). Although the first measured value is not representative for the whole water column and the second one includes some effects of resuspension, their arithmetic mean of 2.19 μg/m^2/year seems to be a good approximation of the actual rate. Yet another test of the STATRIM model results is a map of bottom sediment mercury concentrations (Fig. 7) by Covelli et al. (1999) which implicitly confirms the computed distribution of the particulate and of the total HgII (Fig. 6(b) and (a)).

The G6 case simulation attempted to predict the probable changes in mercury concentrations in the Gulf due to a 90% reduction of both HgII and MeHg in the Soča River. Therefore, only 10% of the mercury from the G5 case was released at the discharge site of the Soča River. Except for the reduction at the source, all data remained the same as for the G5 case, which enabled a direct comparison of the results. In general, the concentrations of HgII and MeHg in the Gulf decreased linearly by 90%. Some minor changes of the role of other sources and sinks were also observed. For example, the atmosphere contributed only 0.3% to the mercury sources in G5 (Table 1), while its share increased to 3.2% in G6. However, these results were based on a fundamental model assumption that all the Hg in the system is equally available to participate in the Hg cycle, and there are no processes in the model which would limit concentrations of HgII or MeHg as the loads increase (e.g. due to chemical precipitation or saturation of binding sites on solids).

5. Discussion

A mercury mass balance for the Gulf of Trieste has been established which has revealed the dominant influence of the Soča River as the main source, and of sedimentation as the main sink of mercury. The inflow by the residual current from the open sea contributes only 5% to the total input, while outflow by the residual current is somewhat higher, with 11% of the total output. The atmospheric deposition is almost negligible, with a contribution of only 0.2% to the total input.

A two-dimensional depth-averaged mercury transport and fate model STATRIM was developed. It enables the elaboration of 2D (space dependent) Hg mass balances for the Gulf and the determination of corresponding specific fluxes as a result of different scenarios; i.e; different combinations and intensities of sources and sinks. During model verification, the observed and predicted results agreed within an order of magnitude. It was not possible to reach a higher level of accuracy at the time, mainly due to insufficient field data and computer hardware limitations. However, the application of partition coefficients speeded up the transport computation by a factor of three, as only two advection-dispersion equations needed to be solved instead of six in the case of the explicit description of both the HgII and MeHg compounds in all three forms. This is important because coupled water quality models such as STATRIM are typically very time-consuming.

The simulations have confirmed the expected spatial distribution of mercury in the sediments and in the water column. Most of the mercury is either deposited in the northern part of the Gulf (Fig. 6) or carried to the open sea by the residual current. In present average conditions, the amount of Hg in the whole water body of the Gulf is approximately 73 kg. This is distributed among HgII in dissolved (54.6%), particulate (45.0%) and plankton (0.4%) fractions, and MeHg having the respective fractions of 83.0%, 16.5% and 0.5%. Due to insufficient measurements, the model cannot yet answer the question of whether the main source of MeHg is production in the Gulf itself or loading from the Soča River watershed. The STATRIM model is being augmented by the development of a 3D unsteady integrated model, with plans to add a food chain module for methylmercury. However, the present model represents a sound method for modelling marine situations which need to address spatial variations in mercury concentrations due to hydrodynamics and sediment transport.

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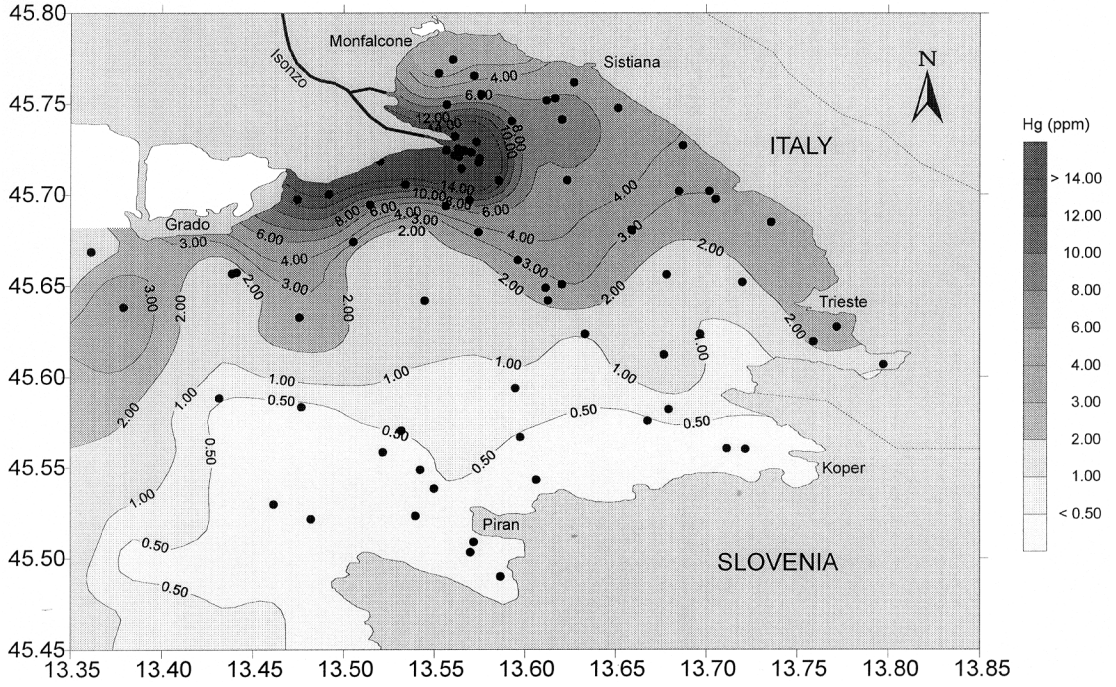

Fig. 7. Areal distribution of mercury in the sediments of the Gulf of Trieste (μg/g) and locations of sampling points. By kind permission adapted from Covelli et al. (1999).

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