EN-SIN
Enhanced Biogeochemical Modeling and Simulation

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Review: Augusta Bay mass-balance steady-state equation

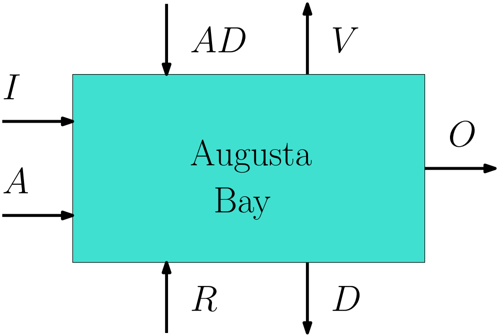
Steady-state mass balance equation of HgT (total mercury) (**Sprovieri et al. (2011)**):

$$I + A + AD + R = O + D + V \tag{1}$$

where

- I is the total H_g influx from the Mediterranean seawater
- A is the dissolved H_g input anthropogenic activities
- AD is the atmospheric H_g deposition
- R is the H_g resuspension/release from sediments
- O is the H_g outflow from the basin
- D is the sedimentary deposition and burial
- V is the H_g evasion to atmosphere

Review: Augusta Bay mass-balance steady-state equation



- The underlying assumption is that the **quantity of contaminant** in the Augusta basin is approximately **constant**.
- The Augusta Bay is henceforth referred to as SIN (acronym for *Sito di Interesse Nationale*).

Review: Augusta Bay mass-balance dynamic equation

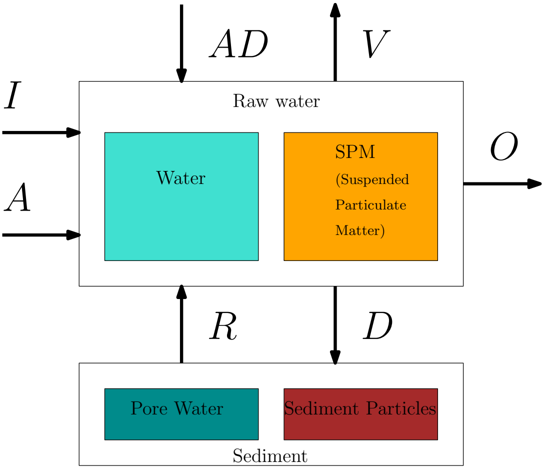
- Moving beyond the equilibrium assumption, a first step is to generalize the steady-state equation to take into account a possibly non-zero variation of contaminant in the Augusta Basin:

$$\dot{Q}_{RawWater}(t) = I(t) + A(t) + AD(t) + R(t) - O(t) - D(t) - V(t) \tag{2}$$

  where the meaning of the time-varying quantities are analogous to the steady-state case.
- In order to take into account of all the chemical and physical phenomena involved in (2), we will adopt and properly modify some known models.

Review: River model

The River model was developed in the context of the two EU-funded projects 2FUN and 4FUN and implemented in the MERLIN-Expo tool.



Review: River model equations

River model equations:

$$
\begin{aligned}
\dot{Q}_{RawWater}(t) = & -\lambda_{water} Q_{RawWater}(t) + EliminationBiota(t) - UptakeBiota(t) \\
& + SoilWashoff(t) + AD(t) - V(t) + A(t) \\
& + FlowRiver(t)\left(C_{WaterUpstream}(t) - C_{Water}(t)\right) \\
& + S_{river}\left(F_r(t) C_{MassSed}(t) - F_d(t) C_{SPM}(t)\right) \\
& + S_{river} MTC_{WaterSed}\left(C_{PoreWaterSed}(t) - C_{DissWater}(t)\right) \\
\dot{Q}_{MassSed}(t) = & \; S_{river}\left(F_d(t) - F_r(t)\right) \\
\dot{Q}_{ChemicalSed}(t) = & -\lambda_{sed} Q_{ChemicalSed}(t) \\
& - S_{river}\left(F_r(t) C_{MassSed}(t) - F_d(t) C_{SPM}(t)\right) \\
& - S_{river} MTC_{WaterSed}\left(C_{PoreWaterSed}(t) - C_{DissWater}(t)\right)
\end{aligned}
$$

Meaning of the state variables:

- $Q_{RawWater}$: quantity of contaminant in Raw Water $[mg]$
- $Q_{MassSed}$: quantity (mass) of Sediment $[g]$
- $Q_{ChemicalSed}$: quantity of contaminant in Sediment $[mg]$

Review: River model equations

River model equations:

