A GIS model-based assessment of the environmental distribution of γ-hexachlorocyclohexane in European soils and waters

P. Vizcaíno*,[1], A. Pistocchi

EC, DG JRC, Institute for Environment and Sustainability, Ispra (VA), Italy

An spatially-explicit multimedia modelling strategy was applied to describe the historical distribution of γ-HCH in European soils and surface waters.

Keywords:
γ-HCH
Lindane
Modelling
Environmental concentrations
Surface waters

A B S T R A C T

The MAPPE GIS based multimedia model is used to produce a quantitative description of the behaviour of γ-hexachlorocyclohexane (γ-HCH) in Europe, with emphasis on continental surface waters. The model is found to reasonably reproduce γ-HCH distributions and variations along the years in atmosphere and soil; for continental surface waters, concentrations were reasonably well predicted for year 1995, when lindane was still used in agriculture, while for 2005, assuming severe restrictions in use, yields to substantial underestimation. Much better results were yielded when same mode of release as in 1995 was considered, supporting the conjecture that for γ-HCH, emission data rather that model structure and parameterization can be responsible for wrong estimation of concentrations. Future research should be directed to improve the quality of emission data. Joint interpretation of monitoring and modelling results, highlights that lindane emissions in Europe, despite the marked decreasing trend, persist beyond the provisions of existing legislation.

1. Introduction

Hexachlorocyclohexane (HCH) is an organochlorine compound largely used as an insecticide since the 1940s in the whole world for all kinds of crops (Li et al., 1996), but also with non-agricultural purposes as reported by the World Health Organization (WHO) (IPCS, 1991). HCH has two commercial forms: technical HCH with a content of 8–15% of γ-HCH, and lindane, with 99% of γ-HCH. Technical HCH was phased out during the 1970s and 1980s (Breivik et al., 1999) and its usage has recently been reported to have ceased globally (Li et al., 2003). Since the 1980's, lindane is considered the dominant source of γ-HCH (Gusev et al., 2005a).

The application of lindane is mainly to soil as pesticide (Breivik et al., 1999), but its volatility and a sufficiently long atmospheric lifetime have lead to a global transport. The major process controlling removal rate of lindane in soils is volatilization. Due to its physico-chemical properties and its relatively high solubility and low polarity compared to other organochlorines, γ-HCH can be detected in all environmental compartments, including water, sediments, air and biota (Willett et al., 1998), where it tends to accumulate. Lindane enters surface water as a result of runoff from agricultural land. When released to water, lindane is not expected to volatilize significantly (IPCS, 1991; UNECE, 1998). Lindane is very stable in fresh water as well as in salt water environments. It is removed from the water column through secondary mechanisms, such as adsorption to the sediment or to fish through the gills, the skin or ingestion. Due to its toxic effects to wildlife and humans, lindane use was reduced since the late 1970s and severe restrictions are currently applied: in particular, lindane was listed in the Aarhus Protocol on POPs of the Convention on Long-Range Transboundary Air Pollution (CLRTAP) (UNECE, 1998), and its use was allowed only for six specific non aerial applications. Lindane has been recently considered for being listed in Annex A of the Stockholm Convention as a substance to be eliminated (UNEP, 2007). In Europe, use of lindane has been banned or severely restricted since the mid-1990s (IHPA, 2006). It has also been included in the List of Chemicals for Priority Action of the OSPAR Convention for the Protection of the Marine Environment of the Northeast Atlantic (OSPAR, 2007) and is listed under the European Water Framework Directive (WFD) (Pistocchi, 2005), as a priority hazardous substance (Decision No 2455/2001/EC of the European Parliament and of the Council, 2001).

γ-HCH has been extensively studied in Europe; estimates of emission, monitoring data and models of its fate and transport in different media have been produced throughout the years. In spite of this body of knowledge, however, our capabilities to quantify

global and European γ-HCH emissions remain rather limited. Large uncertainties in the information reported arise from ambiguities on whether reported use refers to the active ingredient or also diluting agents, to technical HCH or lindane, and from the fact that use of γ-HCH is sometimes estimated from total pesticide usage (Breivik et al., 1999). The contributions to total emissions of post-ban continuing use of lindane are also quite difficult to estimate, although these sources may significantly affect current environmental concentrations (Breivik et al., 2004). At present, the only comprehensive source of information at European scale is provided by the European Monitoring and Evaluation Programme (EMEP) (CEIP, 2009), consisting of official data reported by countries on emissions to atmosphere, and expert estimates (Pacyna et al., 1999). The latter are affected by high uncertainty, and may be even substantially modified from one year of reporting to another. According to information available at the time of preparing this paper (CEIP, 2009) γ-HCH emissions in Europe have experienced an important decrease in most countries since lindane ban in 1995, and France accounts for about half of the total emission to the atmosphere.

