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Modelling Environmental Fate and Transport of POPs and Metals using the Fugacity/Aquivalence approach: Two Aquatic Environments as a Case Study

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Abstract

Multimedia environmental modelling is an useful tool to integrate the information necessary for the understanding of the mechanisms that drive the functioning of a complex system and to simulate its response to both natural and anthropogenic changes. The fundamental concept is that any chemical introduced into the environment is distributed between the components of the ecosystem according to its chemical-physical properties and those of each compartment. Fugacity (for the organics) and aquivalence (for non volatile chemicals) are used as equilibrium criteria. In this paper examples of multimedia modelling in two aquatic environments are shown. In the first case a pre-assembled level III fugacity model was used to screen the fate of PCB-118 in Lake Maggiore, using literature data. In the second example, the model was adapted to the Venice Lagoon accounting for spatial differences and water circulation. Modelled chemicals were octachlorodibenzodioxin/furan (OCDD and OCDF), PCB-180, Pb and Cu. The results described fairly well the fate of these chemicals in term of dominant processes, source apportionment and losses from the system. However, the available dataset for the Venice Lagoon is still not enough for a complete validation of the model. Consequently, the collection of field data on the key processes that drive contaminant variability is fundamental in order to extend its use as a decision supporting tool.

1 Introduction

Persistent organic pollutants and metals in aquatic environments are chemicals of concern due to their potential to negatively impact aquatic organisms and then humans. Over the past century industrial activities have contaminated many valuable coastal ecosystems. Moreover, due to the growth of the population, cities are becoming bigger and bigger, progressively incorporating the surrounding rural areas. These megacities require and use enormous amounts of energy and materials, metabolizing them and generating large quantities of waste products and pollutants, thus resulting in unsustainable conditions that adversely affect ecological integrity and diversity, human health and well-being.

In order to manage contaminants in the environment, it is important to identify and quantify their sources, transport mechanisms and fate. This can be achieved through the integration of measurements

and the use of models. The advantage of models is that they assemble a wide array of information into a common framework. Furthermore, models allow determining process rates that are difficult to measure and permit the simulation of future scenarios for the assessment of the environmental response to natural or anthropogenic influences, such as new or reduced contaminant inputs, and climate changes. In this way, models will assist decision-makers in system management. They will also be useful tools for the orientation of further research and the results will be fundamental for the design of monitoring programmes that can provide the highest number of essential information with the minimum cost.

At present, Multimedia Models represent the most used instruments, thanks to their applicability to every type of environment and the capability to integrate and quantitatively describe different processes within and between compartments. The fundamental concept of multimedia modelling is that any chemical introduced into the environment is distributed between the various components of the ecosystem (e.g., air, water, soil, sediments, biota, etc.) according to its chemical-physical properties and those of each compartment.

Mackay et al. [1] introduced a family of multimedia, mass balance models that use fugacity as an equilibrium criterion. Fugacity, which accounts for the escaping tendency, has units of pressure (Pa) and can be viewed as the partial pressure that a chemical exerts as it attempts to escape from one phase to another. When equilibrium is achieved, the chemical will have the same fugacity in all phases. At environmental (low) concentrations, fugacity is linearly related to chemical concentration through the "fugacity capacity" Z, which expresses the capacity of a phase, or environmental medium, to hold a chemical. The largest is Z, the largest is the quantity of chemical that can be stored in a phase. The fugacity approach is suitable for not highly reactive organic compounds with a measurable vapour pressure.

The integrated models developed so far are unique for their applicability to many contaminants and their linkage of chemical loadings to potential health effects to human and ecosystem receptors. The current state of model development is summarized below.

1. Fate Model. The fate model component is based on the QWASI (Quantitative Water Air Sediment Interaction) model [1]. Over the years the models were extensively adapted, as described below:
    i. to take into consideration both volatile (hydrophobic organics) and non-volatile (metals) chemicals, [2] introduced the "aquivalence" formulation. Aquivalence (i.e. equivalent aqueous concentration, set as 1.00 for water) is analogous to fugacity as an equilibrium criterion, and Z values can be derived;
    ii. to model metals that exist as multiple, interconverting species, [3, 4] expanded the aquivalence formulation to assess the fraction of chemical species in each phase.
    iii. the multispecies model has been loosely coupled with a speciation/complexation model to create a connected TRANsport-SPECiation model [5]. This model (TRANSPEC) allows estimation of metal speciation in the aqueous phase (including binding

to DOC in the colloidal phase) and complexation to solids that is governed by binding with Fe oxyhydroxides. In this way, [5] coupled MINEQL+ [6] with the multispecies aquivalence fate model to estimate the fate of Zn in a contaminated lake. The coupled model has also been applied to estimate the fate of Hg in a reservoir [7].