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\begin{aligned}
\dot{Q}_{RawWater}(t) = & -\lambda_{water} Q_{RawWater}(t) + EliminationBiota(t) - UptakeBiota(t) \\
& + SoilWashoff(t) + AD(t) - V(t) + A(t) \\
& + FlowRiver(t)\left(C_{WaterUpstream}(t) - C_{Water}(t)\right) \\
& + S_{river}\left(F_r(t) C_{MassSed}(t) - F_d(t) C_{SPM}(t)\right) \\
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\dot{Q}_{MassSed}(t) = & \; S_{river}\left(F_d(t) - F_r(t)\right) \\
\dot{Q}_{ChemicalSed}(t) = & -\lambda_{sed} Q_{ChemicalSed}(t) \\
& - S_{river}\left(F_r(t) C_{MassSed}(t) - F_d(t) C_{SPM}(t)\right) \\
& - S_{river} MTC_{WaterSed}\left(C_{PoreWaterSed}(t) - C_{DissWater}(t)\right)
\end{aligned}
$$

Meaning of the parameters:

- S_{river}: surface area of the river $[m^2]$
- λ_{water}, λ_{sed}: degradation rate in water/sediment $[1/unit\ time]$
- $MTC_{WaterSed}$: Mass Transfer Coefficient $[m/unit\ time]$

Review: Biogeochemical models

- It can be shown that the river model is a single-compartment model that is approximately consistent with the underlying continuous model described by a general advection-diffusion-reaction equation

$$\frac{\partial c}{\partial t} = \nabla \cdot (D \nabla c) - \nabla \cdot (\vec{v} c) + \sigma.$$

- Examples of relevant continuous models are
  - Dutkiewicz et al. (2009);
  - Hernandez et al. (2014);
  - Ryabov (2008);
  - Valenti et al. (2017).
- In particular, the river model equations aggregate continuous concentration distributions by means average compartmental concentrations and cumulative quantities of contaminant.

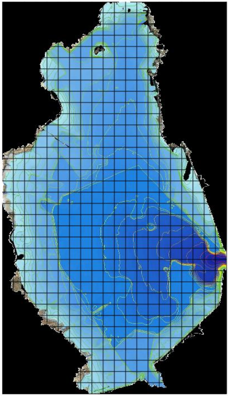
Review: Biogeochemical models

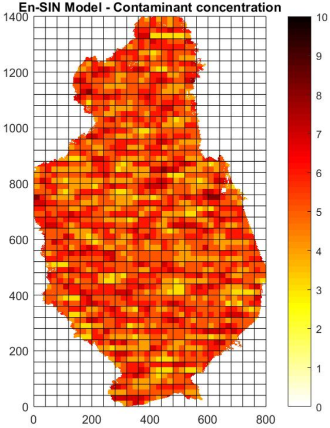
- In recent works, new biogeochemical models reproduce the dynamics of mercury concentration in marine ecosystems by using a WASP approach, which is used to discretize a water body in three dimensions by means of interconnected zero dimensional boxes (water or sediment compartments).
- The WASP approach does not allow to localize the zones within the zero dimensional boxes where the mercury concentration takes on the maximum value. Conversely, this aspect is of paramount importance for the Italian sites investigated in our studies.
- The previous analyses do not include neither the study of the spatio-temporal dynamics of phytoplankton distributions nor the investigation of the mechanism responsible for absorbtion of mercury within the phytoplankton cell in marine ecosystems.

The EN-SIN model

- In CISAS, we modify the aforementioned existing models and develop an advection-diffusion-reaction model for the 3D domain of the Augusta Gulf, reproducing the spatio-temporal behaviour of the concentrations of three mercury species (inorganic, organic, elemental) observed in water, pore water and sediment particles.
- In the model, we also consider the partition of methyl-mercury and inorganic mercury into dissolved (water and pore water) and particulate phases (Suspended Particulate Matter and Sediment particles). Moreover, the effects of deterministic (seasonal) variations of environmental variables are taken into account.
- The numerical method used exploits a finite volume scheme in explicit form. The differential equations of the model are solved by performing a centered-in-space differencing for the diffusion terms, and a first-order upwind-biased differencing for the advection terms. The increment of the spatial variables is set at 454.6 m for the x- and y-direction, and 5.0 m for the z-direction, while the time step is fixed at 0.125 h.