Finally, γ-HCH has long atmospheric residence time (Wittlinger and Ballschmiter, 1987; Breivik and Wania, 2002; Atkinson et al., 1999), and therefore air concentration in Europe may be affected by emissions occurring in remote regions (e.g. North America, Southeast Asia), where lindane is still used in agriculture (Tuduri et al., 2006) but where detailed and accurate information on emissions is equally lacking (Tuduri et al., 2006; Li, 2004).

γ-HCH air concentration and deposition have been included in many monitoring programs over the past years (Bartnicki et al., 2004; Jaward et al., 2004; EMEP, 2009; Buijsman and Van Pul, 2003; Van Drooge et al., 2004), highlighting that the main atmospheric removal mechanism is deposition, especially in wet form above land surfaces due to the relatively high solubility in water; dry deposition may be more important above sea surfaces (Buijsman and Van Pul, 2003). Concentrations show clear season patterns with highest concentrations during spring-summer that could be explained due to agricultural applications still allowed in some countries (Ma et al., 2003).

γ-HCH measurements in European soils are rare e.g. (Wenzel et al., 2002). However, γ-HCH has been subject to extensive monitoring in European rivers as one of the identified priority hazardous substances under the WFD (Directive, 2000/60/EC) and few databases were created (EIONET, 2009; Catalonian Water Agency database, 2009; von der Ohe, 2008; ARGE-Elbe monitoring programme, 1995–2005) showing also a seasonal distribution and a trend of decreasing of concentrations along the years. Oceans are considered to be a sink of HCH's coming both from atmospheric deposition and continental loads from rivers, and a long-range transport medium (Wania and Mackay, 1999); as such, they have also been intensively monitored (Lakaschus et al., 2002; Ilyina et al., 2006).

Several models have been used so far to describe environmental behavior of γ-HCH in Europe and reflect a clear decrease in lindane mean concentrations in different media along the last decades. Some of these models have been developed within specific projects at large scale and fine resolution, providing much higher accuracy of the fate of γ-HCH in specific environments. That is the case of the POPCYCLING-Baltic Model (Breivik and Wania, 2002), the CoZMo-POP model (Zukowska et al., 2005), or the Fantom model (Ilyina et al., 2006). These models refer to limited geographical areas where they have been shown to reproduce quite well the behavior of γ-HCH, but they require site specific environmental parameters and accurate emission data that at larger scale are generally not available with the level of detail achieved in the above quoted examples. With a different approach Dvorska et al. (Dvorská et al., 2009) use measured concentrations to identify potential atmospheric fluxes and emission sources in Central Europe. Other models developed with the more generic objective of assessing the fate of different POP's, have also been applied to describe γ-HCH: among others, the European variant of the BETR (EVnBETR) box model (Prevedouros et al., 2005), and MSCE-POP model (Gusev et al., 2005b), that represents to our knowledge the most advanced implementation. MSCE-POP model predicts concentrations of γ-HCH in atmosphere, rain, soil and ocean, and model results have been tested against monitoring data from EMEP stations in Europe, showing relatively good agreement for the atmospheric media (Gusev et al., 2007). However the complexity of the model has costs in terms of the flexibility and computational efficiency. Also, MSCE-POP model does not account for the fate of γ-HCH in continental surface waters, which is one of the highest concerns within the current policy framework.

In this paper we apply an alternative strategy to describe the multimedia distribution of γ-HCH in Europe. We compute spatial distributions of air, soil and water concentration for two different emission scenarios, corresponding to estimates for the year 1995 (when γ-HCH was used for agricultural purposes and applied mainly to soil), and year 2005, after the European ban of lindane.

We use a simple spatially-explicit multimedia modelling strategy, referred to as the MAPPE model Pistocchi, 2008, implemented using only built-in geographic information system (GIS) analytical capabilities; with respect to the previous application of the method, Pistocchi, 2008, we extend the calculation to the compartment of inland surface waters, using hydraulic geometry algorithms as presented in (Pistocchi, 2005). Concentrations in atmosphere, soil and water, are predicted from input maps of emissions, landscape and climate parameters considering physico-chemical properties of γ-HCH; results are consistently obtained as GIS maps.

