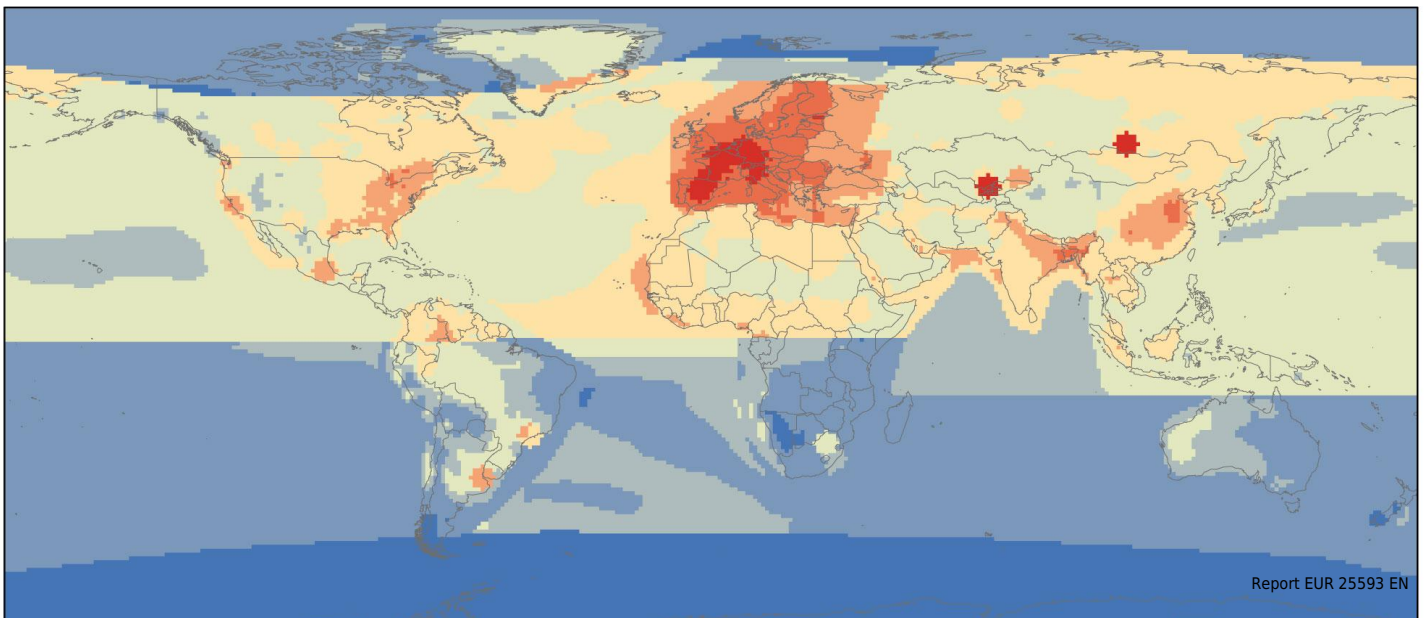# Assessment of Persistent Organic Pollutants load to marine environment by MAPPE-Global model focusing on European regional seas

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In memory of José Manuel Zaldivar Comenges

who inspired us in the environmental modelling

Executive summary

Multimedia mass-balance models are established as scientific and decision-support tools for understanding the behavior of chemical pollutants in the environment. The assessment of POPs load to seas at continental scale is typically performed on the basis of GIS multimedia fate and transport models. These models use data of pollutants' emissions to different environmental media and convert them into predicted concentrations, fluxes and loads using the physico-chemical properties of substances and georeferenced data for landscape and environmental parameters.

MAPPE-Global modeling tool, presented in this work, belongs to the group of the global box models for environmental fate of POPs. This is an explicit GIS model which considers four environmental compartments: atmospheric boundary layer; land; surface water (including rivers and lakes); and oceans/seas world with a resolution of 1^ox1^o for air and oceans and $0.08°$ x $0.08°$ for soil and surface water. Additionally, the land compartment is divided in four categories: soil (agricultural or natural), impervious surfaces (urban or sealed soil), deserts or permanently frozen soils, and forest (split in three sub-categories: deciduous, evergreen broadleaves and evergreen conifers). In MAPPE-Global, each environmental compartment is structured in physical phases (gas, liquid, solid). Accordingly, the fluxes between environmental compartments are composed of a solid, liquid and gas phase. Within each medium, a steady state is assumed so that concentrations between different phases are univocally related through appropriate partition coefficients.

The objectives of this work are twofold:

- to improve performance of MAPPE Global model through developing a simple procedure able to take into account the regional, continental or trans-continental advection transport;

- to assess current and future loads to European regional seas, up to the time horizon of the year 2020, for selected priority or emergency pollutants based on the available pollutants emission inventories.

Potentially the outcome of the present improved version of MAPPE-Global could serve in the assessments of different policy options related to the EU Water Framework Directive (WFD) or Marine Strategy Framework Directive (MSFD) as well as to support the implementation of the European sea conventions as HELCOM (Baltic Sea) (http://www.helcom.fi/), OSPAR (North-East Atlantic) (http://www.ospar.org/), MEDPOL (Mediterranean Sea) (http://www.medpol.unepmap.org/) and BSC (Black Sea) (http://www.blacksea-commission.org/main.asp).

The new developments of MAPPE-Global include, particularly for atmosphere, the quantification of the relocation of chemical masses exported outside of each grid cell as a proxy of diffusive or

advective transport, as well as the accounting of the eventual impact of the long range transcontinental transport in terms of globally "exported or imported" additional emissions. In addition, the present version of the model improves the surface water compartment by introducing a global map of travel times to sea which parameter was considered earlier as a fixed value for a given river basin. Besides, the soil-air gas exchange in the soil compartment was bettered by accounting differences in the global land cover. No further improvement is done in the marine part of the model.

In order to verify MAPPE-Global model, its performance was evaluated versus results of other models or estimates/measurements for sea load of contaminants. This was done qualitatively using EMEP results for global PCB153 distribution in air, soil and sea/ocean derived through the GLEMOS world model. Next, a precise quantitative comparison only for the European continent was done considering Lindane sea load data, EMEP measurement data and model results for air and soil concentrations and simulated data obtained by in-house MAPPE-Europe model.

The estimated error level of MAPPE-Global is about a factor of two which suggests that the model could be considered as a tool for a screening or initial evaluation of chemical risk for POPs at global scale.

The MAPPE-Global is applied in the practical assessments of the chemical loads to the European regional seas. Respecting the current availability of emission data we considered two case studies: the family of PCBs (industrial chemicals potential candidate as an EU priority substance) and the single congener of gamma-HCH (an insecticide banned for agricultural applications in the EU countries since 1995).

The PCBs case study relates to a sum of 22 congeners and considers two emission scenarios: first - the current status relative to the 2010 year; second – a future projection corresponding to the 2020 year. The total amount of 22PCBs released to air equals to 101.03 t for year 2010 and to 50.2 t for year 2020, respectively. The dominant polluters, in both years, are Russia, France and Germany.

The Baseline scenario for Lindane assumes, for the reference year 2005, 86.6 t atmospheric emissions only from European sources and omits the impact of the long range atmospheric transport. The second scenario for Lindane aims to targeting the situation in the year 2020. This scenario (denoted as LRT) suggests no emissions to atmosphere from any European origin due to the banning of this substance but admits that Europe is affected by an unavoidable 'import" of 5.4 t Lindane through trans-continental air transport.

In addition, aiming to ensure a finer model resolution, the model is run over a grid of 30 square km instead of working on the original 100 km resolution. For the same reason, it was restricted the planet computational domain only to the European continent and its surrounding area - Northern African

countries (up to Capricorn tropic), Asian countries around Mediterranean Sea (Turkey, Syria, Israel, Palestine, Lebanon, Jordan and parts of Iraq and Saudi Arabia) and Western Russia (up to the 45th meridian) plus Moldova, Ukraine, Belarus and part of Georgia.

According to the MAPPE-Global model, the extended European area is exporting to the marine water 3.7 t of 22PCBs in 2010 and 1.9 t in 2020, respectively. The observed reduction of 49% of the riverine load from year 2010 to year 2020 reflects the difference in the 22PCBs emissions. The riverine load represents about 4% of the total air emissions of 22PCBs. In both scenarios, the most affected seas are the Mediterranean Sea (ca.35% from the total) followed by Northern (ca. 21.5%) and Black sea (ca. 19%). It was estimated that the European seas will receive by atmospheric deposition about 7.9 t of 22PCBs in the 2010 and ca. 4t in the 2020. This is two times more when comparing to the entire riverine discharge of 22PCBs for these years.

MAPPE-Global forecasts 10.1 t riverine sea load of Lindane under the Baseline scenario and 0.26t in the case of LRT meaning 97% reduction compared to the baseline option. The riverine loads represent 11.7% and 5%, respectively, from the total annual air emissions of Lindane. The highest discharges are observed for Atlantic Ocean – in Baseline scenario 2.2t (21.8% from the total) and for LRT 0.06t (23%); and Mediterranean Sea - Baseline 3.5t (34.7%) and LRT 0.04t (15.4%). For the gamma-HCH, likewise for the PCBs, it was found that the atmospheric deposition over the European seas dominate the river input to the coastal zone. Under the Baseline scenario, the total air deposition (50.2t/y) is about 5 times higher than the riverine component of the sea load. However, in the case of LRT scenario, probably due to the very low amount of Lindane present in the atmosphere, the air deposition (in total 0.2 t/y) is equivalent to the riverine load of Lindane.

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1. Introduction

Multimedia mass-balance models are well-established as scientific and decision-support tools for understanding the behavior of chemical pollutants in the environment (MacLeod et al., 2010), particularly for the Persistent Organic Pollutants (POPs) (Wania and Mackay, 1999). These models were important in establishing the link between chemical emissions in industrialized regions and pollutants' presence at any location of the Earth including remote areas as the Arctic (MacLeod et al., 2011). Besides, the assessment of POPs load to seas at continental scale is typically performed on the basis of explicit GIS multimedia fate and transport models. These models use data of pollutants' emissions to different environmental media and convert them into predicted concentrations, fluxes and loads using substances' physico-chemical properties and landscape and environmental parameters data (Pistocchi, 2008; Pistocchi et al., 2010; Marinov et al, 2011).

For instance, the European spatially resolved geo-referenced **M**ultimedia **A**ssessment of **P**ollutant **P**athways in the **E**nvironment (MAPPE) fate and exposure model (Pistocchi, 2008) is applied in the case studies of Lindane (Vizcaino and Pistocchi, 2010), PCBs (Pistocchi et al, 2010b) and Trifluralin (Pistocchi et al., 2009). Other examples, based on modeling platforms similar to MAPPE-Europe, are BETR (Prevedouros et al, 2004), POPCYCLING-Baltic (Breivik and Wania, 2002) and MSCE-POP (Gusev et al., 2006; Gusev et al., 2009). These models are discussed in a benchmarking exercise related to a recent scenario analysis of priority chemicals load to European regional seas aimed to support the EU Marine Strategy Framework Directive and Water Framework Directive (Marinov et al., 2011).

However, apart being persistent, many POPs possess a considerable long range atmospheric transport potential, thus, they undertake practically a global distribution whatever their emission sources (single or multiple) are or wherever they happen. Therefore, in order to properly simulate the POPs environmental spreading, the development of Earth scale applications is needed.

Recent cases of global POPs box models include: Globo-POP (Wania and Mackay, 1995; Wania et al., 1999), long-range transport and multimedia partitioning of semivolatile organic compounds model (Lammel et al., 2001), BETR-World (Toose et al., 2004), BETR-Global (MacLeod et al., 2005), and Global EMEP Multi-media Modelling System - GLEMOS (Travnikov and Jonson, 2011) of the European Monitoring and Evaluation Programme (EMEP).

For example, BETR-Global multimedia contaminant fate model (MacLeod et al., 2005) has a latitudinal zone structure and describes the global environment on a 15° grid. The 2005 version of BETR Global was used to simulate the global fate and transport of PCBs (MacLeod et al., 2005), and the transport and deposition of a set of persistent organic substances to the North American Great

Lakes (MacLeod et al., 2004). A modified version of the model capable of simultaneously modeling the fate and transport of a weak acid and its conjugate base was developed to study the global mass balance and transport of perfluorinated acids (Armitage et al., 2009a, b). The model was recently used to analyze the global mass budget of PCBs and the effects of a climate change scenario on their steady-state global distribution (Lamon et al., 2009). Most recently, as part of the work of the Task Force on Hemispheric Transport of Air Pollutants, BETR Global has been applied to quantify intercontinental source receptor relationships for persistent organic pollutants in support of the Convention on Long-range Trans-boundary Air Pollution (CLRTAP) (Gusev et al., 2010).

EMEP also continues the development of global scale modeling tools i.e. GLEMOS (Travnikov and Jonson, 2011). This simulation framework is aimed to provide effective means for multi-scale simulations of the environment pollution with various contaminants. Application of the framework on a global scale allows assessing intercontinental transport of long-lived pollutants and its contribution to pollution levels in the EMEP region. The key feature of GLEMOS is the modular architecture providing a flexible approach to multi-pollutant and multi-media simulations. The latter are important in studying of long-term cycle and accumulation of substances as mercury and POPs.

Apart of the world scale POPs box models, referred above, the Life Cycle Assessment studies for toxicity characterization widely used similar but simplified global models for quantification of chemicals exposure (not only POPs) as: USES-LCA (Huijbregts et al., 2000; Van Zelm et al., 2009), CalTOX (Hertwich et al., 2001), IMPACT 2002 (Pennington et al., 2005), IMPACT North America (Humbert et al., 2009), USEtox (Rosenbaum et al., 2008) and GLOBOX (Sleeswijk and Heijungs, 2010).

In addition, aiming to overcome the limitation of box-type models, fully 3-D dynamical models have been developed to describe the atmospheric transport of POPs on regional (Ma et al., 2003), hemispheric (MCSE-POP, Gusev et al., 2005) and global scales (Semeena et al., 2006 and GEM/POPs, Gong et al., 2007). The model simulations include industrial chemicals as Polychlorinated biphenyls (PCBs), the organochlorine insecticides, e.g. Dichlorodiphenyltrichloroethanes (DDTs), and the Polyhalogenated compounds, some being pesticides as Hexachlorocyclohexanes (HCHs).