The EN-SIN model





Dynamics of the dissolved mercury concentration

On the basis of the overall equation for the mass conservation of the state variables in dissolved phase, we devise a PDE system which describes the dynamics of (dissolved) mercury concentration for the three different species (Hg^0, Hg^{II},$MMHg$) and SPM concentration, within the 3-D domain of Augusta basin:

$$\begin{aligned}\frac{\partial Hg^0}{\partial t} = \; & +\frac{\partial}{\partial x}\left[D_x \frac{\partial Hg^0}{\partial x}\right] - \frac{\partial}{\partial x}(v_x Hg^0) + \frac{\partial}{\partial y}\left[D_y \frac{\partial Hg^0}{\partial y}\right] - \frac{\partial}{\partial y}(v_y Hg^0) + \frac{\partial}{\partial z}\left[D_z \frac{\partial Hg^0}{\partial z}\right] \\ & - \frac{\partial}{\partial z}(v_z Hg^0) + k_{Ph-de} \cdot MMHg - (k_1 + k_3) \cdot Hg^0 + (k_2 + k_4) \cdot Hg^{II}\end{aligned}$$

$$\begin{aligned}\frac{\partial Hg^{II}}{\partial t} = \; & +\frac{\partial}{\partial x}\left[D_x \frac{\partial Hg^{II}}{\partial x}\right] - \frac{\partial}{\partial x}(v_x Hg^{II}) + \frac{\partial}{\partial y}\left[D_y \frac{\partial Hg^{II}}{\partial y}\right] - \frac{\partial}{\partial y}(v_y Hg^{II}) + \frac{\partial}{\partial z}\left[D_z \frac{\partial Hg^{II}}{\partial z}\right] \\ & - \frac{\partial}{\partial z}(v_z Hg^{II}) + (k_1 + k_3) \cdot Hg^0 - (k_2 + k_4) \cdot Hg^{II} + S_L^{II} + S_{DOM}^{II} - S_{SPM}^{II}\end{aligned}$$

$$\begin{aligned}\frac{\partial MMHg}{\partial t} = \; & +\frac{\partial}{\partial x}\left[D_x \frac{\partial MMHg}{\partial x}\right] - \frac{\partial}{\partial x}(v_x MMHg) + \frac{\partial}{\partial y}\left[D_y \frac{\partial MMHg}{\partial y}\right] - \frac{\partial}{\partial y}(v_y MMHg) \\ & + \frac{\partial}{\partial z}\left[D_z \frac{\partial MMHg}{\partial z}\right] - \frac{\partial}{\partial z}(v_z MMHg) - K_{Ph-de} \cdot MMHg + S_L^{MM} + S_{DOM}^{MM} - S_{SPM}^{MM}\end{aligned}$$

$$\begin{aligned}\frac{\partial SPM}{\partial t} = \; & +\frac{\partial}{\partial x}\left[D_x \frac{\partial SPM}{\partial x}\right] - \frac{\partial}{\partial x}(v_x \cdot SPM) + \frac{\partial}{\partial y}\left[D_y \frac{\partial SPM}{\partial y}\right] - \frac{\partial}{\partial y}(v_y \cdot SPM) \\ & + \frac{\partial}{\partial z}\left[D_z \frac{\partial SPM}{\partial z}\right] - \frac{\partial}{\partial z}(v_z \cdot SPM) - \frac{\partial}{\partial z}(w_s \cdot SPM) + S_L^{SPM}\end{aligned}$$

Dynamics of the dissolved mercury concentration

The load of dissolved mercury released by particulate organic matter (S_{DOM}) is given by:

$$S_{DOM} = \quad + \sum [\lambda_i \cdot m_{b_i} \cdot b_i \cdot PHg_i]$$

Here, the parameters and variables are defined into Phytoplankton model and NP model (see Merlin-Expo papers, 2015, and Dutkiewicz et al. 2009).
The adsorption rate of suspended particulate matter for dissolved mercury (S_{SPM}) is obtained by Zhang et al. (2014), as follows:

$$S_{SPM} = \quad -\frac{\partial}{\partial z} \left[NPP \cdot (pe - ratio) \cdot \left(\frac{z}{z_0}\right)^{-0.9} \cdot \left(\frac{k_D}{f_{oc}}\right) \cdot Hg(z) \right]$$

Dynamics of the total mercury concentration

Dissolved mercury concentration (DHg) and total mercury concentration (THg) in the position (x,y,z) within the Augusta basin at time t, are given by:

$$
\begin{aligned}
DHg &= Hg^0 + Hg^{II} + MMHg \\
THg &= Hg^0 + Hg^{II} + MMHg + Hg^{II} \cdot k_{D_1} \cdot SPIM + Hg^{II} \cdot k_{D_2} \cdot SPOM \\
&\quad + MMHg \cdot k_{D_3} \cdot SPIM + MMHg \cdot k_{D_4} \cdot SPOM + \sum_i PHg_i b_i
\end{aligned}
$$