Results and discussion are presented, highlighting potentials and limitations of spatially-explicit fate modelling of chemicals at the European scale as a supplement to detailed numerical modelling and, in certain circumstances, as a cheaper and more practical alternative.

2. Materials and methods

2.1. Emissions, γ-HCH properties, landscape and climate parameters

Emissions were derived from the estimates of total atmospheric emissions per country (CEIP, 2009) used by (Gusev et al., 2007) for the MSCE-POP model.

For the year 1995, when γ-HCH was still used as a pesticide, emissions were considered to follow the same mode of application as the one followed in the POPCYCLING-Baltic model (Breivik and Wania, 2002), i.e. 17.5% of total release of γ-HCH as applied to the atmosphere, 80%, to soil and 2.5%, to continental fresh water. Emissions to the different media were calculated from the estimated emissions to atmosphere. Also seasonal variations in the distribution of emissions according to

Table 1
Physical–chemical properties for γ-HCH and degradation rates considered for model simulations.

	Log Kow at 25 °C	LogKaw at 25 °C	MW (g/mol)	Kdeg air (h-1)	Kdeg soil (h-1)	Kdeg water (h-1)
MAPPE	3.7[a]	−3.81[b]	290.85[c]	5.27*E-04[d]	3.21*E-04[d]	7.91*E-15[e]
MSCE-POP[f]	3.9	−3.81		6.98*E-10	7.56*E-04	1.95*E-05
Literature-derived values	3.83[g]	−3.91[g]		3.0.2*E-04 [h]	(1.2E-04 – 2.1–E-03)[i]	

a (Harner and Bidleman, 1998); b (Kucklick et al., 1991); c (Mackay et al., 1997); d calculated from information in (Atkinson et al., 1999); e (Zukowska et al., 2005); f (Gusev et al., 2007) g (Xiao et al., 2004) h (UNEP, 2003) i (Mathur & Sana Jadu, 1973).

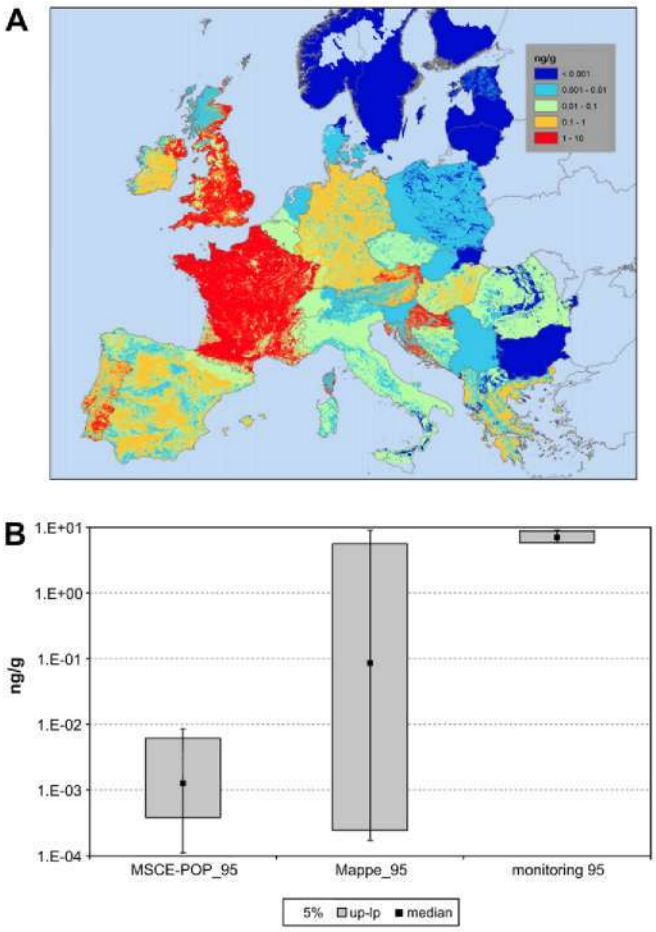

Fig. 1. (A) Estimated concentrations of γ-HCH in soils for the year 1995, in (ng/g); (B) comparison of ranges of soil concentrations (ng/g).

(Bartinickl et al., 2005), were considered: 10% of annual emission in February, 15% in March, and 25% monthly from April to June. We considered emissions to soil and water to follow agricultural land uses extracted from the extended CorineLandCover (CLC) 2000 (European Comission, 2000), as proposed in (Pistocchi et al., 2009).