The modeling tool presented in this work, MAPPE-Global, belongs to the group of the global POPs box models. MAPPE-Global is a worldwide explicit GIS model for multimedia fate of POPs which considers the four environmental compartments: atmospheric boundary layer; land; surface water (including rivers, lakes and reservoirs); ocean and seas (Pistocchi et al., 2011b). Additionally, the land compartment is divided in four categories: soil (agricultural or natural), impervious surfaces (urban or sealed soil), deserts or permanently frozen soils, and forest (in turn split in three sub-categories:

deciduous, evergreen broadleaves and evergreen conifers). These categories are represented through a covering percentage of the surface area of each computational cell. In MAPPE-Global each environmental compartment is structured in physical phases (gas, liquid, solid). Accordingly, the fluxes between environmental compartments are composed of a solid, liquid and gas phase. Within each medium, a steady state is assumed so that concentrations between different phases are univocally related through appropriate partition coefficients.

Since a detailed description of MAPPE-Global is already provided in Pistocchi et al. (2011b), in this report we will remind only the basic model features and focus on the model enhancement, based on a simple "advection" concept used to improve the model outcome by bettering the estimates of chemical concentrations, fluxes and load to seas. Then, after the model verification, the MAPPE-Global shall be used in several applications in order to estimate chemicals load to the European seas in terms of riverine discharge and atmospheric deposition.

Thus, the objective of work is twofold:

- to improve performance of MAPPE Global model through developing a simple procedure able to take into account the regional, continental or trans-continental advection transport;

- to assess current and future loads to European regional seas, up to the time horizon of the year 2020, for selected priority or emergency pollutants with available emission inventories or by developing policy oriented emission scenarios.

2. Improvement of MAPPE-Global model

The first version of MAPPE-Global (Pistocchi et al., 2011b) computes only removal rates for a chemical substance with given physical-chemical properties in an evaluative environment for the entire world with a resolution of $1^{o}x1^{o}$ for air and oceans and $0.08° x 0.08°$ for soil and surface water. The model considers three major types of chemicals fate processes: degradation; vertical and horizontal transport; and diffusive transport.

In MAPPE-Global the chemical degradation, which may be due to a number of biological, physical or chemical processes as photolysis, hydrolysis, chemical and biological transformation, is assumed to follow a simple linear law, i.e. it is sufficiently well described by the chemical half-life. The half-lives may spatially vary according to a number of factors, such as pH, soil moisture, OH concentration, sun irradiance and temperature. For simplicity, the model considers only the dependence of the degradation on temperature.

MAPPE-Global distinguishes the transport of chemicals in "vertical" and "horizontal" processes. The former includes transfer between compartments "inside" computational cells, e.g. wet and dry deposition from the atmosphere over land and oceans; volatilization from soil or water bodies, water column sedimentation, sink through particle settling to deep sea, etc. The latter includes the removal outside of the cell, e.g. runoff and erosion fluxes from soil to stream network; wind advection from atmospheric cells to the surrounding or faraway ones; the current advection for marine environment. However, while the vertical chemical transport is properly treated in the model, so far the "horizontal" elimination processes are considered practically only for cases when computing local concentrations or mass-fluxes from isolated single emission sources.

Besides, MAPPE-Global assumes that the diffusive transport is essentially the gas absorption from the atmosphere to surfaces (land and ocean) and the volatilization from land and ocean. Thus, no dispersive or diffusive horizontal transport between cells is presently considered.

In conclusion, the first version of MAPPE Global does not explicitly compute chemical advective and diffusive transport in space, but only the local fate of a substance at each grid cell; therefore, the model is not able to properly compute the chemical concentrations. Obviously, in order to correctly assess the pattern of contamination originated from spatially distributed emissions, a full 3-D transport model must be used. However, MAPPE Global calculates the chemical mass fluxes that are available for transport outside of the cell, in addition to local concentrations from local emissions, which gives a possibility to further improve the model performance. The way the new MAPPE-Global version works is explained below.

Grounding on the MAPPE Global features described above, the present model version first computes for a given chemical an initial estimate for the mass $M_{init,x}$ (kg) in each grid cell as an algebraic combination of maps of emissions E_x (kg/y) and the total removal rate K_x (y^{-1}) (for details see Pistocchi et al., 2011b):

$$M_{init,x} = \frac{E_x}{K_x}$$

where x indicates air, soil, or ocean environmental compartment.

For instance, the total atmospheric removal rate K_{air} (y^{-1}) (details are provided in the Annex) is:

$$K_{air} = \left(\frac{(K_{part} + (1-\phi)K_{gas} + K_{wet})}{ABL} + K_{\deg a} + \frac{u_{10}}{X} \right) \cdot 3600 \cdot 24 \cdot 365$$

where K_{part}, K_{wet} and K_{gas} are the rates of dry and wet deposition and gas exchange (all in m/s); Φ is the chemical fraction in aerosol phase (-); ABL (m) is the height of the atmospheric boundary layer; $K_{deg,a}$

is the degradation rate in air (s^{-1}); while the last term represents the air intramedium transport or dilution by the wind advection. Here u_{10} (m s^{-1}) is the wind speed at *10*m height and *X* (m) is the size of the calculation cells (approximately *100000* m corresponding to 1 degree resolution). Then, the last term into K_{air} formula (so called advection rate) quantifies the fraction of the air to be moved out of the computational cell through its lateral borders with the u_{10} speed. Obviously, the extreme case of no advection air removal rate ($K_{air\_no\_adv}$) is missing this part.

Similarly, the overall removal rate for soil compartment K_{soil} (y^{-1}) (for details see the Annex) is:

$$K_{soil} = \left(\frac{86400 \cdot (K_{er} + K_{vl}) + K_Q}{h} + 86400 \cdot K_{deg,s} \right) \cdot 365$$

where K_{er}, K_{vl} and K_Q are the rates of erosion, volatilization and diffusion runoff (m/s), respectively; $K_{deg,s}$ is the degradation rate in soil (s^{-1}); while *h* (m) is the soil layer thickness, set to 0.3m.

Once again, the total ocean removal rate K_{sea} (y^{-1}) (for details see the Annex) is calculated as:

$$K_{sea} = \left(\frac{K_{settl} + K_{volat}}{MLD} + K_{deg,w} + \frac{u}{X} \right) \cdot 3600 \cdot 24 \cdot 365$$

where K_{settl} and K_{volat} are the rates of sea settling and volatilization (m/s); *MLD* (m) is the ocean mixing layer depth, $K_{deg,w}$ is degradation rate in sea water (s^{-1}); while *u* (m/s) is the average ocean current velocity and *X* (m) is the size of the calculation cells (approximately *100000* m corresponding to 1 degree spatial resolution).

Formerly, based on the first estimate for the chemical mass M_x, the pollutant fluxes L_x (kg/y) available to be transported out of the computational cells are computed as (valid only for air and ocean medium):

$$L_x = M_{init,x} K_{adv,x}$$

where $K_{adv,x}$ (y^{-1}) are the maps of advection removal rates in different media associated to wind in the atmosphere or currents in the oceans. Subsequently, the mass-fluxes found on the initial chemical mass estimates could be further used aiming at bettering and completing the calculation procedure of MAPPE Global.

The new developments of MAPPE-Global include, particularly for atmosphere, the quantification of the local and regional or continental relocation of the chemical masses exported outside of each grid cell as a proxy of diffusive or advective transport, as well as the accounting of eventual impact of the long range transcontinental transport in terms of globally "exported or imported" additional emissions. In addition, the present version of the model improves the surface water compartment by introducing a global map of travel times to sea which parameter was considered earlier as a fixed value for a given

river basin. Besides, the soil-air gas exchange in the soil compartment was bettered by accounting differences in the global land cover. No further improvement is done in the marine part of the model. All details of the model progress are explained bellow.

For example, as a new element in the model, in particular for atmosphere, we perform a local chemical mass redistribution using a "neighboring" GIS operation in order to take into account the "horizontal" diffusive chemical propagation. This procedure is thought to ensure in the model a previously missing diffuse spreading of chemicals from emission cells over the adjusted ones.

Besides, for persistent chemical substances, intending to calculate the total chemical mass per pixel for a given zone (for example continent or sea), we assume that all chemical masses exported outside of the grid cells belonging to this spatial object, are altogether well and homogeneously mixed by advection processes. Then, an additional chemical mass could be added to the initial one already found in each grid cell according to the local chemical fate conditions. The additional mass is specified simply as a mean value of what is moved out of cells where the emissions occurred, by averaging the exported quantities over the entire spatial zone of concern but taking into account the specific removal capacity of each location.

In addition to the local or regional relocation of chemicals as a proxy of diffusive or advective transport, MAPPE-Global is evolved to account for an eventual impact of the long range transcontinental transport in terms of globally "exported or imported" emissions. Potentially, the trans-boundary extra mass could be associated with an additional deposition over land which originated from external emission sources. Aiming to quantify the transcontinental impact, we follow the approach and the estimates developed by EMEP after detailed modeling study on source-receptor relations at continental and global scales (Gusev et al, 2006).

Hence, the present variant of MAPPE Global evaluates the chemical mass per grid cell in a given area (valid for atmospherics layer) as a sum of the initially estimated amount and the supplements of the regionally advected or trans-boundary transported quantities:

$$M_{tot,x} = M_{init,x} + M_{add,x} + M_{ext,x}$$

Even though we expect that the proposed approach will improve the predictive capacity of the MAPPE-Global model, obviously it will not be capable yet to produce outcomes equivalent to those of the complex 3D mechanistic models or their surrogates based on source-receptor relationships. However, as it will be shown in the next section, the simple concept (algorithm) used to account for the impact of advection or transcontinental transport by adding the extra masses yields sufficiently reasonable results, in particular for screening purposes of chemical fate and sea load at continental and global scale.

When chemical mass in atmosphere has been estimated, we are ready to calculate the pollutant atmospheric deposition, mass in soil and the liquid or sediment discharge from soil to freshwater bodies. The latter were used as additional diffusive sources to complement eventual direct emissions to the soil or surface water as already described in Pistocchi et al., (2011b).

Moreover, in the earlier version of MAPPE-Global, the surface water is considered only as a "transit" compartment which conveys the chemicals originated from land to the marine environment accounting for the exponential decay and the inland retention time of the fresh water. However, a single retention parameter is used for all locations inside a given river basin; this is specified as the average retention time for the entire basin which is a reasonable solution only for small watersheds. To overcome this problem, the second version of the model was improved by introducing a global map of surface water travel times to sea, calculated similarly to the European variant of MAPPE model (Pistocchi, 2008). Actually, the last modification is applied only to the chemical loads in liquid form, due to the practical difficulty to assign relevant values for sediment resident times for each catchment; thus, we assume as before that the entire chemical load with sediments is eventually delivered to the ocean/sea coast (Pistocchi et al., 2011b).

Lastly, the new version of MAPPE-Global improves the surface water compartment by adding a more precise calculation of the liquid or sediment load to streams by separately considering the atmospheric deposition over cultivated or natural soil and fresh water bodies along with the excluding as contributors the urbanized and sealed soils or deserts and permanently frozen land zones.

Based on the above assumptions, the current version of MAPPE-Global is built on the following chain of formulas, starting from air and following the "natural" consequence air-soil-surface water-ocean, which are mathematically written as (here the emissions and removal rates are considered on annual basis):

$$M_{init,air} = \frac{E_{emis\_air}}{K_{air}}$$

$$L_{adv,air} = M_{init,air} * K_{adv,air}$$

$$M_{add,air} = \frac{\sum_{emit\_cells} L_{adv,air} / K_{air\_no\_adv}}{N_{tot\_cell}}$$

$$M_{tot,air} = M_{init,air} + M_{add,air} + M_{ext,air}$$

$$Dep_{air} = M_{tot,air} * K_{dep}$$

$$M_{tot,soil} = \frac{Dep_{air} + E_{emis\_soil}}{K_{soil}}$$

$$Load_{liq} = M_{tot,soil} * Load_Q$$

$$Load_{sed} = M_{tot,soil} * Load_S$$

$$Load_{liq\_basin} = \int_{river\_basin\_area} (Load_{liq} + Dep_{air} + E_{emis\_riv\_liq}) * \exp(-\frac{\ln 2 * \tau}{DT50_w}) dA$$

$$Load_{sed\_basin} = \int_{river\_basin\_area} (Load_{sed} + E_{emis\_riv\_sed}) dA$$

$$Load_{tot\_basin} = Load_{liq\_basin} + Load_{sed\_basin}$$

$$M_{tot,ocean} = \frac{Dep_{air} + Load_{tot\_basin} + E_{emis\_sea}}{K_{sea}}$$

Here N_{tot_cells} is the total number of cells in the considered domain, $K_{air\_no\_adv}$ means the atmospheric removal rate without advection, K_{dep} is air deposition rate, $Load_Q$ is the runoff from soil in liquid form, τ is time of travel to the river outlet, $DT50_w$ is the half-life chemical dissipation in water for dissolved phase, $Load_S$ is the run-off with sediments; all these parameters are provided in Pistocchi et al., (2011b). Also it is worth mentioning that the formula for $M_{tot,ocean}$ is practically valid close to the sea coast. If one would want to consider the situation far away from the coastal line, as a first approximation it could be enough to take into account the atmospheric deposition and to "redistribute" the sea load and the direct emissions to sea using a procedure similar to this applied for air.

Finally, the global maps of pollutant concentrations are calculated by dividing the total mass per cell to the volume of the computational cell for each medium. In the case of air, the volume is calculated multiplying the cell area by the atmospheric boundary layer height, while for ocean and for land, mixing layer and soil depths are respectively considered.

3. Model verification

In order to verify the output of MAPPE-Global model, we compare its performance versus results of other models and estimates of sea load derived by measurements. Firstly, this was done qualitatively against EMEP model results for global PCB153 distribution in air, soil and sea/ocean water derived through the GLEMOS world model (Travnikov and Jonson, 2011). Secondly, we did a precise quantitative comparison only for the European continent contrasting MAPPE-Global results for two scenarios of Lindane air emissions (Marinov et al., 2011) versus sea load data (OSPAR Commission,

2011; Ilyina et al., 2008) as well as measured or modeled air and soil concentrations. The assessments are separately presented below.