According to Zhang et al. (2014), the suspended particulate matter is defined as follows:

$$SPM = SPIM + SPOM$$

In particular, the particulate organic matter (POM) in dissolved-phase and the suspended particulate inorganic matter (SPIM) are given by:

$$POM = SPOM = f_{org} \cdot SPM; \qquad SPIM = (1 - f_{org}) \cdot SPM$$

Dynamics of nutrient concentration and phytoplankton abundance

The dynamics of SPM concentration is coupled to those of phytoplankton abundances. To reproduce the spatio-temporal behaviour of phytoplankton abundance, we use a NP model which takes into account three processes: net growth (reaction term); active/passive movement (taxis/advection term); movement due to turbulence (diffusion term).

$$\begin{aligned}\frac{\partial b_i}{\partial t} = \quad & +\frac{\partial}{\partial x}\left[D_x \frac{\partial b_i}{\partial x}\right] - \frac{\partial}{\partial x}(v_x b_i) + \frac{\partial}{\partial y}\left[D_y \frac{\partial b_i}{\partial y}\right] - \frac{\partial}{\partial y}(v_y b_i) \\ & + \frac{\partial}{\partial z}\left[D_z \frac{\partial b_i}{\partial z}\right] - \frac{\partial}{\partial z}(v_z b_i) - \frac{\partial}{\partial z}(w_i b_i) + b_i \cdot min\left(f_{I_i}(I), f_{R_i}(R)\right) - m_{b_i} b_i\end{aligned}$$

$$\begin{aligned}\frac{\partial R}{\partial t} = \quad & +\frac{\partial}{\partial x}\left[D_x \frac{\partial R}{\partial x}\right] - \frac{\partial}{\partial x}(v_x R) + \frac{\partial}{\partial y}\left[D_y \frac{\partial R}{\partial y}\right] - \frac{\partial}{\partial y}(v_y R) \\ & + \frac{\partial}{\partial z}\left[D_z \frac{\partial R}{\partial z}\right] - \frac{\partial}{\partial z}(v_z R) - \sum_i \frac{b_i}{Y_i} \cdot min\left(f_{I_i}(I), f_{R_i}(R)\right) + \sum_i \varepsilon_i \cdot m_{b_i} \cdot \frac{b_i}{Y_i}\end{aligned}$$

The light intensity $I(x, y, z, t)$ is assumed to depend on the site (x,y) considered, and to decrease exponentially with the depth z, according to Lambert-Beer's law

$$I = I_{in} \exp\left\{ - \int_0^z \left[\sum a_i \cdot chl\, a_i + a_{bg}\right] dZ \right\}$$

Boundary conditions at the water-atmosphere interface – Elemental mercury

The mercury flux at the water-atmosphere interface (z=0) is obtained by the River Model and Bagnato et al. (2013), as follows:

$$\left[D_z \frac{\partial Hg^0}{\partial z} - v_z Hg^0 \right] \Bigg|_{z=0} = \phi_{dep} - \phi_{GEM} =$$
$$= \frac{Hg_{gas-atm} \cdot Pr}{\Delta t} + MTC_{water-atm} \cdot \left(Hg_{gas-atm} - H \cdot Hg^0|_{z=0} \right)$$

The gas phase overall mass transfer coefficient ($MTC_{water-atm}$) is calculated according to The River model as follows:

$$MTC_{water-atm} = \frac{MTC_{water-atm,w} \cdot MTC_{water-atm,g}}{MTC_{water-atm,w} + H \cdot MTC_{water-atm,g}}$$

Here, the water film mass transfer coefficient ($MTC_{water-atm,w}$) and the gas film mass transfer coefficient ($MTC_{water-atm,g}$) are given by:

$$MTC_{water-atm,w} = 0.108 \cdot (u_{wind})^{1.64} \cdot \left(\frac{PM_{CO_2}}{PM_{molar}}\right)^{0.25}$$

$$MTC_{water-atm,g} = 864 \cdot (0.2 \cdot u_{wind} + 0.3) \cdot \left(\frac{PM_{H_2O}}{PM_{molar}}\right)^{0.3}$$

Boundary conditions at the water-atmosphere interface – Inorganic mercury and methyl-mercury

Inorganic mercury concentration

The inorganic mercury flux at the water-atmosphere interface (z=0) is obtained by the River Model and Bagnato et al. (2013), as follows:

$$\left[D_z \frac{\partial Hg^{II}}{\partial z} - v_z Hg^{II}\right]\Big|_{z=0} = Wetdep_{part} + Wetdep_{gas} + Drydep_{part} = \frac{Hg^{II}_{atm} \cdot Pr}{\Delta t}$$