2. Food Web Model. The models of [8, 9] use the fugacity approach to estimate the uptake and transfer of hydrophobic organic contaminants in aquatic food webs. The food web model was applied in Lake Ontario [10], Lake Winnipeg [11] and Lake Ellasjoen (Bear Island, Norway, [12]).
3. Risk Assessment. A general risk assessment framework, applicable to ecosystem and human receptors, was developed [13, 14]. The approach is suitable for chronic exposure to low contaminant levels over the life-time. For ecological risk assessment, the method considers a first tier assessment that compares modelled contaminant concentrations in water and/or sediment with toxicological benchmarks for these media (e.g., [15, 16]. The second tier considers specific organisms and their intake rates of contaminants. The total daily intake (TDI), set for people, is then compared to suitable toxicological benchmark doses to obtain a hazard quotient.
4. Multimedia Urban Model (MUM). It was implemented by [17, 18] to describe the transport and fate of chemicals in urban areas. In addition to air, water, sediment, soil and vegetation compartments, the MUM takes into consideration the organic film that covers impervious surfaces (building walls, windows, streets, etc.) and enhance the mobility of chemicals through the wash off processes.

Despite its many advantages, an extensive modelling may be expensive because it requires a suitable amount of input data and a high degree of expertise, especially in the calibration and validation steps. Else, the uncertainty associated to complex models may be particularly high, and in most cases the simplest approach (identification of source-to-sink pathways) is commonly used. In this paper examples of application of fugacity multimedia models are presented for two aquatic environments that have both experienced strong anthropogenic pressures in the last decades. In the first case the level III QWASI model of [1] was applied as screening tool for the fate of PCB-118 in Lake Maggiore, whereas in the second one a more extended approach was adapted to the Venice Lagoon to assess the fate of various chemicals.

2 Methodological approach

The Level III Quantitative Water Air Sediment Interaction or QWASI model of [1], as modified by [19], which represents an aquatic environment with three well-mixed homogeneous bulk compartments (water, upper sediment layer and lower sediment layer, Figure 1), was used. Dissolved and particulate phases (e.g. suspended sediment and sediment pore water) are in equilibrium within each bulk compartment. The atmosphere is considered as an infinite source to the system with a constant con-

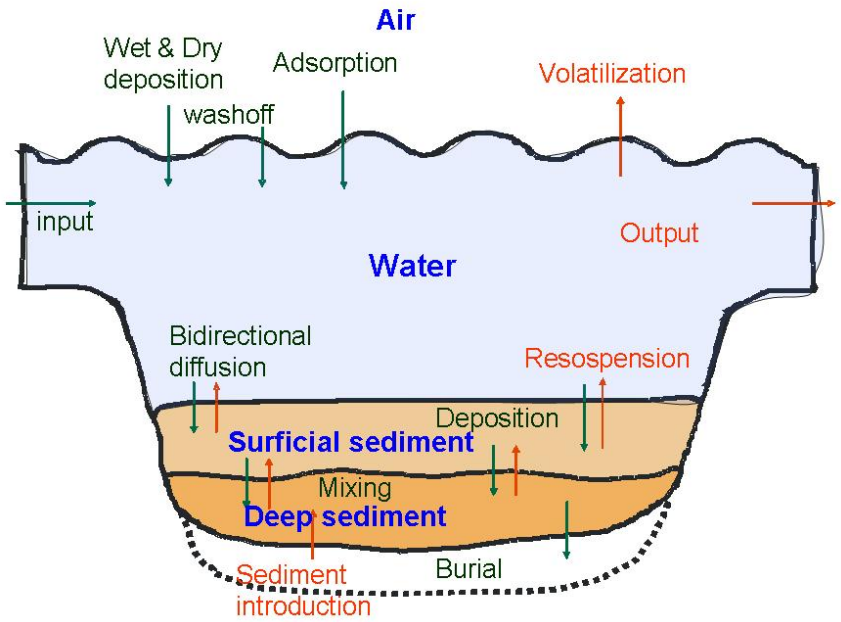

Figure 1: Diagram showing compartment and processes considered in the QWASI model. Input to the system are shown in green, whereas outputs are reported in red.

centration. Figure 1 summarizes all the inter media transport processes (both diffusive and advective) taken into account for the model formulation.