3.1 **PCBs**

Intending to keep similarity to the application of EMEP-GLEMOS world model (Travnikov and Jonson, 2011), the new version of MAPPE-Global was run for the sole PCB153 congener. For the same reason we forced the model with PCB153's air emissions for 2009 (their spatial distribution is shown in Figure 1) as estimated (maximum scenario) by Brevnik et al. (2007). Accordingly, the total global amount released to air for this year equals to 7.37 tonnes. In particular, the dominant polluters are Europe (42.8 % from the world total), North America (19.1 %), Russia (8.9%), China (4.9%), Brazil (2.15%) and India (1.61%). Inside of Europe, the major contributing countries are the industrial ones, i.e. France (26.9 % out of European contribution), Germany (18.7 %), etc.
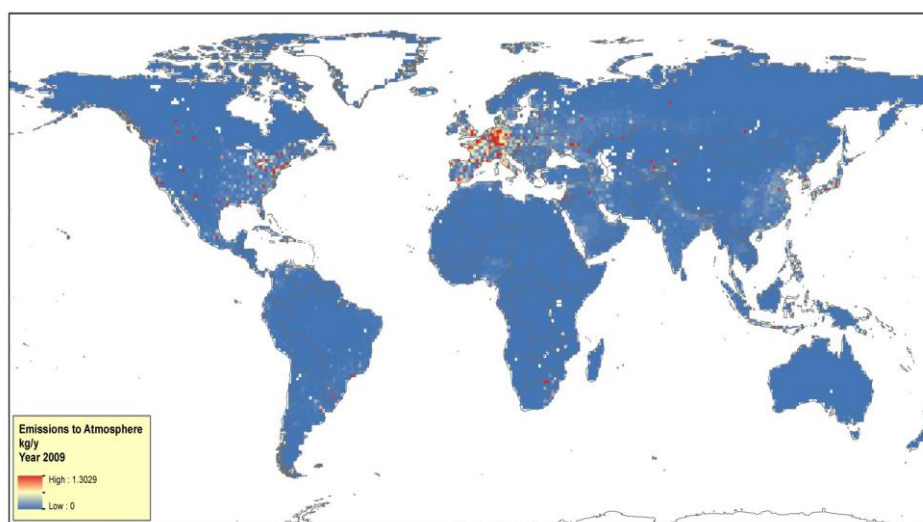
Figure 1: Emissions of PCB153 to atmosphere in 2009 year (Brevnik et al., 2007)

The MAPPE-Global run for PCB153 assumes as input the following reference physico-chemical properties, taken from USEtox model database (Rosenbaum et al., 2008): Molecular weight = 292 [g/mol]; $K_{ow} = 1.26 \ 10^{+7}$ [-]; $K_{aw} = 1.68 \ 10^{-2}$ [-]; the degradation rates in air = $4.0 \ 10^{-7}$ [s^{-1}], soil = $2.1 \ 10^{-7}$ [s^{-1}] and water = $5.7 \ 10^{-7}$ [s^{-1}].

The PCB153 concentration maps, produced basing on the above model input by MAPPE-Global, for air (plus atmospheric deposition), soil and ocean compartment are presented in Figure 2. The visual assessment of these results could be followed comparing with the output of the EMEP-GLEMOS model given in Figure 3. The comparison allows concluding that a general agreement of the global distribution trend certainly can be observed for all environmental compartments.

Indeed, in the case of atmosphere (Figure 2a and Figure 3a), it was found that both models forecast a similar spatial distribution both in longitudinal and latitudinal direction and the air concentrations are in the same order of magnitude. According to MAPPE-Global, the annual average atmospheric concentration of PCB153 - global mean = 0.36 pg/m3 and SD = 0.55 (here and below SD means Standard Deviation) – can be more precisely characterized by an higher concentrations for the Northern hemisphere (mean = 0.61 pg/m3; range from 0.047 to 9.86 pg/m3) when compared to the Southern one (mean = 0.12 pg/m3; range from 0.003 to 2.31 pg/m3). It is worth mentioning that the European continent, in particular, shows exceptionally elevated PCB153 air concentrations (mean = 2.21 pg/m3; SD = 1.54 pg/m3) followed by India (mean = 1.21 pg/m3; SD = 0.54), eastern and western coast of USA (mean = 1.01 pg/m3; SD = 0.64) and China (mean = 0.83 pg/m3; SD = 0.57). Besides these hot zones, the simulated PCB153 atmospheric concentrations at poles (mean = 0.14 pg/m3) are also alike identified by the both models.

The atmospheric deposition of PCB153 congener (global mean = 0.017 µg/m2/y; SD = 0.085) is shown in Figure 2b. It was not possible to compare directly the MAPPE-Global results for this parameter with those of the EMEP since they did not publish any results about it for year 2009. However, the modeled air depositions relative to year 2006 in the extended European region of EMEP (Gusev et al., 2008) are in practice quite higher (European mean=0.2 µg/m2/y; range 0.01-1.5 µg/m2/y) compared to ours for 2009. Probably this discrepancy is caused by the different parameterization of chemical fate processes in the atmosphere or, more importantly, it is determined by the variability in the geo-referenced climatic input data, used in the both models, rather than due to the inequality of air emissions for 2006 and 2009. The latter hypothesis is confirmed by Shatalov et al. (2011). They found that, for air, the temperature is the key factor affecting the model results for the Southern European countries; for Northern ones the key factors are vegetation and precipitation, while, in the case of Western and Central European countries, the precipitation is the dominant environmental parameter. For the air deposition, ibid, the temperature is the first priority factor for Western countries; for all the other European countries, the essential parameter is wind direction together with the vegetation, in particular for Western and Central European countries.

The soil concentrations of PCB153 in the top 5cm soil horizon, found after the MAPPE-Global application, are depicted in the Figure 2c (global mean = 0.57 pg/g; SD = 1.55). Even though the spatial pattern is similar, the values computed by MAPPE-Global are up to one order of magnitude lower than the ones (Figure 3b) reported in the EMEP (Travnikov and Jonson, 2011). Obviously, the reason for this deviation is the fact that GLEMOS output is built on higher atmospheric deposition, as explained in the paragraph above. The same fact explains several soil hotspots identified by MAPPE-Global in the equatorial forest zones in South America, Africa and Indonesia which are not present at all in the EMEP results.
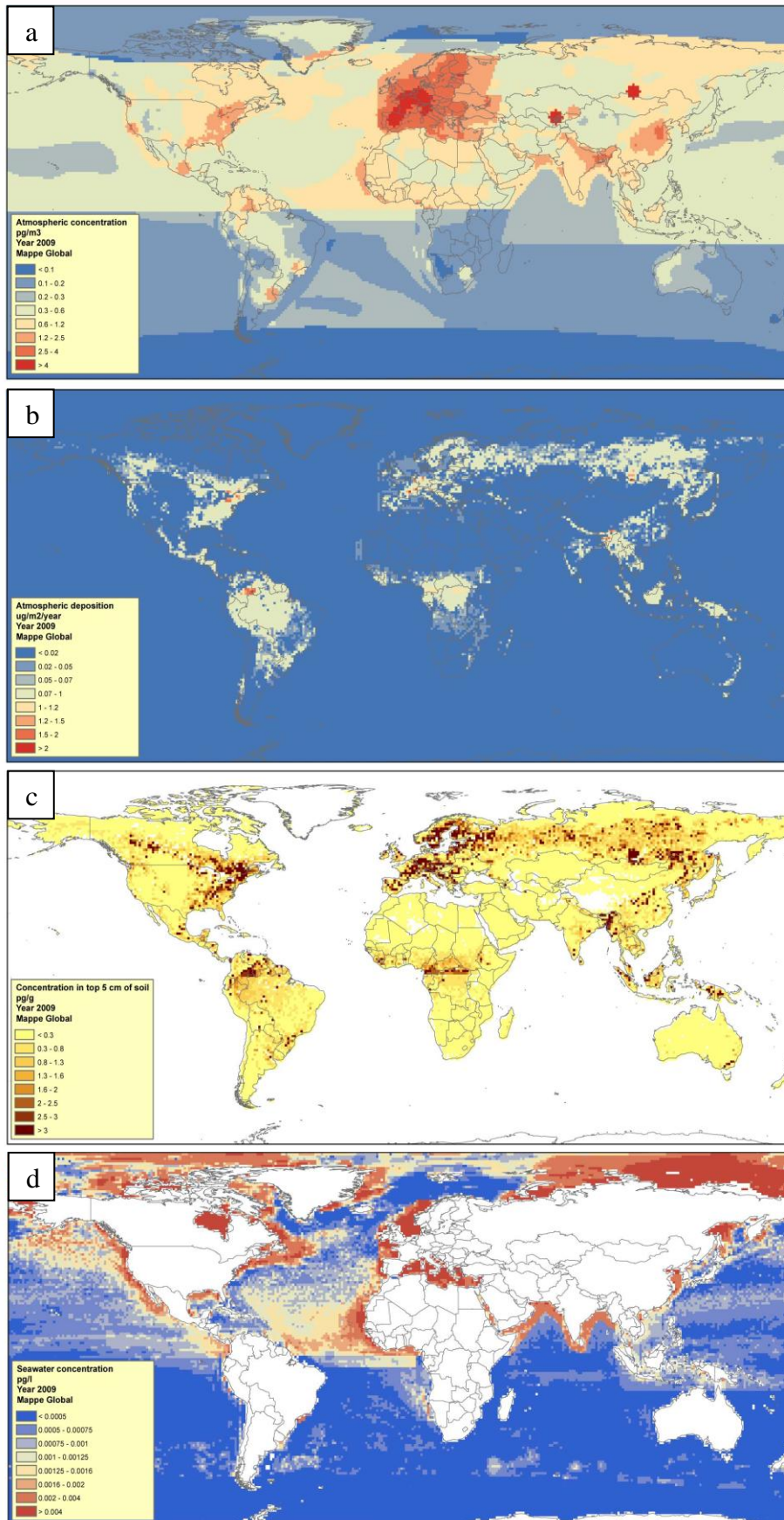
Figure 2: PCB153 annual mean air concentration (a), atmospheric deposition (b), mass in soil (c), and seawater concentration (d) under 2009 emissions to atmosphere (Brevnik et al., 2007) by MAPPE-Global model.
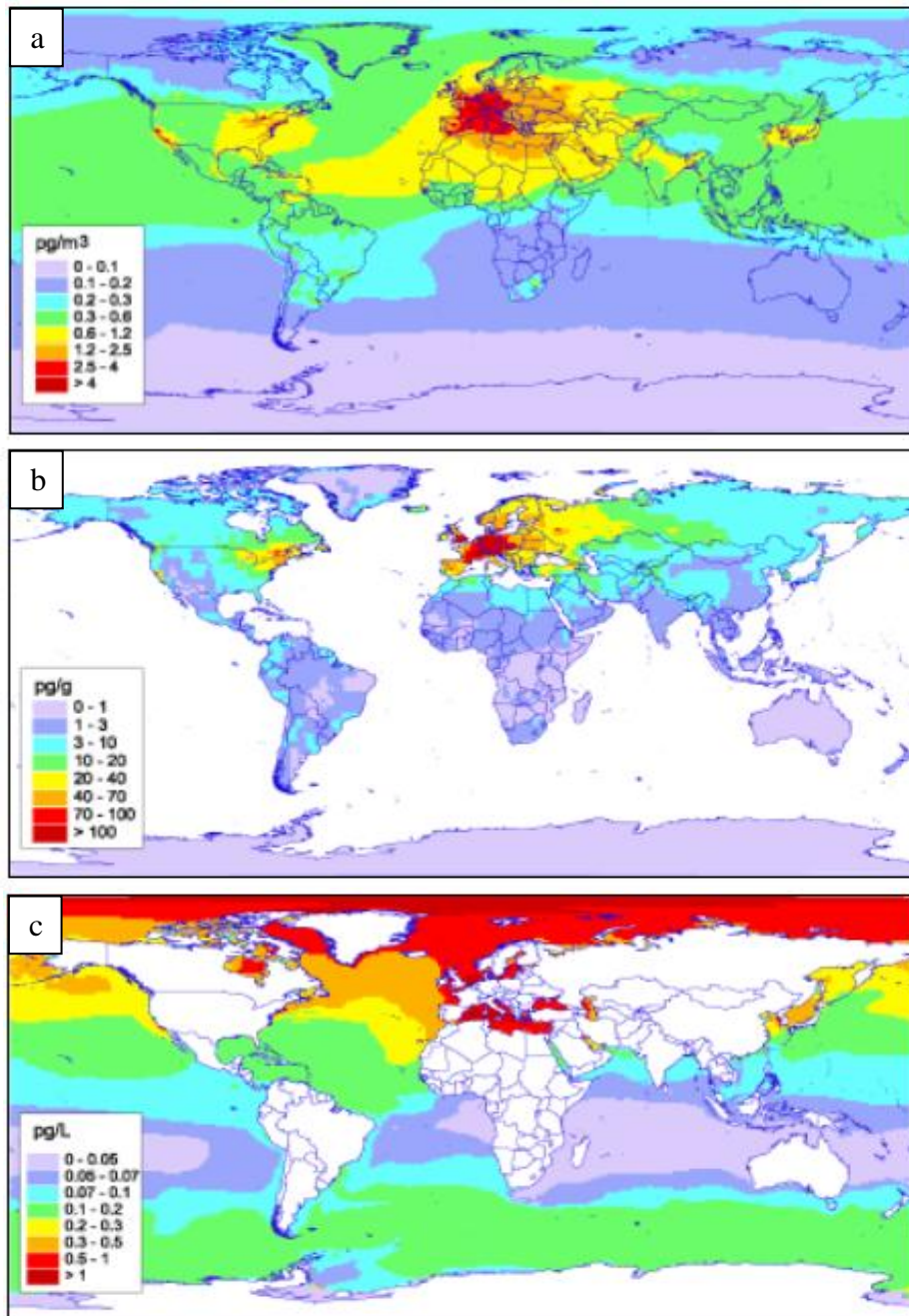
Figure 3: Spatial distribution of PCB153 annual mean concentration in surface air layer (a), in the top 5 cm of soil (b) and in surface seawater (c) under 2009 emissions (Brevnik et al., 2007) by GLEMOS model (taken from Travnikov and Jonson, 2011)

Concerning seawater concentrations (global mean = 0.001 pg/L; SD = 0.002), we found reasonable match of MAPPE-Global outcome (Figure 2d) with the general trend reported by EMEP (Figure 3c). The figures equally show a typical horizontal belt of higher values in the northern hemisphere and consequently a gradual decrease towards the equator. There are anyway differences in the way these values decrease, since MAPPE-Global model does not consider any advection transfer between different sea zones. Besides, looking at both models results, it is evident a significant difference of the reported values (up to 2 orders of magnitude). However, it should be stressed out that the values reported by MAPPE-Global actually represent the contamination inside the entire sea mixing layer (varying from 0.15m up to 552 m; mean=58m), while the EMEP model merely refers to the top sea water surface (probably up to 1m depth). In addition, the MAPPE-Global identifies buffer zones of elevated values along the continental coastlines, which are not mapped by the GLEAM model.