Methyl-mercury concentration

The methyl-mercury flux at the water-atmosphere interface (z=0) can be neglected because the methyl-mercury concentration is very low in atmosphere ($MMHg_{atm} \simeq 0$). Therefore, we set:

$$\left[D_z \frac{\partial MMHg}{\partial z} - v_z MMHg\right]\Big|_{z=0} = Wetdep_{part} + Wetdep_{gas} + Drydep_{part}$$
$$= \frac{MMHg_{atm} \cdot Pr}{\Delta t} = 0$$

Boundary conditions at the water-atmosphere interface – SPM, nutrient and phytoplankton

SPM concentration

The vertical SPM flux at the water-atmosphere interface (z=0) is obtained by the River model as follows:

$$\left[D_z \frac{\partial SPM}{\partial z} - v_z SPM \right] \Bigg|_{z=0} = Drydep \simeq 0$$

where *Drydep* is the surface dry deposition flux of particles $[mg \cdot m^{-2} \cdot h^{-1}]$ (see the River model). This flux can be neglected if the SPM concentration is very low in atmosphere. **Nutrient concentration and phytoplankton abundance**

For the nutrient (phospates) and phytoplankton populations, we assume no flux through the water-atmosphere interface (Valenti et al. 2017). Therefore, we set the vertical fluxes at the boundaries of domain as follows:

$$\frac{\partial R}{\partial z}\Bigg|_{z=0} = 0, \qquad \left[D_z \frac{\partial b_i}{\partial z} - (w_i + v_z) b_i \right] \Bigg|_{z=0} = 0.$$

Boundary conditions at the water-sediment interface – Inorganic mercury

The inorganic mercury flux at the water Ű sediment interface ($z = z_b$) is calculated as a function of time in each position (x,y) of the domain (Schulz and Zabel, 2006):

$$\left[D_z \frac{\partial Hg^{II}}{\partial z} - v_z Hg^{II}\right]\bigg|_{z=z_b} = -J_{sed} = \varphi_{sed} \cdot D_{sed} \cdot \frac{\partial Hg^{II}}{\partial z} = \varphi_{sed} \cdot \frac{D_{w-in}}{\theta^2} \cdot \frac{\partial Hg^{II}}{\partial z} = \\ = MTC^{II}_{sed-water} \cdot \left(Hg^{II}_{pw} - Hg^{II}_{dw}\right)$$

In accordance with Melaku Canu et al. (2015), we calculate the inorganic mercury concentration in the pore water as a function of time, by considering the molecular diffusion within the sediment, as follows:

$$\frac{dHg^{II}_{pw}}{dt} = +K_{demeth} \cdot MMHg_{pore-water} - K_{meth} \cdot Hg^{II}_{pw} + \frac{\partial}{\partial z}\left[\varphi_{sed} \cdot \frac{D_{w-in}}{\theta^2} \cdot \frac{\partial Hg^{II}_{pw}}{\partial z}\right]$$

The inorganic mercury concentration in the pore water at the initial condition (t=0) is estimated as follows:

$$Hg^{II}_{pw}(0) = (1 - k_{MMHg}) \cdot k \cdot THg_{sed} \cdot SPM_{sed}$$

Boundary conditions at the water-sediment interface – Methyl-mercury

The methyl-mercury flux at the water Ű sediment interface ($z = z_b$) is calculated as a function of time in each position (x,y) of the domain (Schulz and Zabel, 2006):

$$\left[D_z \frac{\partial MMHg}{\partial z} - v_z MMHg \right] \Bigg|_{z=z_b} = -J_{sed} = \varphi_{sed} \cdot D_{sed} \cdot \frac{\partial MMHg}{\partial z}$$
$$= \varphi_{sed} \cdot \frac{D_{w-or}}{\theta^2} \cdot \frac{\partial MMHg}{\partial z} = MTC^{MM}_{sed-water} \cdot (MMHg_{pw} - MMHg_{dw})$$

In accordance with Melaku Canu et al. (2015), we calculate the methyl-mercury concentration in the pore water as a function of time, by considering the molecular diffusion within the sediment, as follows:

$$\frac{dMMHg_{pw}}{dt} = -K_{demeth} \cdot MMHg_{pw} + K_{meth} \cdot Hg^{II}_{pw} + \frac{\partial}{\partial z} \left[\varphi_{sed} \cdot \frac{D_{w-or}}{\theta^2} \cdot \frac{\partial MMHg}{\partial z} \right]$$