The model consists of a set of equations (Table 1) that define the Z values for each compartment of Figure 1, including both dissolved and particulate phases.

All transport processes are expressed in common mathematical terms as D values (mol $Pa^{-1}h^{-1}$), defined as:

$$D = GZ = kAZ$$

where G (m^3h^{-1}) is the flow rate of a medium (e.g., air, water, suspended particles), k(m h^{-1}) is a mass transfer coefficient, and A($m^{2)}$ is the area across which the chemical mass transfer is occurring. The rate of inter-media transport (molh^{-1}) is thus:

$$N = Df = GC$$

A mass balance equation is written for each compartment to represent the change in chemical mass with time. All input and removal pathways are assumed to occur simultaneously and instantaneously once a contaminant enters the system. The general mass balance equation for compartment b and chemical j is:

$$V_b Z_b \frac{df_{bj}}{dt} = E_{bj} + \sum(D_{abj} f_{aj}) - f_{bj} \sum D_{bj}, \quad (1)$$

where V_b (m^3) is the volume of compartment b, f_{aj} is the fugacity (Pa) of chem-

ical j in compartment a, Z is the fugacity capacity for organics ($molm^{-3}Pa^{-1}$), E_{bj} ($molm^{-3}$) is the direct emission, Dabj ($molPa^{-1}{\cdot}m^{-3}$) is the transport rate moving chemical j from compartment a to b, and Dbj is the transport rate removing chemical j from compartment b. For metals, fugacity is replaced with aquivalence [2] in Equation 1.

In order to account for metal chemistry in each phase, the speciation-complexation model TRANSPEC [5] calculates two system- and species-specific values of distribution coefficients K_ds: K_{dCD} (colloidal-to-dissolved phases) and K_{dPD} (particulate-to-dissolved phases) for both total metal and its species, based on ambient aqueous phase chemistry. K_ds are used to calculate constituent species' Z values required for the weighted averaged bulk Z used in the fate and transport model [3].

3 Model Application to Lake Maggiore

The original QWASI model [1, 20] was applied under steady-state conditions as a simple exercise to describe the fate of 2,3',4,4',5-Pentachlorobiphenyl (PCB-118 according to IUPAC nomenclature), a "dioxin like" congener included also in the seven PCB indicator set (EFSA, 2005). The model software is freely available at the Canadian Environmental Modelling Centre website (CEMC, 2007).

The lake was considered as a whole and its environmental characteristics were taken from [21] and references therein. They were: lake proprieties (lake dimension, concentration and density of solids in the environmental compartments, organic carbon fractions of solids), water and sediment flows, atmospheric deposition parameters and mass transfer coefficients for diffusive transports. The physical-chemical proprieties of PCB-118 (water solubility, vapour pressure, melting point, log K_{ow}) were determined through the EPISUITE tool developed by the US Environmental Protection Agency's office for Pollution Prevention and Toxic and Syracuse Research Corporation (USEPA 2009). An emission of 2 $kg{\cdot}y^{-1}$ is assumed to be supplied to the lake, whereas the concentration in inflow water was considered as low as 4 pg L^{-1}. A bulk atmospheric PCB-118 concentration of 6.83 x $10^{-3}ngm^{-3}$, determined by Castro Jìmenez et al. [22] as averaged sum of measured gaseous and aerosol bound concentrations in the Ispra area of Lake Maggiore, was considered as model input. Any removal through degradation was assumed negligible.

Model output includes: chemical inputs to the system, Z and D values, fugacities, concentrations and amounts of chemical in each compartment, mass balances and residence times and details of process rates in a summary diagram. In particular, Figure 2 summarizes the transport processes and the resulting environmental fate of PCB-118 in the compartments of the lake.

The modelled surficial sediment concentration (3.44 ngg^{-1}) is close to the average PCB-118 surficial value in the Ispra Bay, determined by [22].

The residence time of PCB -118 in the system resulted 2.66 years.