3.2 Gamma-HCH

In order to test MAPPE-Global for Lindane (gamma-HCH) two scenarios for atmospheric emissions have been considered: BAU - business as usual and "ban" – assuming only unintended European emissions equal to the 'equivalent import" of the transcontinental air transport from remote sources of pollution outside of Europe (Marinov et al., 2011). In both cases, the emissions are supposed to be continuous during the years.

For instance, the BAU scenario is built on the available EMEP emission data (Gusev et al., 2006; Gusev et al., 2009) with a baseline year 2005. It assumes in total 92 tonnes of Lindane being released from fewer industrial applications or agricultural seeds treatment in Europe, mainly in UK, Belgium, France, Spain, Portugal, Italy, Croatia and Greece, plus trans-continental transport from sources outside of European continent. An illustrative map of Lindane air emissions under BAU scenario is presented in Figure 4.

In contrast, the "ban" scenario respects the current situation in Europe and adopts only low release of Lindane to air from industrial applications like solvent and products use. This motivates assuming that Lindane emissions are spatially distributed according to population density in Europe (Marinov et al., 2011). However, as the exact amount of the European emissions of Lindane is unknown, the "ban" scenario is built on the EMEP's approximation for the atmospheric long-range transport of Lindane in the Northern hemisphere, estimated to be about 5.4 tonnes per year (Gusev et al., 2006; Gusev et al., 2009).

Then, based on the above scenarios, we ran MAPPE-Global aiming to calculate the environmental fate of Lindane starting from atmosphere and continuing with soil and surface water which, at the end, allows estimating the Lindane load to European seas. In these runs we assumed the following physico-

chemical properties of Lindane: Molecular weight = 291 [g/mol]; $K_{ow} = 5012$ [-]; $K_{aw} = 2 \cdot 10^{-5}$ [-]; degradation rate in air = $1.87 \cdot 10^{-7}$ [s^{-1}], soil = $1.13 \cdot 10^{-8}$ [s^{-1}] and water = $1.13 \cdot 10^{-8}$ [s^{-1}] (Rosenbaum et al., 2008).
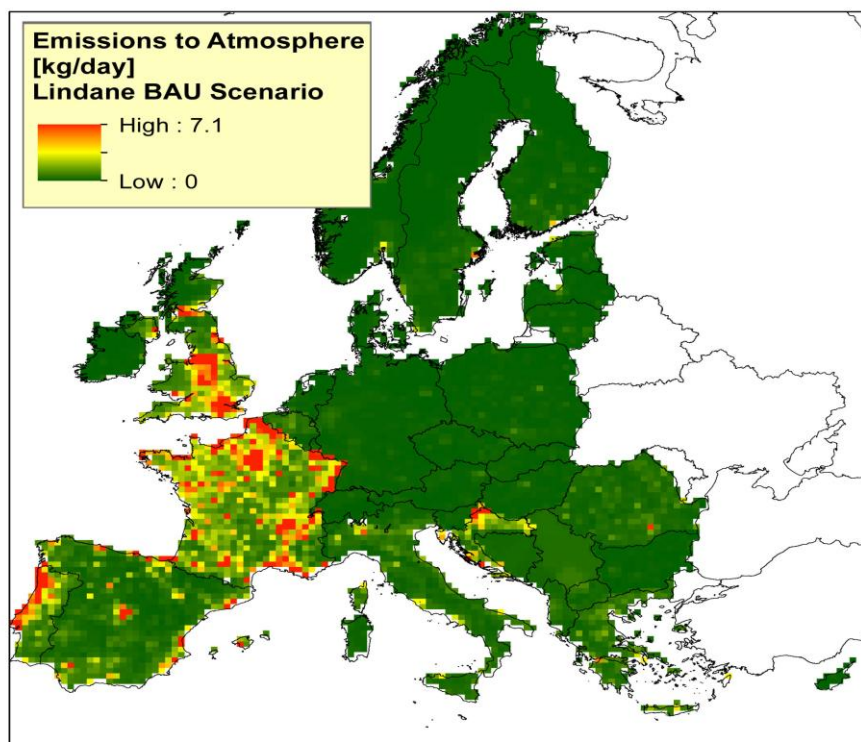
Figure 4 - Spatial distribution across Europe of Lindane air emissions under BAU scenario (Gusev et al., 2006; Gusev et al., 2009). BAU assumes as a reference year 2005 considering annually 92 t were released from fewer industrial applications or agricultural seeds treatment mainly in UK, Belgium, France, Spain, Portugal, Italy, Croatia and Greece.

Firstly, the MAPPE-Global model results for Lindane are compared under BAU emission scenario on the Figure 5 considering the calculated annual mean air concentrations against measurements and mass in soil versus the outcome of an establish multimedia model. The evaluation of atmospheric part of MAPPE Global is performed with data having a good European coverage using two different sources: EMEP data for the period 2004-2007 (www.emep.int) and passive samplers observations for 2005 (Pozo et al., 2009) and 2006 (Helse et al., 2011). The assessment of soil results of MAPPE Global is done against results of MSCE-POP model of EMEP. We found that MAPPE Global tends to overestimate the atmospheric concentrations, in particular the small ones in the range 1-30 pg/m^3 , which leads to a lower correlation coefficient (R^2=0.24) between the model results and measurement data. In addition, the detected discrepancy in the air concentrations eventually propagates in the other MAPPE model compartments, for example soil one, because in this case we also found a weak correlation (R^2=0.18) of MAPPE results with those of MSCE-POP model of EMEP.
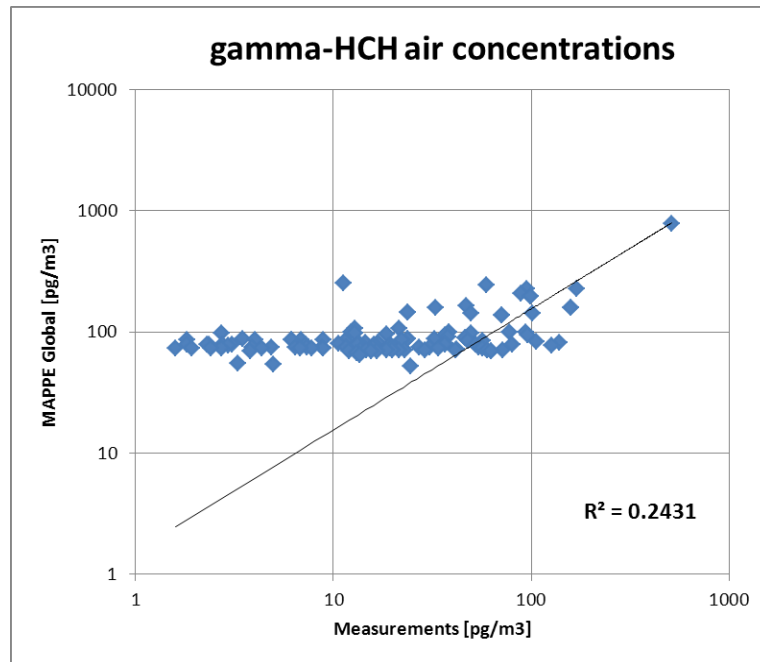
(a) – evaluation of atmospheric results of MAPPE Global model against measurements with a good European coverage using EMEP data for the period 2004-2007 (www.emep.int) and passive samplers observations for 2005 (Pozo et al., 2009) and 2006 (Helse et al., 2011).
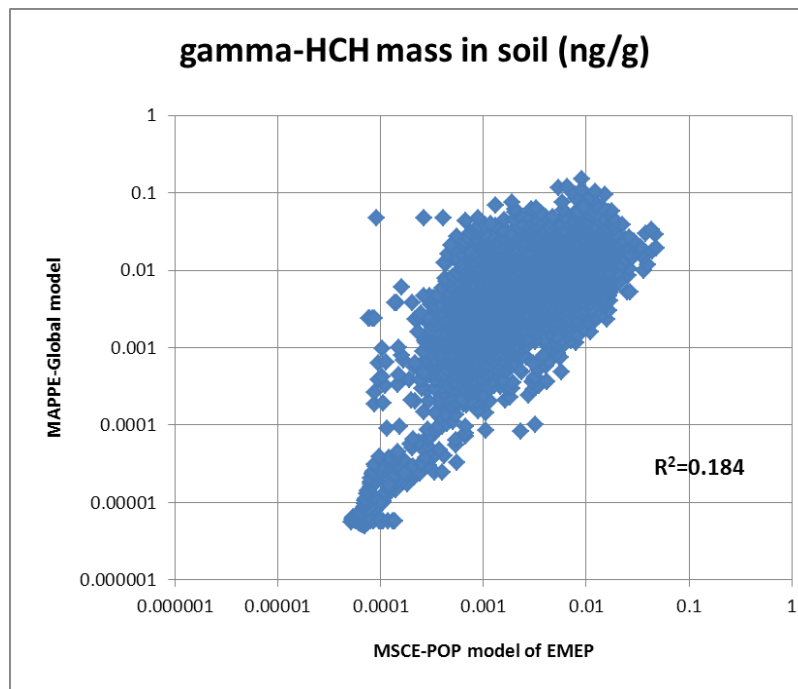
(b) - evaluation of soil results of MAPPE Global against results of MSCE-POP model of EMEP for annual average Lindane mass in soil.

Figure 5 – Comparison of Lindane annual mean (a) -air concentrations and (b) - mass in soil calculated by MAPPE-Global model under BAU emission scenario. BAU assumes as a reference year 2005 considering annually 92 t were released from fewer industrial applications or agricultural seeds treatment mainly in UK, Belgium, France, Spain, Portugal, Italy, Croatia and Greece.

The illustrative maps of Lindane air and soil concentrations under the BAU scenario, found by MAPPE-Global and MAPPE-Europe models, are presented in parallel in Figure 6. MAPPE-Global estimates for Europe an average air concentration of 0.74 pg/m^3 (SD=0.53) and a mean mass in soil of 5.01 μg/m^2 (SD=5.57) while the MAPPE-Europe version gives lower values of 0.23 pg/m^3 and 1.24 μg/m^2, respectively. In both cases, the spatial patterns of the results are quite similar, apart from the soil concentrations in Scandinavian countries. However, the elevated soil concentrations of Lindane observed there, as simulated by MAPPE-Global, are actually realistic. They depend on the higher organic carbon content of the soil, typical of this part of Europe which causes extended contaminants accumulation in soil. Thus, in general, we could conclude that, despite of the observed discrepancies, MAPPE-Global is working well for atmospheric as well as for soil compartment.

In addition, Figure 6 provides insight about matching (through scatter diagrams) between numerical results produced by both models at a grid level (again for the BAU test case). The observed R^2 - correlation coefficients equal for air to 0.67 and for soil to 0.21 (mainly because of the deviations in Northern Europe) - in fact confirmed one more times the conclusion about MAPPE-Global performance stated above. It is worth mentioning that during the model comparison under 'ban" scenario conditions, we arrived to similar conclusions as those drawn already for BAU scenario study.

Then, as a further important step of MAPPE-Global verification, we compared the riverine load of Lindane to seas calculated by the European and Global model versions considering the BAU and "ban" scenarios for Lindane air emissions. This assessment showed (see Table 1) that the new version of MAPPE-Global reasonably calculates the range of regional sea loads but tends in general to underestimate them by 40 to 60%, except in the case of North Sea for which one could track up to 3 times overestimation. This discrepancy might be due to the incomplete consideration of air advection by MAPPE-Global model, which leads to lower atmospheric deposition and consequently results in reduced chemical mass in soil and decreased sea loads. Oppositely, the artificial redistribution of the chemical mass exported from emission cells, in particular over Northern Europe, together with the higher soil organic matter found there, lead to an increase of load to North and Baltic Sea. Among the European seas, the load of Lindane to Mediterranean Sea is better predicted for both scenarios.