The methyl-mercury concentration in the pore water at the initial condition (t=0) is estimated by the total mercury concentration (THg) and the specific weight (SPM) measured in the sediment, as follows:

$$MMHg_{pw}(0) = k_{MMHg} \cdot k \cdot THg_{sed} \cdot SPM_{sed}$$

Boundary conditions at the water-sediment interface – Elemental mercury, nutrient and phytoplankton

Elemental mercury concentration
Since we can neglected the elemental mercury flux at the water Ű sediment interface ($z = z_b$), we set:

$$\left[D_z \frac{\partial Hg^0}{\partial z} - v_z Hg^0 \right] \bigg|_{z=z_b} = 0$$

Nutrient concentration and phytoplankton abundance
For the nutrient (phosphates) we fix the nutrient concentration at the other boundaries equal to the values measured during the oceanographic survey. According to these assumptions, we set:

$$R(x, y, z_b) = R_{in}(x, y, z_b).$$

For phytoplankton populations, we assume no flux through the water-sediment interface (Valenti et al. 2017). Therefore, we set the vertical fluxes at the boundaries of domain as follows:

$$\left[D_z \frac{\partial b_i}{\partial z} - (w_i + v_z) b_i \right] \bigg|_{z=z_b} = 0$$

Boundary conditions at the water-sediment interface – SPM

The vertical SPM flux at the water Ű sediment interface ($z = z_b$) depend on two processes (River Merlin-Expo model, 2015): the deposition flux of particles and the resuspension of particles. These are described by the following boundary condition:

$$\left[D_z \frac{\partial SPM}{\partial z} - v_z SPM \right] \Bigg|_{z=z_b} = w_s \cdot SPM(z_b) \cdot exp\left(-\frac{\tau}{\tau_d} \right) - F_R$$

In particular, the resuspension flux of particles can be estimated, according to Melaku Canu et al. (2015) or the River model, as follows:

$$F_R = (w_r + w_b) \cdot SPM_{sed} = min(e_{max}; \lambda_c \cdot SPM_{sed} \cdot \Delta h_u) \cdot exp\left(-\frac{\tau_r}{\tau} \right)$$

It is worth to stress that the bed shear stress is obtained by using the quadratic drag law, in which we insert the numerical and experimental findings acquired for the Augusta basin. According to this definition (see Umgiesser et al., 2004), the bed shear stress is given by following equation:

$$\tau = \rho_w \cdot \left(\frac{g}{(k_s \cdot H^{1/6})^2} \right) \cdot (v_x^2 + v_y^2)$$

Boundary conditions (lateral fluxes) – Dissolved mercury

The Augusta basin is considered as closed except to inlets, rivers and sewerage. Therefore, we fix for the three mercury species (Hg^0, Hg^{II},$MMHg$) the following lateral fluxes at boundaries of the domain:

$$\left[D_x \frac{\partial Hg}{\partial x} - v_x Hg\right] = \left[D_y \frac{\partial Hg}{\partial y} - v_y Hg\right] = 0$$

For all points of basin where rivers and sewerage are localized, we set:

$$\left[D_x \frac{\partial Hg}{\partial x} - v_x Hg\right] = INPUT_{x_{point-source}} = \left(\frac{Q_{source}}{A_{source}}\right)\bigg|_x \cdot Hg_{source}$$

$$\left[D_y \frac{\partial Hg}{\partial y} - v_y Hg\right] = INPUT_{y_{point-source}} = \left(\frac{Q_{source}}{A_{source}}\right)\bigg|_y \cdot Hg_{source}$$

Boundary conditions (lateral fluxes) – Dissolved mercury

The lateral fluxes of dissolved mercury concentration at inlets (Scirocco and Levante) of the basin (Salvagio Manta et al., 2016) as a function of depth and time are given by:

$$\begin{aligned}\phi_{x_{inlet}}(z,t) &= \left[D_x \frac{\Delta Hg}{\Delta x} + v_{x_{inlet}}(z,t)\cdot Hg_{ext}(z)\right] \\ &= \left[D_x \frac{\Delta Hg}{\Delta x} - v_{x_{inlet}}(z,t)\cdot Hg_{int}(z,t)\right]\end{aligned}$$

$$\begin{aligned}\phi_{y_{inlet}}(z,t) &= \left[D_y \frac{\Delta Hg}{\Delta y} + v_{y_{inlet}}(z,t)\cdot Hg_{ext}(z)\right] \\ &= \left[D_y \frac{\Delta Hg}{\Delta y} - v_{y_{inlet}}(z,t)\cdot Hg_{int}(z,t)\right]\end{aligned}$$