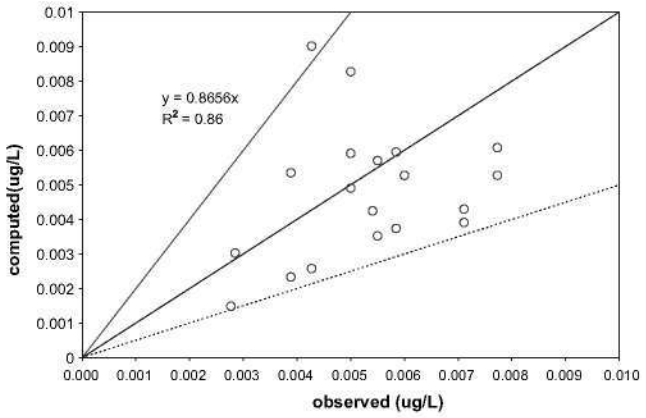

Fig. 3. Comparison of concentration in water of γ-HCH in 1995 in µg/l predicted by MAPPE and observed in monitoring stations (1:2 line and 2:1 factor lines are displayed).

Unlike 1995, for the year 2005, lindane was already banned as a pesticide: for this reason, differences not just in terms of absolute quantities but also in terms of mode of release into the environment should be considered. In the absence of more accurate information on the 2005 use profiles of γ-HCH, we assumed emissions to happen only to air, as in the case of the MSCE-POP model simulations (A. Gusev, 2009, personal communication). An alternative assumption would consider emissions following the same distribution as in 1995 (i.e. 17.5% to air, 2.5% to water and 80% to soil). This assumption seems rather conservative, since in 2005 it is likely that the use of γ-HCH as a pesticide is substantially reduced following ban or restrictions in Europe. We will discuss later how this assumption will be used to interpret monitoring data.

Details on emissions used in our simulations are included in the supporting information (Table S1 and Fig. S1 and S2).

Physical–chemical properties that determine environmental phase partitioning and degradation rates are functions of seasonally and spatially variable phase temperatures.

Table 1 summarizes physico-chemical properties for γ-HCH considered in our calculation, including partition coefficients, and degradation rate constants in air, soil, and water. In order to test model consistency and specifically intercomparability with the MSCE-POP model, physico-chemical properties used in MSCE-POP as well as adjusted values of these properties taken from literature-derived values, are included.

Landscape and climate parameters used in the calculations are thoroughly described in (Pistocchi et al., 2006). Likewise, a complete description of the MAPPE modelling strategy is available in (Pistocchi, 2008, 2005).

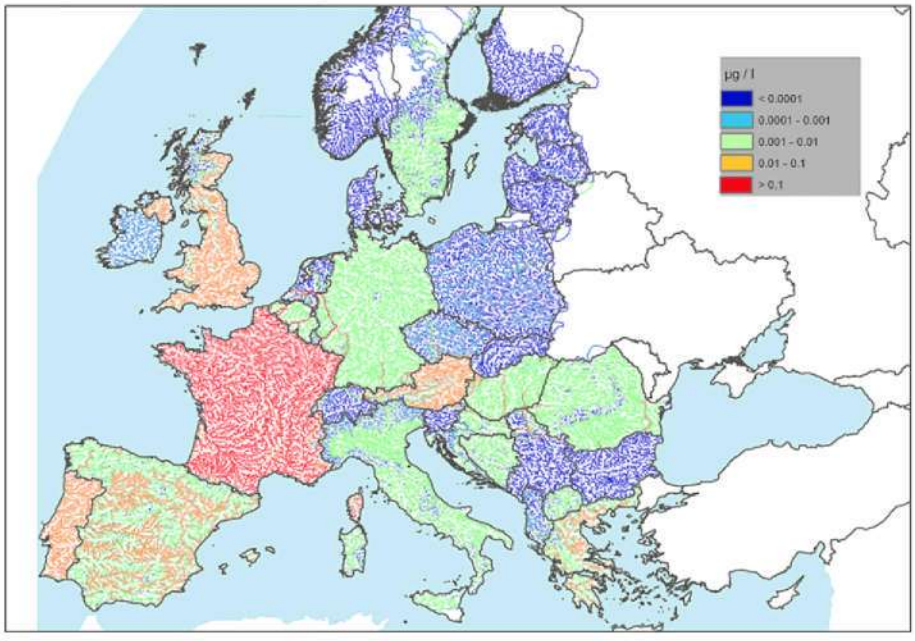

Fig. 2. Estimated concentrations of γ-HCH in continental surface waters for the year 1995 in (µg/l).