Moreover, Ilyina et al. (2008) estimated ca. 1 tonne of gamma-HCH load to North Sea in 2001, based on measurements for the major contributing rivers. Logically, under the BAU scenario of year 2005, MAPPE-Europe forecasts lower amount of 0.4 t but it seems that MAPPE-Global over-estimates the expected sea load, forecasting a load of 1.3 t (as shown in Table 1). However, the OSPAR Commission reported for year 2009 the following riverine inputs of gamma-HCH: to North Sea – lower = 0.074 t/y and upper = 0.186 t/y; to Atlantic Ocean – lower = 0.047 t/y and upper = 0.677 t/y (OSPAR Commission, 2011). When, comparing these values to the forecasts for both models (see

25

Table1), we found that MAPPE-Global in practice reasonably approaches the lower OSPAR estimates for Northern Sea and Atlantic Ocean under the "ban" scenario (calculating 0.06 t/y and 0.08 t/y) and overestimates the upper ones according to the BAU scenario (yielding 2 t/y and 1.3 t/y).
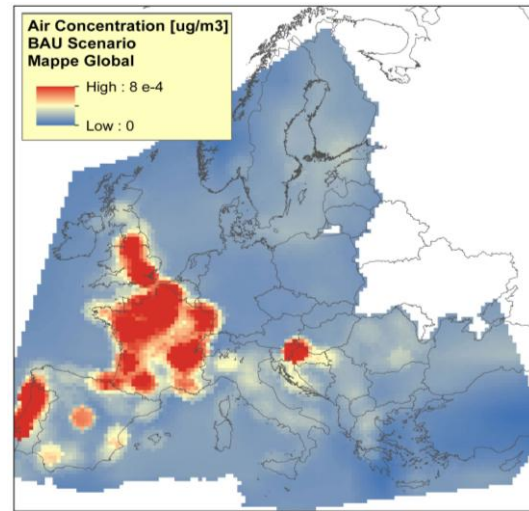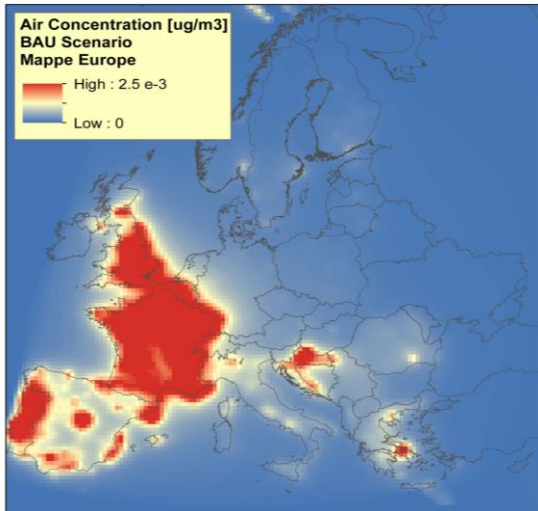
(a) - air concentrations
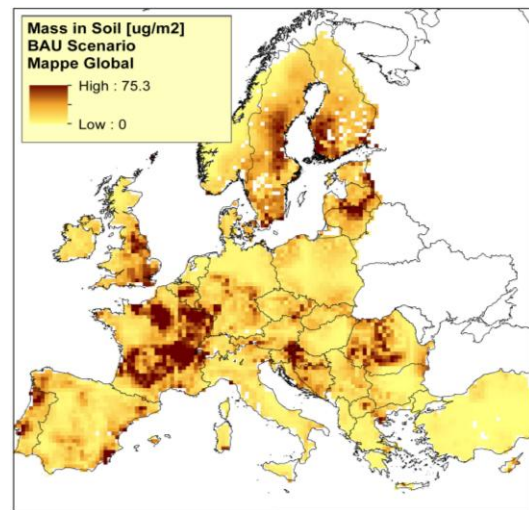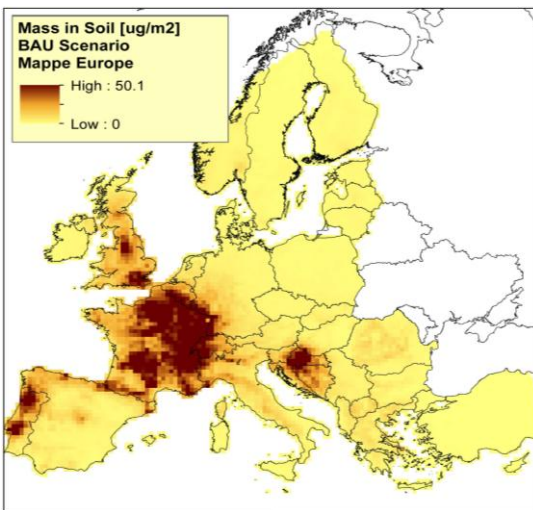
(b) - mass in soil
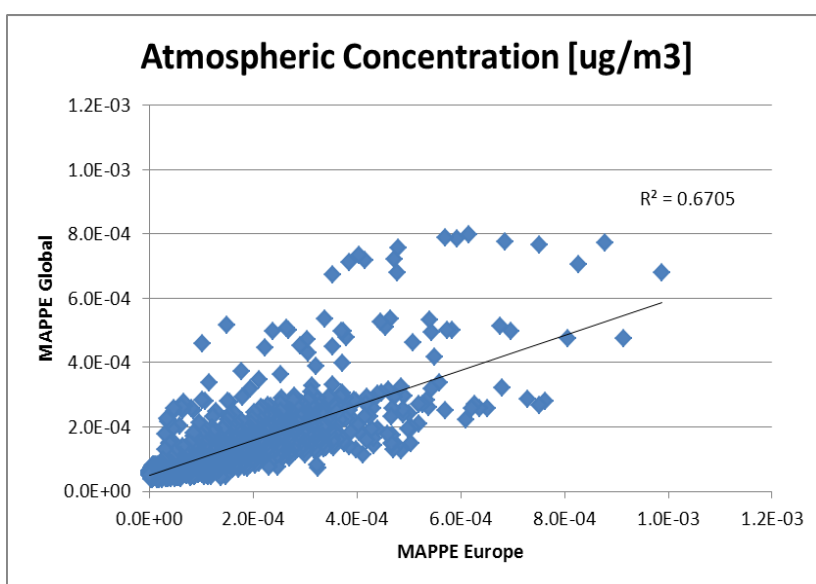
(c) − correlation between modelled air concentrations.
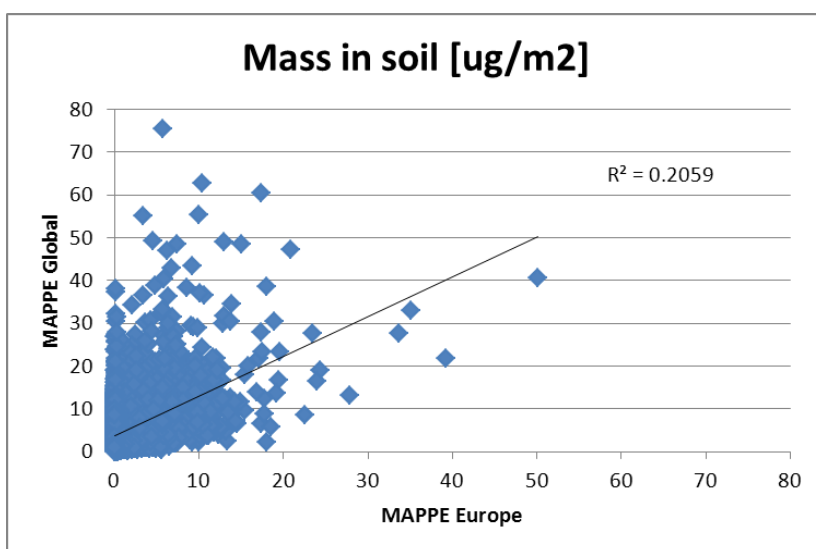
(d) − correlation between modelled mass in soil.

Figure 6 - Comparison of Lindane annual mean atmospheric concentrations and mass in soil calculated by MAPPE-Global and MAPPE-Europe at grid scale level under BAU emission scenario. BAU assumes as a reference year 2005 considering annually 92 t are released from fewer industrial applications or agricultural seeds treatment mainly in UK, Belgium, France, Spain, Portugal, Italy, Croatia and Greece.

Load to European seas	Scenario					
	BAU (2005)			BAN (current status)		
	MAPPE Europe	MAPPE Global	Ratio (Global/Europe)	MAPPE Europe	MAPPE Global	Ratio (Global/Europe)
Atlantic ocean	6.13	1.99	0.32	0.09	0.064	0.71
Baltic sea	0.2	1.02	5.10	0.1	0.082	0.82
Black sea	2.3	1.07	0.47	0.26	0.076	0.29
Mediterranean sea	3.4	2.72	0.80	0.12	0.12	1.00
Northern sea	0.4	1.32	3.30	0.03	0.082	2.73
Total	12.43	8.12	0.65	0.59	0.42	0.72

Table 1 – Comparison of Lindane riverine load to European seas estimated by the European and Global version of MAPPE model under BAU and "ban" emission scenarios. BAU assumes as a reference year 2005 considering annually 92 t were released from fewer industrial applications or agricultural seeds treatment mainly in UK, Belgium, France, Spain, Portugal, Italy, Croatia and Greece. The "ban" scenario is built on the EMEP's approximation for the atmospheric long-range transport of Lindane in the Northern hemisphere, estimated to be about 5.4 t/y.

In summary, the testing of MAPPE-Global for PCB153 and gamma-HCH allows concluding that, given its coarser spatial resolution (1x1 degree) and the simplicity of the employed modeling approach for advection, the MAPPE-Global model produces compatible results compared to observations or outcome of more refined models. The estimated error level of MAPPE-Global model is about a factor of two, which suggests that the model could be considered as a tool for a screening or initial evaluation of chemical risk for POPs at global or continental scale.

4. Assessment of loads to the European seas

MAPPE-Global modeling tool (described in the second section of this report), after being assessed versus existing data or results from other models (comparison is shown in the third section), is ready to be applied in practical assessments of the chemical loads to the European regional seas. Respecting the current availability of emission data, we considered two case studies – the family of PCBs (industrial chemicals potential candidate as an EU priority substance) and the single congener of gamma-HCH (an insecticide banned for agricultural applications in the EU countries since 1995).

Aiming to ensure a finer model resolution that would guarantee a more accurate assessment of load to European seas, in both occasions, we ran the model over a grid of 30 km instead of working on the original 100 km spatial resolution adopted at global scale. For the same reason we restricted the planet computational domain only to the European continent and its surrounding area - Northern African countries (up to Capricorn tropic), Asian countries around Mediterranean Sea (Turkey, Syria, Israel, Palestine, Lebanon, Jordan and parts of Iraq and Saudi Arabia) and Western Russia (up to the 45th meridian) plus Moldova, Ukraine, Belarus and part of Georgia.

4.1 PCBs

The PCBs case study relates to a group of 22 congeners including 2 dichlorobiphenyls, 3 trichlorobiphenyls, 2 tetrachlorobiphenyls, 6 pentachlorobiphenyls (like PCB153 considered in the section 3.1), 6 hexachlorobiphenyls, 1 heptachlorobiphenyls and 2 octachlorobiphenyls. As commonly accepted (Pistocchi, 2008; Pistocchi et al., 2010; Rosenbaum et al., 2008), the physical-chemical properties used as a model input relative to the whole PCB group are the same as those already reported in paragraph 3.1.

In order to evaluate the impact of emission reduction, throughout the PCBs exercise, we considered two emission scenarios: first - the current status relative to the year 2010; second – a future projection corresponding to the year 2020. Both scenarios are built on estimates for PCBs emissions (maximal values) as calculated by Brevnik et al. (2007). Accordingly, the total amount released to air in the considered study area equals to 101.03 t for year 2010 (see Figure 7) and to 50.2 t for year 2020, respectively. The dominant polluters are, in both years, Russia (responsible for 17.1% of the total emissions in 2010 and 12.2% in 2020), France (15.7% and 18.3%) and Germany (13.6% and 12.9%).

The MAPPE-Global results for atmospheric concentration, air deposition and mass in soil for the sum of 22 PCBs congeners, modelled under air emission in 2010, are presented in Figure 8. Obviously, the spatial patterns of all of them follow the distribution of the 22PCBs emissions. For example, the cumulative concentrations of the sum of 22 PCB congeners in the atmosphere (see Figure 8a) - mean = 84.5 pg/m3 and SD = 29.3 - show higher values in a vast area located in the central part of Europe -

mean=160 pg/m3 and SD=60 - with smaller hotspots spread around the study area where the main urban zones are located. Consequently, the atmospheric deposition - mean = 2.18 μg/m2/year and SD = 4.8 (see Figure 8b) - and mass in soil - mean = 0.41 μg/m2 and SD = 0.8 (see Figure 8c) - are more equally spread and, especially in the Eastern part of the studied domain, the values homogeneously cover a continuous area with a less evident presence of hot-spots.
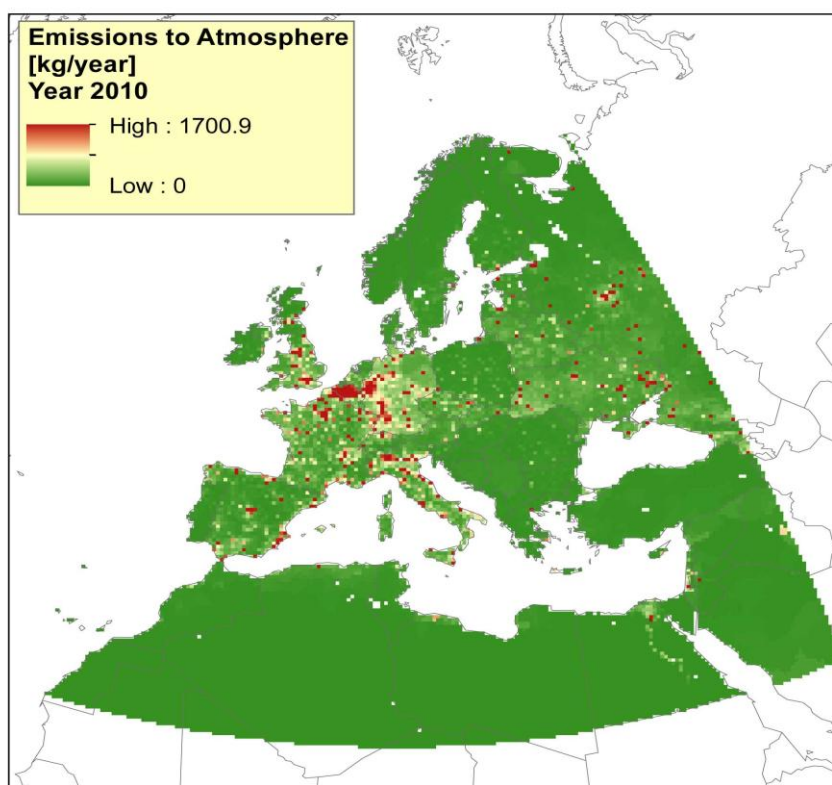
Figure 7 – Spatial distribution of of modelled air emission in 2010 for a sum of 22 PCB congeners including 2 dichlorobiphenyls, 3 trichlorobiphenyls, 2 tetrachlorobiphenyls, 6 pentachlorobiphenyls, 6 hexachlorobiphenyls, 1 heptachlorobiphenyls and 2 octachlorobiphenyls. The total amount released to air across the considered study area equals to 101 tonnes.
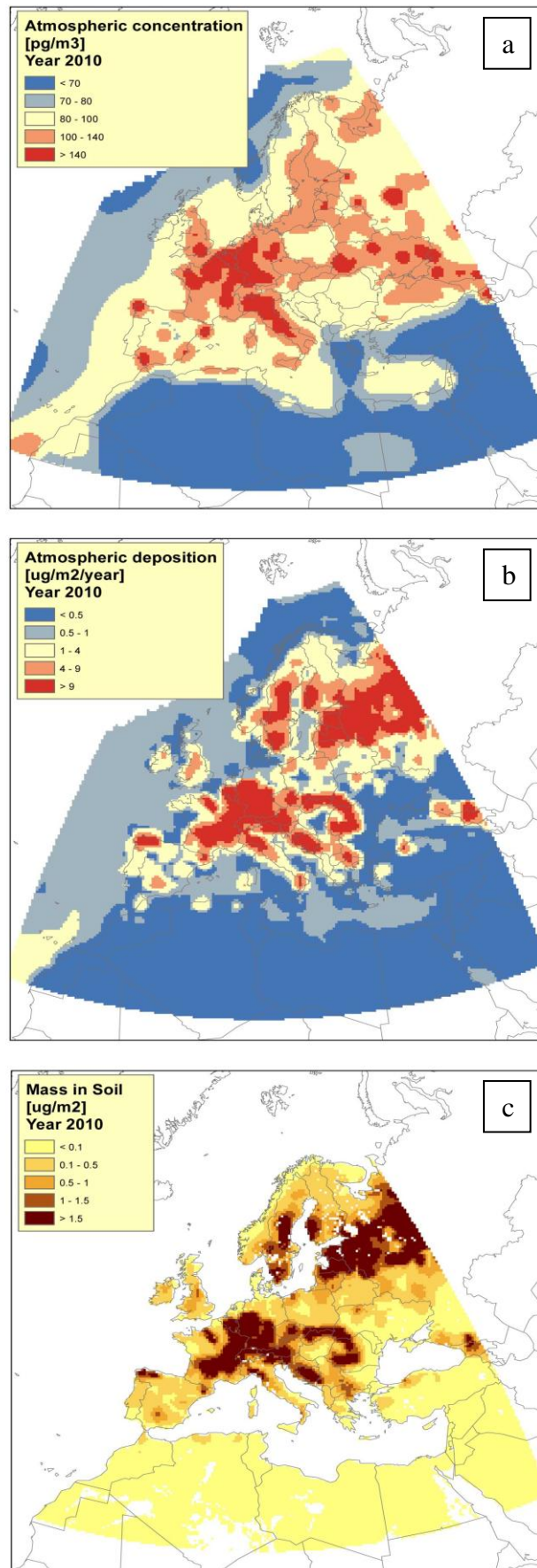
Figure 8 - Spatial distribution of atmospheric concentration (a), deposition (b) and mass in soil (c) of a sum of 22 PCBs congeners under modelled air emission in 2010.