Mass balance of mercury in Augusta basin

Symbol	Interpretation	Value
O_{Lev_1}	*THg* outflow from Levante inlet to open sea	0.191
O_{Sci_1}	*THg* outflow from Scirocco inlet to open sea	0.112
O_1	*THg* outflow from the basin to the open sea	0.303
$R_{Hg_1^{II}}$	Hg^{II} release from the sediment of the basin	3.028
R_{MMHg_1}	*MMHg* release from the sediment of the basin	0.346
R_1	*DHg* release from the sediment of the basin	3.374
V_1	GEM evasion from basin to atmosphere	$5.26 \cdot 10^{-4}$

Table: Mass balance of mercury in Augusta basin (scenario 2% THg_{sed}) in $Kmol/year$.

Mass balance of mercury in Augusta basin

Symbol	Interpretation	Value
O_{Lev_2}	*THg* outflow from Levante inlet to open sea	0.319
O_{Sci_2}	*THg* outflow from Scirocco inlet to open sea	0.185
O_2	*THg* outflow from the basin to the open sea	0.504
$R_{Hg^{II}_2}$	Hg^{II} release from the sediment of the basin	4.542
R_{MMHg_2}	*MMHg* release from the sediment of the basin	0.519
R_2	*DHg* release from the sediment of the basin	5.061
V_2	GEM evasion from basin to atmosphere	$7.74 \cdot 10^{-4}$

Table: Mass balance of mercury in Augusta basin (scenario 3% THg_{sed}) in $Kmol/year$.

Mass balance of mercury in Augusta basin

Symbol	Interpretation	Value
O_{Lev_3}	*THg* outflow from Levante inlet to open sea	0.575
O_{Sci_3}	*THg* outflow from Scirocco inlet to open sea	0.330
O_3	*THg* outflow from the basin to the open sea	0.905
$R_{Hg^{II}_3}$	Hg^{II} release from the sediment of the basin	7.570
R_{MMHg_3}	*MMHg* release from the sediment of the basin	0.865
R_3	*DHg* release from the sediment of the basin	8.434
V_3	GEM evasion from basin to atmosphere	$12.71 \cdot 10^{-4}$

Table: Mass balance of mercury in Augusta basin (scenario 5% THg_{sed}) in $Kmol/year$.

Mass balance of mercury in Augusta basin

Symbol	Interpretation	Value
A	Input of dissolved mercury from anthropogenic activities	0.000
AD	Atmospheric mercury deposition	$n.d.$
D	Amount of mercury recycled into Augusta Bay	$n.d.$

Table: Mass balance of mercury in Augusta basin in $Kmol/year$.

Boundary conditions (lateral fluxes) – SPM

In accordance with the boundary conditions for dissolved mercury concentration, the Augusta basin is considered as closed except to inlets, rivers and sewerage. Therefore, we fix the following lateral fluxes at boundaries of the domain:

$$\left[D_x \frac{\partial SPM}{\partial x} - v_x SPM\right] = \left[D_y \frac{\partial SPM}{\partial y} - v_y SPM\right] = 0$$

For all points of basin where rivers and sewerage are localized, we set:

$$\left[D_x \frac{\partial SPM}{\partial x} - v_x SPM\right] = INPUT_{x_{point-source}} = \left(\frac{Q_{source}}{A_{source}}\right)\bigg|_x \cdot SPM_{source}$$

$$\left[D_y \frac{\partial SPM}{\partial y} - v_y SPM\right] = INPUT_{y_{point-source}} = \left(\frac{Q_{source}}{A_{source}}\right)\bigg|_y \cdot SPM_{source}$$

Boundary conditions (lateral fluxes) – SPM

The lateral fluxes of SPM concentration at inlets (Scirocco and Levante) of the basin as a function of depth and time are given by:

$$\phi^{SPM}_{x_{inlet}}(z,t) = \left[D_x \frac{\Delta SPM}{\Delta x} + v_{x_{inlet}}(z,t) \cdot SPM_{ext}(z)\right]$$
$$= \left[D_x \frac{\Delta SPM}{\Delta x} - v_{x_{inlet}}(z,t) \cdot SPM_{int}(z,t)\right]$$

$$\phi^{SPM}_{y_{inlet}}(z,t) = \left[D_y \frac{\Delta SPM}{\Delta y} + v_{y_{inlet}}(z,t) \cdot SPM_{ext}(z)\right]$$
$$= \left[D_y \frac{\Delta SPM}{\Delta y} - v_{y_{inlet}}(z,t) \cdot SPM_{int}(z,t)\right]$$