2.2. Model calculations

The model operates under steady state conditions, however different time to steady state in the different media should be accounted for; it is assumed that the time to steady state in atmosphere is shorter than 1 month and monthly variations are described in terms of successions of steady states. In surface water, transition from concentrations of the month before to the next are computed by using an exponential decay where the decay rate embeds all decay mechanisms (see details of the algorithms in the following paragraphs). For soils, where the response time is longer, a full transient analytic solution is used which tracks changes from one month to the next by considering piecewise constant parameters during each month.

The model computes concentrations in air using a stationary source–receptor relationship approach (Pistocchi, 2008; Vizcaíno and Pistocchi, in preparation). A complete description of the method is included in (Roemer et al., 2005). Deposition is computed by multiplying atmospheric concentrations by an appropriate deposition rate; average concentration in the soil top 20 cm is computed in cyclostationary conditions allowing to account for the month of the year in which emissions occur, taking into account degradation, advection with runoff and erosion, and volatilization; although emissions in the past may affect concentrations at a given time, the overall persistence of γ-HCH in air, soil and water is relatively short (average calculated values of half life times of few hours, three months and hundred days respectively), so that a steady state calculation can be acceptable as a first approximation of annual average concentrations (Pistocchi and Galmarini, 2008). In order to test the relevance of past history in concentrations of lindane in soils we simulated historical evolution of mass of lindane considering dynamic or steady state conditions. Results show that average concentrations don't change much and consequently a steady state calculation would be acceptable (Fig. S3 of Supporting information). Concentrations in continental water were calculated adding loads from direct water emissions, atmospheric deposition, and leaching and runoff from soils. γ-HCH mass discharge in rivers was computed according to a plug flow model with degradation and volatilization according to the algorithms discussed in (Pistocchi, 2008).

Concentrations in seawater far from the coast were calculated as due to deposition from the atmosphere, while loads from inland water were converted into coastal water concentrations using the conventional box model suggested in the European Technical Guidance Document on risk assessment (European Commission, 2003), which assumes a coastal mixing zone of 40 km by 10 km and 10 m depth, alongshore current of 3 cm s^{-1}, and dispersion coefficient of 50 m^2/s. With this assumption, it is possible to convert loads to seawater into concentrations through a conversion coefficient of 1.4×10^{-4} s/m^3.