This example shows the ability of a simple multimedia fate model to represent the fate and main processes of a chemical in an aquatic system, when its proprieties are well known and processes are properly parameterized. This allows to estimate the ranges of concentration in media (i.e. water

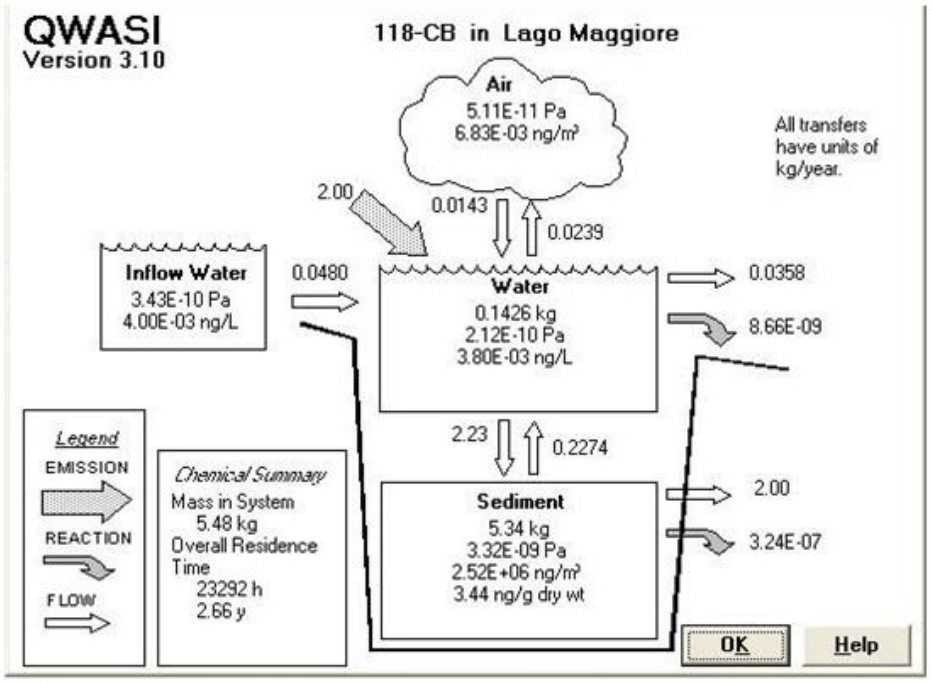

Figure 2: Diagram showing concentration of PCB-118 in air, water and sediment compartments in Lake Maggiore and resulting transport processes: water inflow, wet and dry deposition, rain dissolution, adsorption, volatilization, sediment deposition, resupension, diffusion, burial, emission to water, water outflow. Reaction rates in water and sediment are assumed as negligible.

and sediment) varying the direct emission and the water inflow, and thus to formulate previsions on the response of the system in terms of changing loadings.

4 Model Application to the Venice Lagoon

After a first attempt by [23] a multi media model of the Venice Lagoon has been implemented, while the parametric uncertainty was assessed through a Monte Carlo analysis. Here a summary of model formulation and achieved results is reported, whereas further details are available in [24, 25].

The model was applied to octachlorodibenzodioxin/furan (OCDD and OCDF), 2,2',3,4,4',5,5'-Heptachlorobiphenyl (PCB-180 according to IUPAC nomenclature), Pb and Cu to evaluate their behaviour and fate.

The lagoon was segmented into 10 areas (Figure **??**) according to the analysis of [26] who used a 2-dimensional finite element hydrodynamic model based on the

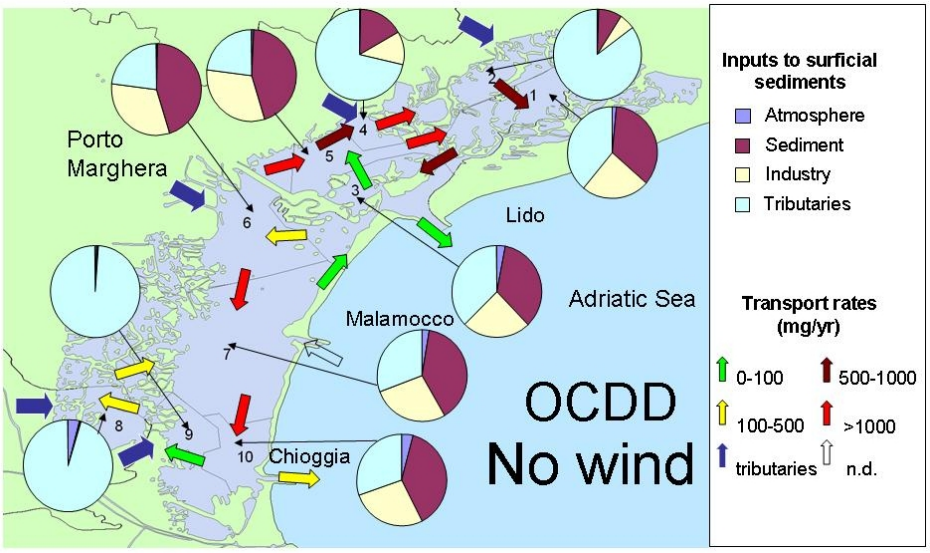

Figure 3: Output of the model showing the ten basins of the Venice lagoon, the direction of the net water movement and the magnitude of OCDD transport rates. The relative importance of OCDD loadings to surficial sediment is also shown.