Boundary conditions (lateral fluxes) – Phytoplankton

The Augusta basin is considered as closed for phytoplankton abundance flux except to inlets and rivers. Therefore, we set the following lateral fluxes at boundaries of the domain:

$$\left[D_x \frac{\partial b_i}{\partial x} - v_x b_i\right] = \left[D_y \frac{\partial b_i}{\partial y} - v_y b_i\right] = 0$$

For all points of basin where inlets and rivers are localized, we set:

$$\left[D_x \frac{\partial b_i}{\partial x} - v_x b_i\right] = \left(\frac{Q_{source}}{A_{source}}\right)\Big|_x \cdot b_{i_{source}}$$

$$\left[D_y \frac{\partial b_i}{\partial y} - v_y b_i\right] = \left(\frac{Q_{source}}{A_{source}}\right)\Big|_y \cdot b_{i_{source}}$$

Also in this case, the lateral fluxes at inlets (Scirocco and Levante) of the basin are given by:

$$\phi^{b_i}_{x_{inlet}}(z,t) = \left[D_x \frac{\Delta b_i}{\Delta x} + v_{x_{inlet}}(z,t) \cdot b_{i_{ext}}(z)\right] = \left[D_x \frac{\Delta b_i}{\Delta x} - v_{x_{inlet}}(z,t) \cdot b_{i_{int}}(z,t)\right]$$

$$\phi^{b_i}_{y_{inlet}}(z,t) = \left[D_y \frac{\Delta b_i}{\Delta y} + v_{y_{inlet}}(z,t) \cdot b_{i_{ext}}(z)\right] = \left[D_y \frac{\Delta b_i}{\Delta y} - v_{y_{inlet}}(z,t) \cdot b_{i_{int}}(z,t)\right]$$

Phytoplankton model

The dynamics of inorganic mercury content in each cell of the i-th phytoplankton population is given by the phytoplankton model (see The Phytoplankton Merlin-Expo model,2015):

$$\frac{dPHg_i^{II}}{dt} = W_{phy_i} \cdot k_{phy,up_i} \cdot Hg^{II} - PHg_i^{II} \cdot (k_{phy,exc_i} + k_{phy,gro_i})$$

To simplify the mercury concentration model we assume that, for all phytoplankton populations, the inorganic (methyl-) mercury content in each cell reaches a fast equilibrium with marine environment. In this condition, we can neglect the gradient of mercury content and obtain the following equations:

$$\frac{dPHg_i^{II}}{dt} = 0 \Rightarrow PHg_i^{II} = (W_{phy_i} \cdot k_{phy,up_i} \cdot Hg^{II})/(k_{phy,exc_i} + k_{phy,gro_i})$$

The same equations can be used to estimate the quantity of methyl-mercury absorbed by phytoplankton cells.

Simulations

- An ENSIN prototype has been developed in C and Matlab.
- 3 simulation scenarios considered.
- Grid-based ENSIN solutions are interpolated to obtain approximately continuous quantities.

Table: Grid-based solutions

THg_{sed}	THg	DHg	MMHg	HgII	SPM	HgIIpw	MMHgpw
2%	Link	Link	Link	Link	Link	Link	Link
3%	Link	Link	Link	Link	Link	Link	Link
5%	Link	Link	Link	Link	Link	Link	Link

Table: Continuous solutions

THg_{sed}	THg	DHg	MMHg	HgII	SPM	HgIIpw	MMHgpw
2%	Link	Link	Link	Link	Link	Link	Link
3%	Link	Link	Link	Link	Link	Link	Link
5%	Link	Link	Link	Link	Link	Link	Link

Simulations

- An ENSIN prototype has been developed in C and Matlab.
- 3 simulation scenarios considered.
- Grid-based ENSIN solutions are interpolated to obtain approximately continuous quantities.

Table: Grid-based fluxes

THg_{sed}	FluxHgIIsed	FluxMMHgsed
2%	Link	Link
3%	Link	Link
5%	Link	Link

Table: Continuous fluxes

THg_{sed}	FluxHgIIsed	FluxMMHgsed
2%	Link	Link
3%	Link	Link
5%	Link	Link

Future work

- Model improvements
- Uncertainty quantification
  - Parameter estimation
  - Prediction reliability
- Finalization of toxicant species of interest
- Modeling toxicant exposure distribution via food
- Development of CISAS modeling webservices
- Connection environment $\rightarrow$ health

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