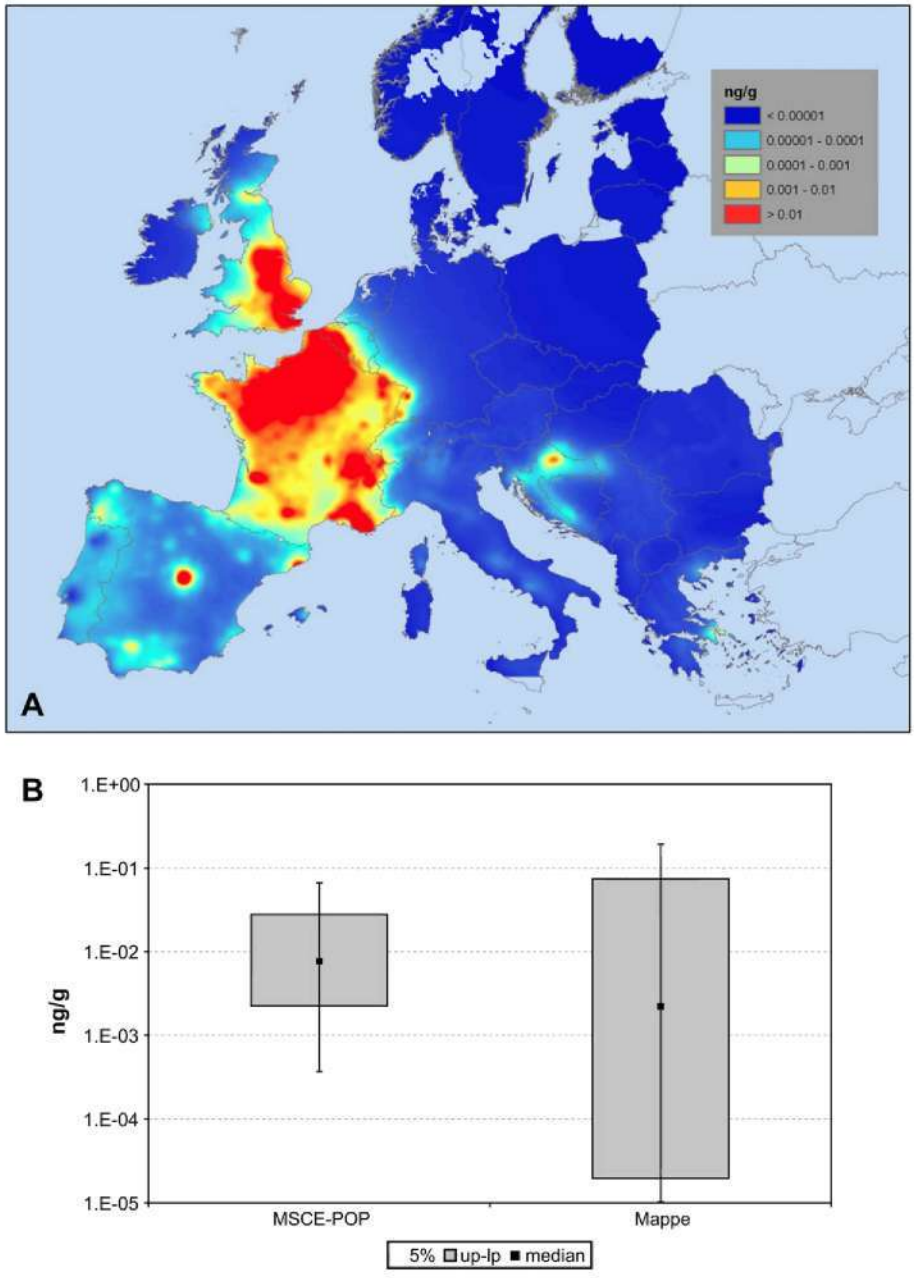

Fig. 4. (A) Estimated concentrations of γ-HCH in soils for the year 2005, in (ng/g); (B) comparison of ranges of soil concentrations (ng/g).

2.3. Model evaluation

Results from our model were compared with monitored inland and seawater concentrations (EMEP, 2009; Buijsman and Van Pul, 2003; Wenzel et al., 2002; EIONET, 2009; Catalonian Water Agency database, 2009; von der Ohe, 2008; Lakaschus et al., 2002; Ilyina et al., 2006; Prevedouros et al., 2005) of which an extensive database was compiled for the different compartments. A map representing monitoring stations in Europe is included in the supporting information (Fig. S4). In the soil compartment, however, we did not find many data for comparison, as it will be discussed below.

Results of concentrations in soil and seawater were compared with the ones of the MSCE-POP model (MSCE-E, 2009 outputs), taken as a benchmark.

3. Results and discussion

3.1. γ-HCH in the atmosphere

In the present paper, we focus on the soil and water compartments only; results for the atmosphere have been presented elsewhere (Vizcaíno and Pistocchi, in preparation) and are only briefly recalled here for completeness. Air concentrations of γ-HCH are in relatively good agreement with EMEP monitoring station data and MSCE-POP model results, and shows a range of 0.01–0.1 ng/m^3 for the year 1995, and 0.001–0.01 ng/m^3 for the year 2005. In 1995, the spatial distribution follows emissions related to agricultural intensity due to the fact that γ-HCH was primarily used in agriculture. In 2005 lindane was already banned or restricted in most European countries, and therefore emissions were first of all computed as proportional to population density to account for all other non-agricultural uses. The calculation was repeated with emissions following agriculture in 2005 as well, yielding to slightly better performance of the model. This may be due to still rather important residual agricultural uses in 2005, as discussed in (Vizcaíno and Pistocchi, in preparation). A clear effect of background concentrations deriving from extra-continental emissions was highlighted. Given the reasonable correspondence with atmospheric concentrations predicted by MSCE-POP and monitored by EMEP for both years, it may be said as a first approximation that the atmospheric part of γ-HCH fate is predicted reasonably well, despite the limited knowledge about emissions.

3.2. γ-HCH in soil and water, scenario 1995

Mass in soil in 1995 is controlled by direct emissions to soil, and follows agriculture intensity (Fig. 1) with high interannual variations