spatial distribution of physical properties (salinity and water residence time) and other water quality parameters. The circulation patterns and net flow estimates from the reference scenario of "no wind", which reflects steady-state hydrologic conditions in the system, were first chosen, assuming mean annual tributary flows and an idealized sinusoidal M2 tide levels at inlets that force water circulation. To account for sediment loss in the central basin of the Lagoon, two additional transport pathways were included in the QWASI model (Figure 1): i) a sediment introduction term defined as the addition of sediment from the lowest sediment compartment into the subsurficial layer and ii) an upward transfer term that moves sediment from the lower to the upper sediment layer.

Compartment specific versions of Equation 1 are solved assuming steady-state or pseudo-steady state. The first approximation is used to represent average long term conditions. The pseudo-steady-state approach, in which the fugacity/aquivalence of the lower sediment layer was specified, is used for in-place pollution where sediment concentrations are not at steady state with respect to current loadings [27].

Our model considers inputs to the lagoon from tributaries, discharges from the industrial area of Porto Marghera, contributions from historically contaminated sediments and atmospheric deposition. Tributary inputs of dissolved and particulate phases of Pb, Cu and PCB-180 were obtained from [28]. Industrial loadings were calculated as the difference between contents in water entering and exiting a facility annually. As far as the contribution of in-place pollution

is concerned, fugacity/aquivalence of the lower sediment (3-20 cm) was calculated from the geometric mean of the measured concentrations from three sediment cores [29, 30]. Bulk atmospheric deposition of PCBs and PCDD/Fs were modelled using direct gas-phase measurements [31]. Metal deposition was calculated from measured PM10 concentration. Atmospheric stack emissions were not explicitly taken into account in the model. The model was written in Visual Basic and runs on a PC in a Windows© environment.

4.1 Model evaluation

We evaluated the model by comparing measured and modelled concentrations for soluble (dissolved and colloidal phases) Pb and Cu in the water column and Pb, Cu, OCDD/F and PCB-180 concentrations in the upper sediment.
Measured and modelled concentrations of all contaminants in water and sediment were within an order-of-magnitude of each other. Among all contributions, industrial loadings of PCB-180 and other contaminants are probably most uncertain. To evaluate the reliability of PCB-180 inputs, several industrial loading scenarios were analyzed. The fraction of industrial emissions retained by the sediment of the industrial canals was estimated by running the model with export fractions varying from 0 to 1, while keeping all other loadings constant. The best fit with measured values corresponded to 10-20% industrial emissions suggesting that the transfer of PCB-180 as well as other contaminants from the canals to the lagoon might be overestimated in the model.

4.2 Source apportionment and contaminant fate

The source apportionment analysis reflected the location of loading sources and the dominant hydrologic circulation pattern of the Lagoon. 50% to 94% of total OCDD/F, PCB-180, Cu and Pb loadings enter the Lagoon in the central basin from industry and in-place pollution, followed by a significant contribution from tributaries. These loads circulate to the northern lagoon, with limited transport to the far southern lagoon. For example, 60 % of total OCDD loadings to basin 1 in the northern lagoon were from in-place pollution and present industrial sources originating from segment 6, whereas nearly 100 % of loadings in basin 9 in the southern lagoon were from tributaries (Figure 3).
Despite $\sim$75 % of Pb and Cu being in the soluble form (dissolved + colloidal phases), their fate, similar to that of OCDD/F and PCB-180, was mediated by particle dynamics (i.e., sediment deposition and resuspension). Moreover, contaminants were lost through lower sediment burial in non-erosive segments.
Water circulation is the dominant contaminant removal pathway from the northern and central basins (22-79% for OCDD/F and PCB-180 56-98% for Cu and Pb). In contrast, removal from the southern basin was dominated by burial (12-70% for all contaminants) further limiting transfer from the central to the far southern lagoon and to the Adriatic Sea (Figure 3). Despite the dominance of export as a sediment removal pathway within the northern and central lagoon, total export of contaminants to the Adriatic Sea through the Lido, Malamocco and Chioggia inlets was minimal under the “no wind” scenario. Less than 19% of total Pb and Cu loadings