On the basis of the results shown above, we calculated the riverine load of 22PCBs to the European seas as shown in Table 2. Overall, the considered extended European area, according to the MAPPE model, is expected to export to the coastal marine water, 3.7 tonnes of 22PCBs in 2010 and 1.9 tonnes in 2020, respectively. The observed reduction by 49% of the riverine load from year 2010 to year 2020 reflects the difference in 22PCBs emissions. It is worth mentioning that the entire riverine load represents about 4% of the total air emissions of 22PCBs. In both scenarios, the most affected seas are Mediterranean Sea (ca.35% from the total) followed by Northern (ca. 21.5% from the European total) and Black sea (ca.19% from the European total).

Load to seas [tonnes/year]	Emissions Scenario	
	2010	2020
Atlantic ocean	0.532	0.272
Baltic sea	0.388	0.190
Black sea	0.741	0.353
Mediterranean sea	1.281	0.691
Northern sea	0.801	0.412
Total	**3.743**	**1.918**

Table 2 – Riverine load to European seas for a sum of a sum of 22 PCB congeners modelled under emissions to air in year 2010 (ca.101t) and year 2020 (ca.50t).

Next, we analyse the riverine load of 22PCBs at the level of river basins (see Figure 9). The results, taking into account the spatial distribution of the 22PCBs' emissions to atmosphere, evidenced the important contribution of the major Central European Rivers. During the year 2010, Rhine was the top "exporter" of 22PCBs to surrounding seas (0.63 t/y; 16.8% from the total), followed by Danube (0.46 t/y; 12.3% from the total), Rhone (0.41 t/y; 10.85% from the total) and Po (0.22 t/y; 6.01% from the total). As expected, in 2020 the model forecasts a lowering of PCBs' sea load; for this year the highest contamination by 22PCBs comes again from the basin of Rhine (0.32 t/y; 16.7% from the total).

Another important component of the 22PCBs load to seas is the deposition from atmosphere that is reported in the Table 3. In this case, due to its wider extension, the highest total air deposition is observed over the North Atlantic Ocean. However, when looking at the average values per square kilometre, the Baltic Sea is the most affected one, receiving about 5 times more than the rest of the study area, probably due to the more intensive cold condensation and higher precipitation rate. In total the European seas are expected to receive by atmospheric deposition about 7.9 tonnes of 22PCBs in

2010 (ca.4 t during 2020), which is two times more comparing to the entire riverine discharge of 22PCBs for the same year (as well valid for the year of 2020).
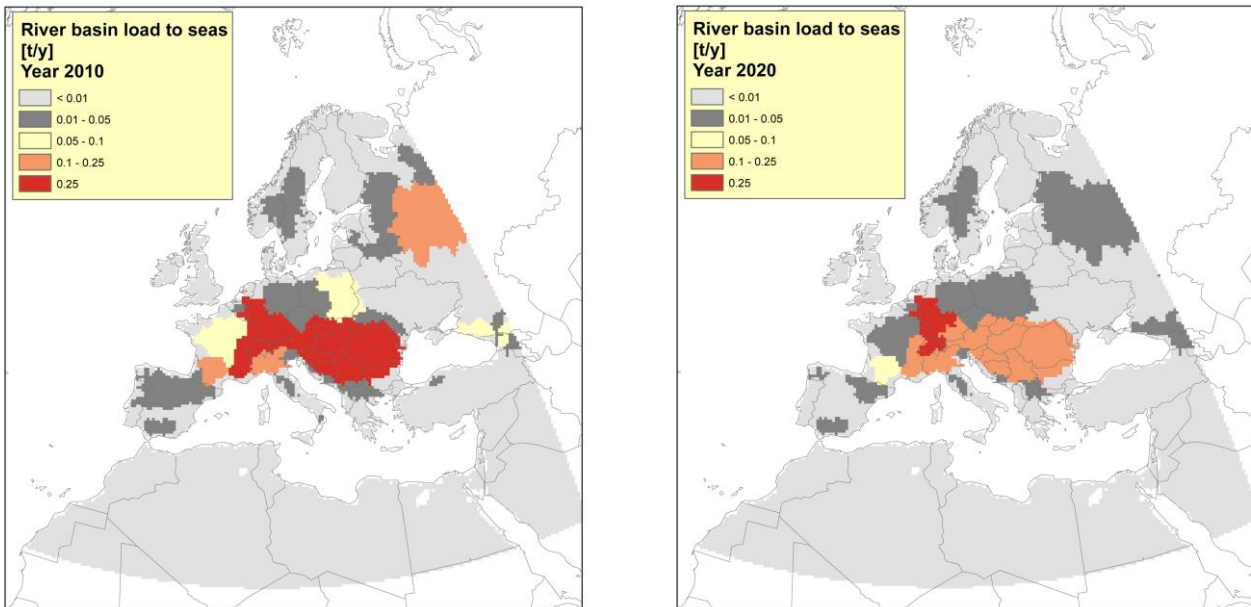
Figure 9 - Riverine load to European seas by river basin for a sum of 22 PCB congeners under modelled emissions to air in year 2010 (101t) and year 2020 (50t).

Atmospheric deposition to seas	Emissions Scenario					
	2010			2020		
	Average [g/km^2/year]	Range [g/km^2/year]	Sum [t/year]	Average [g/km^2/year]	Range [g/km^2/year]	Sum [t/year]
Atlantic ocean	0.70	10.99	3.50	0.35	5.72	1.76
Baltic sea	3.64	28.19	1.56	1.80	10.65	0.78
Black sea	0.84	9.02	0.39	0.42	4.58	0.19
Mediterranean sea	0.75	15.97	1.90	0.39	8.72	0.99
Northern sea	0.87	6.22	0.50	0.44	3.57	0.26
Total			**7.86**			**3.97**

Table 3 - Atmospheric deposition to European seas for a sum of 22 PCB congeners under modelled emissions to air in year 2010 (ca.101t) and year 2020 (ca.50t).

4.2   Gamma-HCH

The second case study applies the same modeling methodology to two emission scenarios for gamma-HCH (Lindane).

The Baseline scenario for Lindane assumes atmospheric emissions only from European sources – being ca.86.6 t/y during the reference year of 2005 according to EMEP data (Gusev et al., 2006; Gusev et al., 2009). Note that this is a lower amount, comparing to what is considered under the BAU scenario in section 3.2, as in this exercise we omit the impact of the long range atmospheric transport. The latter is considered separately in the second emission scenario described below. In more details the emissions during baseline year of 2005 are concentrated in very few European countries as France (responsible for 47 % of the total emissions), United Kingdom (15.4 %), Spain (12.1%) and Portugal (9.1%).

The second scenario for Lindane is denoted as LRT (long range transport) and it aims to evaluate a future projection by targeting the situation in the year 2020. The LRT scenario suggests no emissions to atmosphere from any European origin due to the banning of this substance, but appositely to the baseline scenario it admits that Europe is affected by an unavoidable 'import" of Lindane caused by the trans-continental air transport. We assume that the "external" Lindane emissions amount to5.4 t/y according to recent EMEP figures (Gusev et al., 2006; Gusev et al., 2009). Moreover, we accept that the LRT emissions are homogeneously spread over the whole study area.

The physical-chemical properties used as input for the Lindane model runs are the ones already specified in the section 3.2.

Under the baseline scenario, consistently with the distribution of Lindane emissions, the atmospheric concentrations - mean = 60.5 pg/m3 and SD = 43.1 (see Figure 10a), express higher values close to the emitting countries. Instead, the atmospheric deposition - mean = 3.5 $\mu g/m^2$/year and SD = 43.1 (Figure 10b), and the mass in soil - mean = 2.05 $\mu g/m^2$ and SD = 4.16 (Figure 10c), have a slightly more even pattern due to the advective redistribution of Lindane in the European atmosphere.
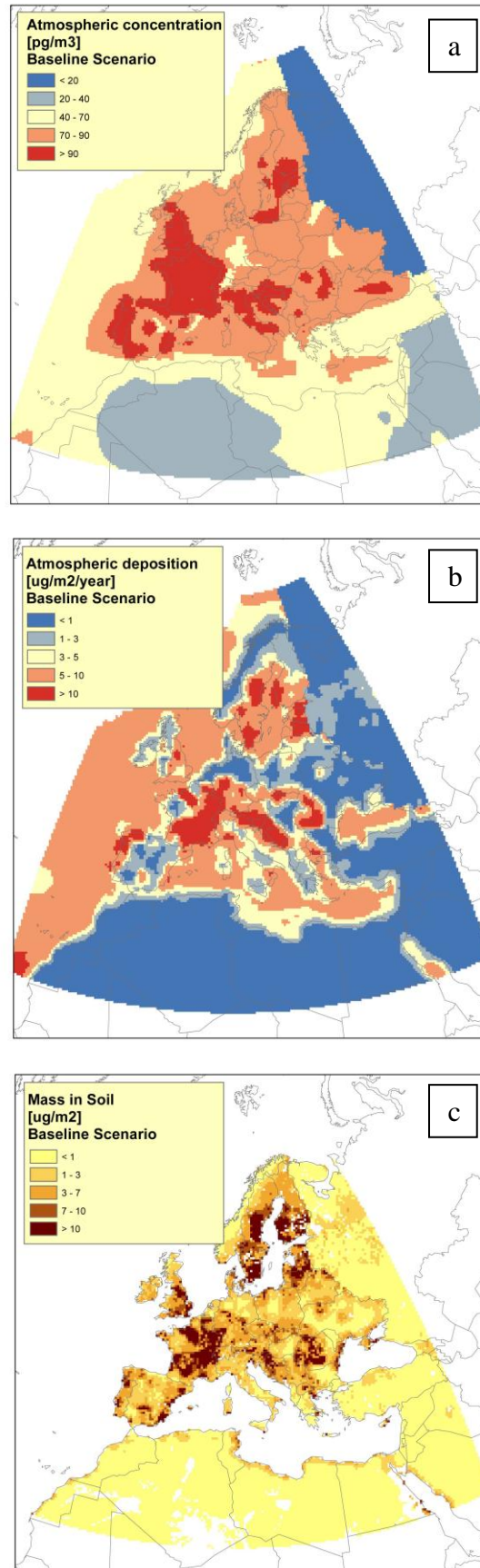
Figure 10 - Spatial distribution of atmospheric concentration (a), air deposition (b) and mass in soil (c) of gamma-HCH modelled under baseline air emission scenario (86.6t) for 2005.

The patterns and figures, observed in the baseline scenario, are changed in the LRT one. Accordingly, MAPPE forecasts the following mean values: atmospheric concentration - mean= 11.7 pg/m^3 and SD=12.6, atmospheric deposition - mean = 0.05 μg/m^2/year and SD = 0.06, and mass in soil - mean = 0.08 μg/m^2 and SD = 0.12, respectively. Despite of the homogeneous distribution of the emissions, unlikely to the baseline scenario, the higher Lindane mass in soil is mainly concentrated in the northern part of the study area, due to the precipitation and to the temperature factor.

Consequently, the estimated riverine sea load of Lindane is shown in the Table 4. In total the European seas are expected to receive 10.1 t under the Baseline scenario and 0.26 t in the case of LRT (97% reduction compared to the baseline option). The riverine loads represent 11.7% and 5%, respectively, from the total air emissions of Lindane. The highest river discharges are observed for Atlantic Ocean – in Baseline scenario 2.2 t (21.8% from the European total) and for LRT 0.06 t (23% from the European total); and Mediterranean Sea - Baseline 3.5 t (34.7% from the European total) and LRT 0.04 t (15.4% from the European total).

Similarly to the PCBs case, the Central European river basins are the main sources of the Lindane surface water pollution transported to seas (see Figure 11). For example, under the Baseline scenario Danube accounts for 12.6 % from the total export followed by Rhone (12.4% from the European total) and Rhine (10.2% from the European total). These proportions are slightly changed (Danube 10.3%, Rhine 5.8%, Wisla 4.3% and Rhone 2.3 % from the European total) when we considered only the trans-boundary atmospheric pollution over Europe according to the LRT scenario. All these explain the higher values of Lindane discharge as well to Black and Northern Sea under both scenarios for Lindane.