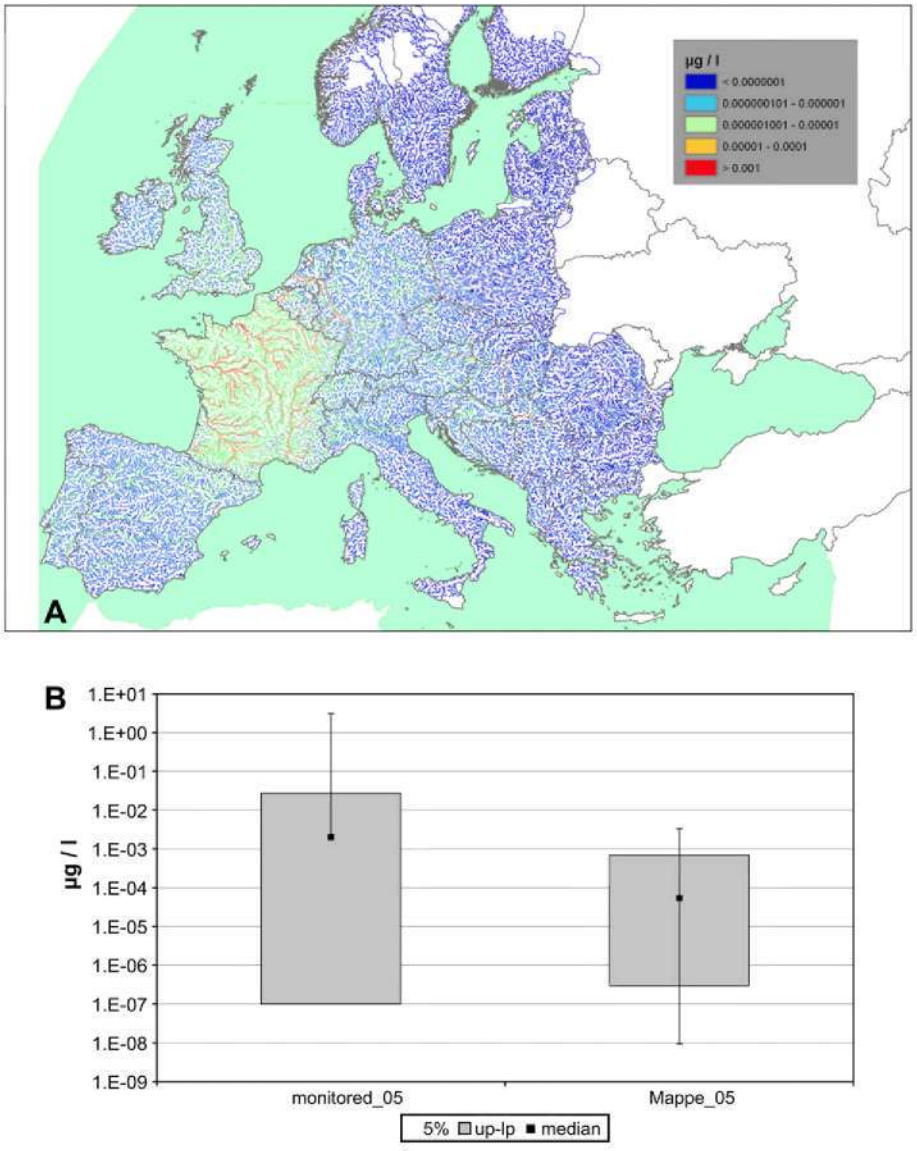

Fig. 5. (A) Estimated concentrations of γ-HCH in continental surface waters for the year 2005 in (µg/l); (B) comparison of ranges of water concentrations (µg/l).

due to differences in emission along the year. Our predicted annual average values of soil concentration of γ-HCH are in the range of 10^{-3}–10 ng/g with median of about 0.1 ng/g, and upper values similar to those reported by (Wenzel et al., 2002), referred to a single location where some contamination from γ-HCH usage nearby was observed in forest soils with high organic carbon content. Concentrations predicted in 1995 are also compatible with values ranging from 1 to 10 ng/g reported elsewhere for soils in Europe (INCHEM dataset, 2008). When compared to the MSCE-POP model results, our predicted concentrations have median values around one hundred times greater. These discrepancies are likely due to the fact that MSCE-POP model considers only atmospheric emissions, ignoring direct γ-HCH emission to soil, and therefore, the only input to soil is deposition. In fact, emissions to soils considered for 1995 by the MAPPE model are around 100 times greater than results of deposition (see Fig. S5 in the Supporting information). Moreover, at locations where MAPPE considers no direct emissions to soils (i.e. non-agricultural land uses), concentrations are predicted consistently with MSCE-POP (see Fig. S6 of Supporting information).

Fig. 2 presents the maps of concentration of γ-HCH in continental surface waters derived from the MAPPE model. In 1995, advective runoff losses from soil is the major process that controls water concentrations, as expected due to the high emissions of γ-HCH to agricultural soils and its physical–chemical properties. The MAPPE model estimates were compared with available monitoring data for 1995 on River Elbe in Germany (25 sampling points) (ARGE-Elbe monitoring programme, 1995–2005). A good correlation between the modelled and observed water concentrations is obtained ($R^2 = 0.86$), accompanied by the reasonable correspondence in terms of orders of magnitude (for most sites the differences were within the factor of two, see Fig. 3), and average values (the ratio between the mean computed and observed concentration is about 0.87).