and less than 2% of total PCB-180 and OCDD/F loadings were exported from the Venice Lagoon to the Adriatic Sea (Figure 3).
Our estimates of annual export rates to the Adriatic Sea, however, likely underestimated actual losses because episodic flooding events in the lagoon were not included in our model parameterization. Ultimately, we found that although substantial sediment-water exchange occurs, net contaminant loss from the Venice Lagoon was through burial, resulting in a high persistence of contaminants in the system.
As a further exercise, the model has been improved considering the two recurring winds in the area: 1) scirocco, a warm wind from SE, blowing year-round, responsible of flooding ("acqua alta") events in Venice (esp. in fall-winter); 2) bora, a strong (up to 30 m s^{-1}), cold NE wind blowing up to 40 day y^{-1} (esp. in winter). The model has been parameterized in the same way as the "no wind" scenario but changing the water circulation according to [26, 32].
Preliminary results shows that, under scirocco wind, deposition/resuspension processes are the main responsible of the spreading of the lagoon contaminants from the industrial area and burial is an important removal mechanism. Bora, in turn, may act as a "cleaning mechanism" for the lagoon by increasing export to the Adriatic sea. In fact the residence time of all the modelled contaminants resulted to be the lowest in this scenario.

4.3 Uncertainty examination

The more complex they are, models are indeed simplifications of reality and as such are inherently uncertain. Model uncertainty derives from both structural and parametric uncertainty. The former not only reflects the inability to capture all the essential components of the real system, but also the difficulty to express them in an unequivocal manner. On the other hand, parametric uncertainty stems from the analytical errors, the imprecision of measurements as well as spatio-temporal parameter variability. This latter source of uncertainty is of particular importance in fate and transport modelling in which the relative effects of individual parameters on model predictions are not well understood and can be contaminant-specific. In this regard, scientific knowledge, expert judgment, and observational data were used to formulate probability distributions and characterize the uncertainty of environmental parameters used in the model applied to the Venice Lagoon. Details of the procedure of uncertainty analysis are presented by [25].
Our analysis demonstrates that the range of model output distributions can vary up to an order of magnitude exhibiting both contaminant and site-specific variability. Generally, we found that the uncertainty of the contaminant concentrations in the Venice Lagoon is characterized by two modes of spatial variability (i.e., the northern and central parts of the Lagoon, and the more isolated southern basin) mainly driven by the local hydrodynamics.
Moreover we also found that the interplay among the in-place pollution in the central Lagoon and sediment burial rates drove the spatial heterogeneity of bulk water and upper sediment concentrations as well as total suspended solids (TSS) concentration.

5 Conclusions

In conclusion these models, developed in a user-friendly environment, are simple and

useful tools for environmental studies of complex systems, where direct measurements of process velocity and concentrations in specific compartments are difficult or too expensive. Moreover, they can also be used in decision-making processes, like risk assessment and regulation. In these latter cases model validation becomes important. However, environmental models can not be validated in the same sense as models of highly reproducible closed systems. Credibility can be improved by using examples in which observed and predicted concentrations are compared, as single values or ranges with identification of dominant sources, fate processes, or partitioning characteristics. Consequently, the numerical output of these models is dependent on the amount of available data.

In case of the Venice Lagoon, despite the large number of studies, the dataset is still not enough for a complete validation of the model, thus the model output, in term of "numbers" should be used with care.

In particular, the uncertainty analysis distinguished between parametric and structural uncertainty. While the former is associated primarily to model parameters that drive the spatial variability of the lagoon, the latter resulted in systematic predictive bias.

Thus, the collection of field data about the key processes that drive contaminant variability in the system and the formulation of well-defined prior distributions for the corresponding parameters is a goal that will assist the calibration and validation of this model. This may be particular important for a proper management of the mobile gates (MOSE) in order to predict the environmental effects after repeated closures.