Load to seas [tonnes/year]	Emissions Scenario	
	Baseline	LRT
Atlantic ocean	2.196	0.059
Baltic sea	1.27	0.044
Black sea	1.584	0.057
Mediterranean sea	3.458	0.059
Northern sea	1.636	0.038
Total	10.144	0.257

Table 4 - Lindane riverine load to European seas considering air emissions under the Baseline (86.6t/y) and LRT (5.4t/y) scenarios.
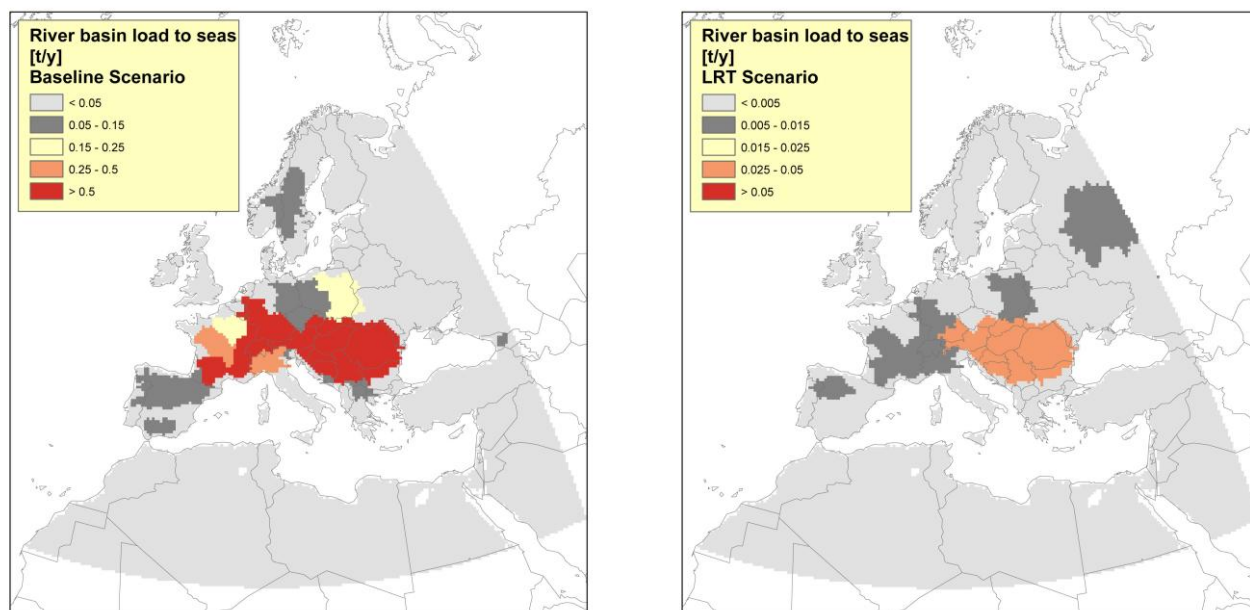
Figure 11 - Gamma-HCH riverine load to European sea per river basin considering air emissions under the Baseline (86.6t/y) and LRT (5.4t/y) scenarios.

Likewise for the PCBs, we concluded that, also in the case of gamma-HCH, the atmospheric deposition (for details see the Table 5) over the European sea basins dominate the river input to the coastal zone. For example, under the Baseline scenario, the total air deposition (50.2 t/y) is about 5 times higher than the riverine component of the sea load. However, in the case of LRT scenario, probably due to the very low amount of Lindane present in the atmosphere, the air deposition (in total 0.2 t/y) is very similar to the riverine load of Lindane.

Atmospheric deposition to seas [tonnes/year]	Emissions Scenario					
	Baseline			LRT		
	Average [g/km^2/year]	Range [g/km^2/year]	Sum [t/year]	Average [g/km^2/year]	Range [g/km^2/year]	Sum [t/year]
Atlantic ocean	5.71	21.04	28.75	0.018	0.235	0.09
Baltic sea	7.56	17.36	3.25	0.063	0.206	0.03
Black sea	4.55	8.79	2.10	0.027	0.237	0.01
Mediterranean sea	4.84	14.89	12.23	0.020	0.191	0.05
Northern sea	6.71	10.09	3.88	0.021	0.239	0.01
Total			**50.21**			**0.20**

Table 5 - Atmospheric deposition of Lindane to the European regional seas considering air emissions under the Baseline (86.6t/y) and LRT (5.4t/y) scenarios.

5. Conclusions

The improvement of MAPPE-Global atmospheric compartment, developed in this work, includes the quantification of the redistribution of chemical masses exported outside of each grid cell as a proxy of diffusive or advective transport, as well as the accounting of the eventual impact of the long range transcontinental transport in terms of globally "exported or imported" additional emissions. In addition, the present version of the model advances the surface water compartment by introducing a global map of travel times to sea which parameter was considered earlier as a fixed value for a given river basin. Besides, the soil-air gas exchange in the soil compartment was bettered by accounting differences in the global land cover. No further improvement is done in the marine part of the model.

The testing of MAPPE-Global for PCB153 and gamma-HCH allows concluding that, given its coarser spatial resolution (1x1 degree) and the simplicity of the employed modeling approach for advection, MAPPE-Global model is able to produce compatible results compared to observations or outcome of more refined models.

The estimated error level of MAPPE-Global model is about a factor of two, which suggests that the model could be considered as a tool for a screening or initial evaluation of chemical risk for POPs at global scale.

Potentially the outcome of the present improved version of MAPPE-Global could serve in the assessments of different policy options related to the EU Water Framework Directive (WFD) or Marine Strategy Framework Directive (MSFD) as well as to support the European sea conventions as HELCOM (Baltic Sea) (http://www.helcom.fi/), OSPAR (North-East Atlantic) (http://www.ospar.org/), MEDPOL (Mediterranean Sea) (http://www.medpol.unepmap.org/) and BSC (Black Sea) (http://www.blacksea-commission.org/main.asp).

The evaluation of the environmental distribution of 22PCBs after emission scenarios, considering the current status for the 2010 year and the future projection for the 2020 year, according to the MAPPE-Global model results, allows concluding that:

- The extended European area is expected to export to the coastal marine water about 3.7 t of 22PCBs in 2010 and 1.9 t in 2020, respectively. The observed reduction by 49% of the riverine load from year 2010 to year 2020 reflects the difference in 22PCBs emissions
- The entire riverine load of 22PCBs represents about 4% of their total air emissions.
- The most affected seas by river discharge of chemical pollutants, in both scenarios, are Mediterranean Sea (ca.35% from the total) followed by Northern (ca. 21.5% from the total) and Black sea (ca.19% from the total)

- During the year 2010, Rhine river was the top "exporter" of 22PCBs to European coastal zone (0.63 t; 16.8% from the total), followed by Danube (0.46 t; 12.3% from the total), Rhone (0.41 t; 10.85% from the total) and Po (0.22 t; 6.01% from the total). As expected, in 2020 the model forecasts a lowering of PCBs' riverine load; for this year the highest contamination by 22PCBs comes again from the basin of Rhine (0.32 t; 16.7% from the total)

- In total, the European seas are expected to receive by atmospheric deposition about 7.9 t of 22PCBs in 2010 and ca.4 t during 2020. This is two times more comparing to the entire riverine discharge of 22PCBs for the same years.

The analysis of the Lindane environmental distribution respecting the Baseline emission scenario - referred to the year 2005, and the LRT (long range transport) scenario - a future perspective for the year 2020, according to MAPPE-Global model, lead to following conclusions:

- The European seas are expected to receive in total 10.1 t under the Baseline scenario and 0.26 t in the case of LRT meaning 97% reduction compared to the baseline option.

- The entire riverine load represents 11.7% and 5% from the total amount of the air emissions of Lindane, respectively, for the Baseline and the LRT scenarios,

- The highest river discharge is identified for Atlantic Ocean – according to Baseline scenario 2.2 t (21.8% from the total) and in LRT case 0.06 t (23% from the total); and for Mediterranean Sea – as for Baseline 3.5 t (34.7% from the total) and LRT 0.04 t (15.4% from the total) scenario

- Under Baseline scenario Danube accounts for 12.6 % from the total riverine export of Lindane followed by Rhone (12.4% from the total) and Rhine (10.2% from the total). The figure is slightly changed (Danube 10.3%, Rhine 5.8%, Wisla 4.3% and Rhone 2.3 %) when only the trans-boundary atmospheric pollution over Europe according to the LRT scenario is considered

- Likewise for the PCBs, also in the case of gamma-HCH, the atmospheric deposition over the European sea basins dominates the river input to coastal zone. According to Baseline scenario, the total air deposition (50.2 t/y) is about 5 times higher than the riverine discharge to seas. However, in the case of LRT scenario, probably due to the very low amount of Lindane present in the atmosphere, the atmospheric deposition (in total 0.2 t/y) is practically equivalent to Lindane riverine load.

6. Annex

Since a detailed description of MAPPE-Global is provided in Pistocchi et al. (2011b) in this report we shall remind only the basic model features by presenting the mathematical formulation of the considered chemical fate and transport processes into the different environmental media.

6.1 Atmospheric compartment

Aerosol partitioning

The mass fraction ϕ (-) of chemical that is in aerosol phase is computed as:

$$\phi = \frac{10^{-2.91} K_{oa} OC}{1 + 10^{-2.91} K_{oa} OC}$$

where K_{oa} (-) is the chemical octanol-air partition coefficient, usually set to K_{ow}/K_{aw} while OC (kg m^{-3}) is the concentration of particulate organic carbon in the atmosphere. Respectively, the K_{ow} (-) is the octanol-water partitioning coefficient and K_{aw} (-) is the air-water partitioning coefficient (non-dimensional Henry's constant). The latter is calculated depending of the atmospheric temperature T *(K)* as:

$$K_{aw} = K_{aw_0} \exp(\gamma T)$$

where K_{aw_0} (-) is the air-water partitioning coefficient at reference temperature and γ (-) is the temperature-degradation coefficient.

Wet deposition

The wet deposition velocity K_{wet} (m s^{-1}) is computed from the annual average precipitation rate P (m day^{-1}) as:

$$K_{wet} = (S\phi + \frac{1}{K_{aw}}(1-\phi))\frac{P}{86400}$$

where S (-) is a scavenging factor usually set to *2*10^5*.

Particle dry deposition

The particle deposition velocity K_{part} (m s^{-1}) is computed from OC and the deposition flux of atmospheric particulate organic carbon F_{OC} (kg m^{-2} s^{-1}), as:

$$K_{part} = \phi \frac{F_{OC}}{OC}.$$

Gas absorption

The absorption velocity of atmospheric chemicals in gas phase depends on the type of ground surface.

The following categories of ground surface are presently considered in the model:

- agricultural or natural (bare) soil
- impervious surface (urban, sealed soil, etc.)
- desert or permanently frozen soil
- forest deciduous
- forest evergreen (broadleaves or conifers)
- water (lakes, reservoirs and rivers; oceans and seas).

Conventionally, the following absorption velocities are given for the three types of forest:

- deciduous: $v_{f,d}$= *0.036* m s^{-1}
- evergreen, broadleaved: $v_{f,b}$= *0.072* m s^{-1}
- evergreen, conifers: $v_{f,c}$= *0.0078* m s^{-1}

The above values are taken from MacLachlan and Horstmann (1998), as measured velocities on oaks (0.036 m s^{-1}) and spruce (0.0078 m s^{-1}) in Germany; in the case of evergreen broadleaved forest it is assumed that the speed is ca. 25%-50% higher than the one for oaks. These velocities are referred to chemicals such as dioxins or polychlorobyphenils, having a molecular weight of about 300 g mol^{-1}, and need to be rescaled for other chemicals.

Therefore, the absorption velocity on forest areas, $K_{gas, forest}$ (m s^{-1}) is specified as:

$$K_{gas,forest} = \left(0.036\,\frac{Dec}{100} + 0.0078\,\frac{Eve}{100}\left(1 - \frac{Bro}{100}\right) + 0.045\,\frac{Eve}{100}\frac{Bro}{100}\right)\left(\frac{300}{MW}\right)^{0.5}$$

where *Dec* is the percentage of deciduous forest cover, *Eve* is the percentage of evergreen forest, and *Bro* is the percentage of broadleaved forest.

The absorption velocity on soils, $K_{gas, soil}$ (m s^{-1}) is evaluated using a two-layer resistance model (Pistocchi, 2005):

$$K_{gas,soil} = \frac{D_a}{\left(\xi h_s + d_a\right)}$$

where h_s = 0.15 m is half of the soil layer thickness (set to 0.3m), ξ (-) is the tortuosity factor $\xi = \frac{\omega^{2/3}}{(\omega - \theta)^2}$; ω (-) and θ (-) are soil porosity and soil water content, d_a is the thickness of the laminar microlayer at the air-soil interface (which is assumed to be negligible compared to ξh), and D_a is the diffusion coefficient of the chemical in air (m^2 s^{-1}).

Then, assuming constant values for both porosity, set to 0.4, and soil water content, set to 0.2, the tortuosity coefficient simply equals to 13.6. The diffusion coefficient in air (m^2/s) can be estimated as Schwarzenbach et al., (1993):

$$D_a = 0.000025 \cdot \left(\frac{18}{MW}\right)^{0.5}$$

where 0.000025 m^2/s is the diffusion coefficient of H_2O in air.

Under these assumptions, $K_{gas, soil}$ (m s^{-1}) becomes

$$K_{gas, soil} = 0.0000123 \cdot \left(\frac{18}{MW}\right)^{0.5}$$

On impervious surfaces (e.g. urban, sealed soils) it is assumed that no absorption occurs. The same assumption was applied to deserts or permanently frozen land.

On water, the velocity of absorption $K_{gas, water}$ (m s^{-1}) is evaluated using a two resistance model (see Pistocchi, 2005 for details) in the form:

$$K_{gas,water} = \frac{v_a v_w}{v_a K_{aw} + v_w}$$

where v_a and v_w are the diffusion velocities (m s-1) in air and water, given by:

$$v_a = \left(\frac{18}{MW}\right)^{0.335} \left(0.002 \cdot u_{10} + 0.003\right)$$

$$v_w = \left(\frac{32}{MW}\right)^{0.285} \cdot \left(0.0000004 \cdot u_{10}^2 + 0.000004\right)$$

As a result, for each grid cell in the model, the gas absorption from atmosphere K_{gas} (m s^{-1}) is calculated as:

$$\mathrm{K}_{gas} = \mathrm{K}_{gas,water}\frac{w}{100} + \left(\mathrm{K}_{gas,forest}\frac{Dec + Eve}{100} + \mathrm{K}_{gas,soil}\left(1 - \frac{Dec + Eve}{100}\right)\right)\left(1 - \frac{Imp}{100}\right)\left(1 - \frac{w}{100}\right)$$

where w is the percentage of the cell that is water, and *Imp* the percentage that is impervious surface. Additionally, the spatial coverage of $K_{gas,forest}$ and $K_{gas,soil}$ respects the presence of the deserts or permanently frozen soils assuming there a zero value.