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Compartment	Z value	Equation
Air	Z_Air	1/(R*Temp)
Aerosol	Z_Aerosol	Kqa*Z_Air
Interface	Z_Interface	Kia*Z_Air
Water	Z_Wat	1/HLC
Suspended Sediment	Z_SusSed	Z_Wat*Den_SusSed*Koc*OC_SusSed/Den_Wat
Upper Sediment	Z_USed	Z_Wat*Den_Sed*Koc*OC_USed/Den_Wat
Lower Sediment	Z_LSed	Z_Wat*Den_Sed*Koc*OC_LSed/Den_Wat
Bulk Air	Z_Bulk_Air	Z_Air + (Z_Aeroaol*Vol_Fr_Aerosol)
Bulk Water	Z_Bulk_Wat	Z_Wat* (1 - Vol_Fr_SS_Wat) + Z_SusSed*Vol_Fr_SS_Wat
Bulk Upper Sediment	Z_Bulk_USed	Z_Wat* (1 - Vol_Fr_Used_Solid) + Z_USed*Vol_Fr_Used_Solid
Bulk Lower Sediment	Z_Bulk_LSed	Z_Wat* (1 - Vol_Fr_Lsed_Solid) + Z_USed*Vol_Fr_Lsed_Solid

R = ideal gas constant = 8.314472 m^3 Pa K^{-1} mol^{-1}
Temp = Absolute temperature (K)
K is a partition coefficient
HLC = Henry's Law Constant (Pa m^3 mol^{-1})
Den is density, Wat is water, SS stand for suspended solid
Vol_Fr stands for volume fraction

Table 1: Definitions of Z values for organics (for metals Z is derived by aquivalence) for each environmental compartments.

References

[1] D. Mackay, S. Paterson, and M. Joy. A quantitative water, air, sediment interaction (QWASI) fugacity model for describing the fate of chemicals in water. *Chemosphere*, 12:1193–1208, 1983.

[2] D. Mackay and M.L. Diamond. Application of the QWASI (Quantitative Water Air Sediment Interaction) fugacity model to the dynamics of organic and inorganic chemicals in lakes. *Chemosphere*, 18:1343–1365, 1989.

[3] M.L. Diamond, D. Mackay, and P.M. Welbourn. Models of multi-media partitioning of multi-species chemicals: the fugacity/aquivalence approach. *Chemosphere*, 25:1907–1921, 1992.

[4] M.L. Diamond, M. Ganapathy, S. Peterson, and C. Mach. Mercury dynamics in the Lahontan Reservoir, Nevada: application of the QWASI fugacity/aquivalence multispecies model. *Water Air and Soil Pollution*, 117:133–156, 2000.

[5] S.P. Bhavsar, M.L Diamond, L.J. Evans, N. Gandhi, J. Nilsen, and P. Antunes. Development of a coupled metal speciation-fate model for surface aquatic systems. *Environmental Toxicology and Chemistry*, 23:1376–1385, 2004.

[6] W.D. Schecher and D.C. McAvoy. MINEQL+ A chemical equilibrium modelling system, Version 4.0 for windows, user's manual. 1998.

[7] N. Gandhi, S.P. Bhavsar, M.L. Diamond, J.S. Kuwabara, M.M. Di Pasquale, and D.P. Krabbenhoft. Development of a mercury speciation, fate, and biotic uptake (BIOTRANSPEC) model: application to Lahontan reservoir (Nevada, USA). *Environmental Toxicology and Chemistry*, 26(11):2260–2273, 2007.

[8] J. Campfens and D. Mackay. Fugacity-based model of PCB bioaccumulation in complex aquatic food webs. *Environmental Science and Technology*, 31(2):577–583, 1997.

[9] F.A.P. Gobas and H.A. Morrison. Bioconcentration and biomagnification in the aquatic environment. pages 189–231, 2000.

[10] F.A.P. Gobas, M.N. Z'Graggen, and X. Zhang. Time response of the Lake Ontario ecosystem to virtual elimination of PCBs. *Environmental Science and Technology*, 29:2038–2046, 1995.

[11] S.B. Gewurtz, N. Gandhi, G.A. Stern, W.G. Franzin, B. Rosenberg, and M.L. Diamond. Dynamics of PCBs in the Food Web of Lake Winnipeg. *Journal of Great Lakes Research*, 32(4):712–727, 2006.

[12] N. Gandhi, S.P. Bhavsar, S.B. Gewurtz, M.L. Diamond, A. Evenset, G.N. Christensen, and D. Gregor. Development of a Multichemical Food Web Model: Application to PBDEs in Lake Ellasjoen, Bear Island, Norway. *Environmental Science and Technology*, 40(15):4714–4721, 2006.

[13] J.A. Archbold. Development of a screening ecological risk assessment model and its coupling with the Multimedia Urban Model. *M.Sc. Thesis. Department of Geography, University of Toronto*, 2003.

[14] J.A. Archbold, H. Hull, and M.L. Diamond. Potential importance of inhalation exposures for wildlife using screening-level ecological risk assessment. *Human and Ecological Risk Assessment*, 13(4):870–883, 2007.

[15] D.S. Jones, G.W. Suter, and R.N Hull. Toxicological benchmarks for screening contaminants of potential concern for effects on sediment-associated biota: 1997 Revision. 1997.

[16] B.E. Sample, D.M. Opresko, and D.W. Suter. Toxicological benchmarks for wildlife: 1996 Revision. 1996.

[17] M.L. Diamond, D.A. Priemer, and N.L. Law. Developing a multimedia model of chemical dynamics in an urban area. *Chemosphere*, 47:1655–1667, 2001.

[18] D.A. Priemer and M.L. Diamond. Application of the Multimedia Urban Model To Compare the Fate of SOCs in an Urban and Forested Watershed. *Environmental Science and Technology*, 36:1004–1013, 2002.

[19] M.L. Diamond. Development of a fugacity/aquivalence model of mercury dynamics in lakes. *Water Air and Soil Pollution*, 111:337–357, 1999.

[20] D. Mackay. Multimedia environmental models: The fugacity approach. 2001.

[21] A. Di Guardo, C. Ferrari, and A. Infantino. Development of a Dynamic Aquatic Model (DynA Model): Estimating Temporal Emissions of DDT to Lake Maggiore (N. Italy). *Environmental Science and Pollution Research*, 13(1):50–58, 2006.

[22] J. Castro-Jimenez, G. Mariani, S.J.Eisenreich, E.H. Christoph, G. Hanke, E. Canuti, H. Skejo, and G. Umlauf. Atmospheric input of POPs into Lake Maggiore (Northern Italy): PCDD/F and dioxin-like PCB profiles and fluxes in the atmosphere and aquatic system. *Chemosphere*, 73:S122–S130, 2008.

[23] M. Dalla Valle, A. Marcomini, A. Sfriso, A.J. Sweetman, and K.C. Jones. Estimation of PCDD/F distribution and fluxes in the Venice Lagoon, Italy: Combining measurement and modelling approaches. *Chemosphere*, 51:603–616, 2003.

[24] J.K. Sommerfreund, N. Gandhi, M.L. Diamond, C. Mugnai, M. Frignani, G. Capodaglio, M. Gerino, L.G. Bellucci, and S. Giuliani. Contaminant fate and transport in the Venice Lagoon: Results from a multi-segment multimedia model. *Ecotoxicology and Environmental Safety*, 73:222–230, 2010.

[25] J.K. Sommerfreund, G.B. Arhonditsis, M.L. Diamond, M. Frignani, G. Capodaglio, M. Gerino, L.G. Bellucci, S. Giuliani, and C. Mugnai. Examination of the uncertainty in contaminant fate and transport modelling: A case study in the Venice Lagoon. *Ecotoxicology and Environmental Safety*, 73:231–239, 2010.

[26] C. Solidoro, D. Melaku Canu, A. Cucco, and G. Umgiesser. A partition of the Venice Lagoon based on physical properties and analysis of general circulation. *Journal of Marine System*, 51:147–160, 2004.

[27] M.L. Diamond. Application of a mass balance model to assess in-place arsenic pollution. *Environmental Science and Technology*, 28:29–42, 1995.

[28] F. Collavini, C. Bettiol, L. Zaggia, and R. Zonta. Pollutant loads from the drainage basin to the Venice Lagoon (Italy). *Environment International*, 31:939–947, 2005.

[29] M. Frignani, L.G. Bellucci, C. Carraro, and S. Raccanelli. Polychlorinated biphenyls in sediments of the Venice Lagoon. *Chemosphere*, 43:567–575, 2001.

[30] M. Frignani, L.G. Bellucci andC. Carraro, and M. Favotto. Accumulation of polychlorinated biphenyls in sediments of the Venice Lagoon and the industrial area of Porto Marghera. *Chemosphere*, 54:1563–1572, 2004.

[31] A. Gambaro, L. Manodori, I. Moret, G. Capodaglio, and P. Cescon. Determination of polychlorobiphenyls and polycyclic aromatic hydrocarbons in the atmospheric aerosol of the Venice Lagoon. *Analytical and Bioanalytical Chemistry*, 378:1806–1814, 2004.

[32] A. Cucco and G. Umgiesser. Modeling the Venice Lagoon residence time. *Ecological Modelling*, 193:34–51, 2006.