Degradation

The degradation processes in the atmosphere are specified by the degradation rate $K_{deg,a}$ (s^{-1}) as follows:

$$K_{\deg a} = \alpha_a \exp(\beta_a T)$$

where α_a (s^{-1}) and β_a (K^{-1}) are the degradation coefficients and temperature T is given in Kelvin degrees.

Atmospheric removal rate

In the expression for total K_{air}, the term for advection should be considered only for a single isolated emission which is an ideal extreme case.

The other extreme case is the situation when emissions occur in a uniform way around the Globe, thus, the advection may be neglected. In this case, one should consider K'_{air} no advection (d^{-1}):

$$K'_{air} = 3600 \cdot \left(\frac{(K_{part} + (1 - \phi)K_{gas} + K_{wet})}{ABL} + K_{\deg a}\right) \cdot 24.$$

Obviously, the real situations should be in between these two extremes.

Deposition

Atmospheric deposition rate Dep (d^{-1}) is the fraction of the atmospheric removal rate in a cell, which quantifies the air intermedia transfer and is computed as:

$$Dep = 3600 \cdot \frac{(K_{part} + (1 - \phi)K_{gas} + K_{wet})}{ABL} \cdot 24$$

Worth mentioning that similarly to the other multimedia box models the atmospheric part of MAPPE Global does not distinguish wind directions. This limitation is likely to underestimate the role of advection on the fate of the persistent organic chemicals. The improvement of atmospheric part of MAPPE-Global is detail commented in the main body of this report.

6.2 Soil compartment

Partitioning

In soil the chemical mass fractions in liquid R_{liq} (-) and solid R_{sol} (-) phases are computed as:

$$R_{liq} = \frac{\theta}{(K_d \rho + \theta + (\omega - \theta)K_{aw})}$$

$$R_{sol} = \frac{K_d \rho}{(K_d \rho + \theta + (\omega - \theta)K_{aw})}$$

where ω (-) and θ (-) are soil porosity and water content, ρ (kg l^{-1}) is the soil bulk density, and K_d (l kg^{-1}) is the chemical solid-liquid distribution coefficient. We assume constant values of porosity, set to *0.4*, and soil water content, set to *0.2*, as well as soil bulk density, set to *1.4* (kg l^{-1}). In addition, the spatial coverage of R_{liq} and R_{sol} respects the presence of the deserts or permanently frozen soils assuming there a zero value.

The chemical solid-liquid distribution coefficient is estimated as:

$K_d=0.41\ OC_s\ K_{ow}$

where OC_s (l kg^{-1}) is the organic carbon content of soils.

Erosion

The K_{er} erosion rate (m s^{-1}) is estimated as:

$$K_{er}=0.001\frac{SSY \cdot R_{sol}}{\rho} = 0.001\frac{SSY \cdot R_{liq} \cdot K_d}{\theta}$$

where *SSY* (kg m^{-2} s^{-1}) is the specific sediment yield and *0.001* is a conversion coefficient.

Volatilization

The volatilization rate K_{vl} (m s^{-1}) from the land is:

$$K_{vl}=K_{aw}\ K_{ga,soils}\ \frac{R_{liq}}{\theta}$$

where $K_{gas,soil}$ is the removal rate from soil excluding sealed, frozen or desert soils as is explained with reference to the air compartment.

The same formulas have been applied to the other types of land surfaces used in the model but accounting for their specific properties (for example substituting $K_{gas,\ soil}$ with $K_{gas,\ forest}$ in the formula for volatilization).

Runoff

The runoff rate K_Q (m d^{-1}) is meant here to include all removal mechanisms through water flows at the catchment scale, i.e. leaching to groundwater and direct runoff to surface water bodies; a further separation between these two mechanisms can be done on the basis of more refined data presently not available for the global scale. In the long term, as all recharge to groundwater is assumed to return to the rivers under steady state conditions, this simplification is equivalent to assuming that the decay of a contaminant through surface and groundwater pathways is the same. This assumption deserves more discussion and is simply given for granted in the current model description.

Then, taking into account the above assumptions, the runoff rate K_Q (m d^{-1}) is simply:

$$K_Q = 0.001 \cdot \frac{Q \cdot R_{liq}}{\theta} / 365$$

where Q is the annual discharge per unit area (mm y^{-1}).

Degradation

The degradation processes in the soil compartment are specified by the degradation rate $K_{deg,s}$ (s^{-1}) as follows:

$$K_{deg,s} = \alpha_s \exp(\beta_s T)$$

where α_s (s^{-1}) and β_s (K^{-1}) are the degradation coefficients and top soil temperature T (K) is assumed to be equal to the atmospheric one.

Water loads

The rate of chemical load in liquid form to surface water bodies, $Load_Q$ (d^{-1}), computed as a fraction of the emission to soils in each cell (emission being direct emission to soil, or deposition from the atmosphere, or the sum of the two), is given by:

$$Load_Q = \frac{K_Q}{h} .$$

Sediment loads

Similarly, the rate of chemical sediment load to surface water bodies, $Load_S$ (d^{-1}), computed as a fraction of the emission to soils in each cell (emission being direct emission to soil, or deposition from the atmosphere, or the sum of the two), is given by:

$$Load_S = \frac{86400 K_{er}}{h} .$$

The soil compartment of MAPPE Global is considered as sufficiently matured and presently no further development of this part of the model is planned.

6.3 Ocean compartment

Water-suspended solids partitioning

In the sea environment, the chemical partitioning between solid and liquid phase is calculated on the basis of the particulate organic carbon POC (kg l^{-1}) suspended in sea water. The POC is estimated according to Legendre and Michaud (1999), as:

$$POC = 10^{-6.79} \chi^{0.51}$$

where χ being the concentration of chlorophyll (μg L^{-1})[1].

Then, the mass fraction of chemical in particulate phase Φ' (-) is:

$$\phi' = \frac{0.41 K_{ow} POC}{1 + 0.41 K_{ow} POC}$$

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[1] Legendre and Michaud (1999) propose the equation log(POC)=2.21+ 0.51 log χ, with both POC and χ in mg m^{-3}. The term 10$^{-6.79}$ arises from converting POC into kg l^{-1}.

Volatilization

The velocity of volatilization from the sea surface to air, $K_{sea,\,vol}$ (m s^{-1}), is evaluated consistently with the two-resistance model for gas absorption, and is:

$$K_{sea,vol} = K_{gas,water} K_{aw}(1 - \phi')$$

Sinking with organic carbon

The velocity of sinking with organic particles, $K_{sea,\,settl}$ (m s^{-1}), is:

$$K_{sea,settl} = \phi' \frac{F'_{OC}}{86400 * POC}$$

where F'_{OC} is the sinking flux of *POC*. The F'_{OC} (Mg m^{-2} day^{-1}) is evaluated according to Baines et al. 1994 (see also Dachs et al., 2002)[2] as:

$$F'_{OC} = 10^{-6.91} \chi^{0.81}$$

Degradation

The degradation processes in the ocean compartment are specified by the degradation rate $K_{deg,w}$ (s^{-1}) as follows:

$$K_{deg,w} = \alpha_w \exp(\beta_w T)$$

where α_w (s^{-1}) and β_w (K^{-1}) are the degradation coefficients and the water temperature T is in Kelvin degrees.

Total ocean removal rate

Similarly to the air compartment, in the expression for total oceanic removal rate the term u/X accounts for intramedium advection transfer, and should be considered for an isolated emission which is an ideal extreme case.

The other extreme case is when emissions occur in a uniform way in space, and advection may be neglected. In this case, one should consider K'_{sea} (d^{-1}) no advection:

$$K'_{sea} = 3600 \cdot \left(\frac{K_{sea,settl} + K_{sea,vol}}{MLD} + K_{deg,w} \right) \cdot 24$$

Again, the real situations should lie in between these extremes.

No further development of the oceanic compartment of MAPPE Global is foreseen at this stage but obviously the further accounting of the ocean currents will improve the simulation of the contaminant fate in oceans and seas.

6.4 Inland water compartment

The inland water compartment is only accounted for as a "transitional" one, through which loads from soil are transferred to oceans, passing through an exponential decay process accounting for the inland retention time of the fresh water. The single parameter that accounts for possible retention is the average retention time of catchments τ (d).

Thus, the rate of load to oceans (d^{-1}) through the surface water, as a fraction of emissions (direct or indirect) occurring in soil, is given by:

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[2] Baines et al., 1994, propose the equation log(F'$_{OC}$)=2.09+ 0.81 log χ, with F'$_{OC}$ in mg m^{-2} day^{-1} and χ in mg m-3. The term 10$^{-6.91}$ arises from converting F'$_{OC}$ into Mg m^{-2} day^{-1} to be divided by POC in kg l^{-1} or Mg m^{-3}.

$$Load = \frac{1}{A} \int_A \left(Load_Q e^{-\frac{\ln(2)\tau}{dt_{50,w}}} + Load_S e^{-\alpha \frac{\ln(2)\tau}{dt_{50,s}}} \right) dA$$

where A is the catchment area, $dt_{50,\ w}$ (d) and $dt_{50,\ s}$ (d) are the half-lives of the chemical in dissolved and sediment phase, respectively, while α is the ratio of the residence time of sediments and the residence time of water in the catchment (see Pistocchi, 2008).

At the present stage of development of the MAPPE Global model, due to the practical difficulty to assign a value of α for each catchment, and considering the uncertainty in half lives in sediments and in *SSY*, we simply assume that all load with sediments is eventually delivered to the oceans, i.e. $\alpha=0$ meaning that the exponent in the second term in the above integral is just unit. Moreover, assuming that τ is a single value for each catchment and the half-life is a non-spatially variable but chemical specific constant, the above expression simplifies to:

$$Load = \frac{1}{A} \left(\int_A Load_Q \, dA \right) e^{-\frac{\ln(2)\tau}{dt_{50,w}}} + \frac{1}{A} \left(\int_A Load_S \, dA \right)$$

In practical terms, the expressions $\left(\int_A Load_S \, dA \right)$ and $\left(\int_A Load_Q \, dA \right)$ are computed in GIS as "zonal operators" with statistics "average" on zones given by the catchments considered in the MAPPE Global model.

The present development of the inland water compartment of the MAPPE Global is explained in the main body of this report.

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Abstract

MAPPE-Global modeling tool belongs to the group of the global box models for environmental fate and transport of POPs. The development of MAPPE-Global for atmosphere includes the relocation of chemical masses exported outside of each grid cell as a proxy of diffusive or advective transport, as well as the accounting of the eventual impact of the long range transcontinental transport in terms of globally "exported or imported" air emissions. In addition, the present version of the model improves the surface water compartment by introducing a global map of travel times to sea which parameter was considered earlier as a fixed value for a given river basin. Besides, the soil-air gas exchange in the soil compartment was bettered by accounting differences in the global land cover. No further improvement is done in the marine part of the model. The estimated error level of MAPPE-Global is about a factor of two, which suggests that the model could be considered as a tool for a screening or initial evaluation of chemical risk for POPs at global scale.

The verified MAPPE-Global is applied in practical assessments of chemical loads to the European regional seas. The PCBs case study relates to a sum of 22 congeners and considers two emission scenarios: first - the current status relative to the 2010 year; second – a future projection corresponding to the 2020 year. The total amount of 22PCBs released to air equals to 101.03 t for year 2010 and to 50.2 t for year 2020, respectively. The Baseline scenario for Lindane assumes, for the reference year 2005, 86.6 t atmospheric emissions only from European sources and omits the impact of the long range atmospheric transport. The second scenario for Lindane aims to targeting the situation in the year 2020. This scenario (denoted as LRT) suggests no emissions to atmosphere from any European origin due to the banning of this substance but admits that Europe is affected by an unavoidable 'import' of 5.4 t Lindane through trans-continental air transport.

According to the MAPPE-Global model, the extended European area is exporting to the marine water 3.7 t of 22PCBs in 2010 and 1.9 t in 2020, respectively. The observed reduction of 49% of the riverine load from year 2010 to year 2020 reflects the difference in the 22PCBs emissions. The riverine load represents about 4% of the total air emissions of 22PCBs. In both scenarios, the most affected seas are the Mediterranean Sea (ca.35% from the total) followed by Northern (ca. 21.5%) and Black sea (ca. 19%). It was estimated that the European seas receive by atmospheric deposition about 7.9 t of 22PCBs in 2010 and ca. 4t in 2020. This is two times more when comparing to the entire riverine discharge of 22PCBs for these years.

MAPPE-Global forecasts 10.1 t riverine sea load of Lindane under the Baseline scenario and 0.26t in the case of LRT meaning 97% reduction compared to the baseline option. The riverine loads represent 11.7% and 5%, respectively, from the total air emissions of Lindane. The highest discharges are observed for Atlantic Ocean – in Baseline scenario 2.2t (21.8% from the total) and for LRT 0.06t (23%); and Mediterranean Sea - Baseline 3.5t (34.7%) and LRT 0.04t (15.4%). For the gamma-HCH, likewise for the PCBs, it is found that the atmospheric deposition over the European seas dominate the river input to the coastal zone. Under the Baseline scenario, the total air deposition (50.2t/y) is about 5 times higher than the riverine component of the sea load. However, in the case of LRT scenario, probably due to the very low amount of Lindane present in the atmosphere, the air deposition (in total 0.2 t/y) is equivalent to the riverine load of Lindane.

Potentially the outcome of MAPPE-Global model could serve in the assessments of different policy options related to the EU Water Framework Directive (WFD) or Marine Strategy Framework Directive (MSFD) as well as to support the implementation of the European sea conventions as HELCOM (Baltic Sea), OSPAR (North-East Atlantic), MEDPOL (Mediterranean Sea) and BSC (Black Sea).

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