3.3. γ-HCH in soil and water, scenario 2005

In 2005 γ-HCH was evaluated in the first instance according to the assumption of only atmospheric emissions following population density distribution, since lindane was already banned for agricultural use and the only input is supposed to come from residual uses of the chemical. Based on these assumptions, computed concentrations and patterns of distribution of γ-HCH in soils presented in Fig. 4, are controlled by atmospheric deposition. The mappe model provides estimates well in line with the MSCE-POP model, although with a wider range of variation as for the 1995 scenario, and lower minimum values of concentrations. These same patterns are observed in ranges of atmospheric deposition (see Fig. S7 of the Supporting information), with also same spatial distribution. Differences in predictions of extreme values of deposition between both models can be explained by the differences in calculation of total deposition, particularly, MAPPE overestimates wet deposition, and underestimates dry deposition with respect to MSCE-POP model.

Spatial distribution of γ-HCH in 2005 is more homogeneous than in 1995 due to the "smoothing" effect of atmospheric deposition that dilutes chemical masses over larger areas with lower gradients. Moreover, as in 2005 γ-HCH emissions are supposed to come from non-agricultural usages, and they are assumed to be proportional to human population density, higher values are predicted in the most densely populated areas for 2005, while for 1995 the hot spots followed agricultural intensity. At a finer scale, the model reflects the importance of organic carbon content of soils for the sorption of γ-HCH (Wania and McLachlan, 2001), with higher values of mass in soils in organic-rich terrestrial areas such as forested regions or peats. Median values are in the order of magnitude of 0.001 ng/g, or 100 times less than in 1995.

Concerning surface water, there is an impressive two to three orders of magnitude reduction in predicted concentrations between 1995 (Fig. 2) and 2005 (Fig. 5A), which is a direct consequence of the assumption of no direct emissions to soils or waters in 2005. In this case the main source for γ-HCH in water is direct deposition, which yields a smoother spatial pattern similar to the case of soil concentration. The relatively homogeneous deposition to water yields a rather small spatial variation of predicted concentrations, and much lower absolute values than would derive from direct emissions to water and runoff from soil.

However, this distribution of predicted concentrations does not correspond to observations at monitoring stations for 2005 (EIONET, 2009; Catalonian Water Agency database, 2009; von der Ohe, 2008; ARGE-Elbe monitoring programme, 1995–2005)

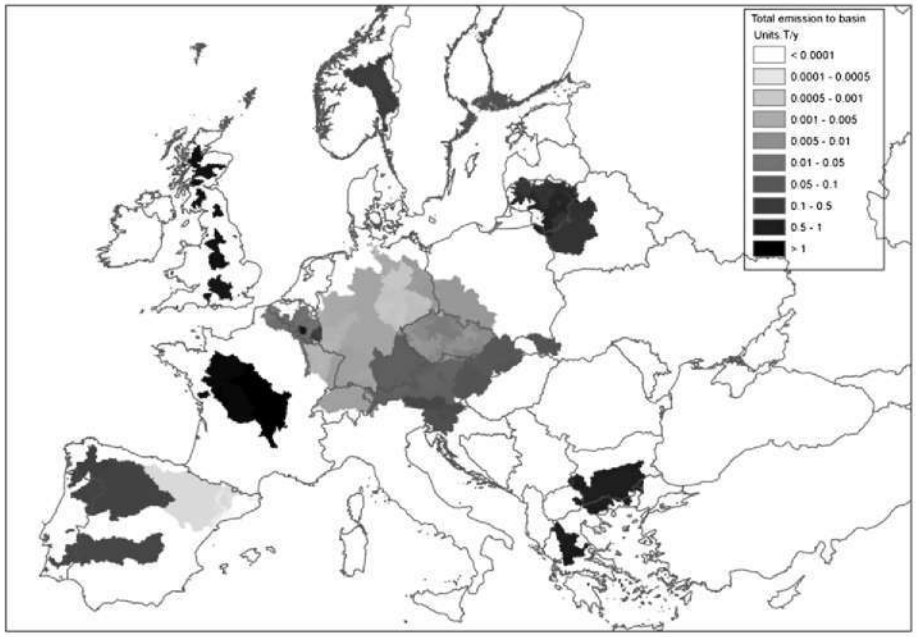

Fig. 6. Estimated emissions of γ-HCH to basins for 2005.

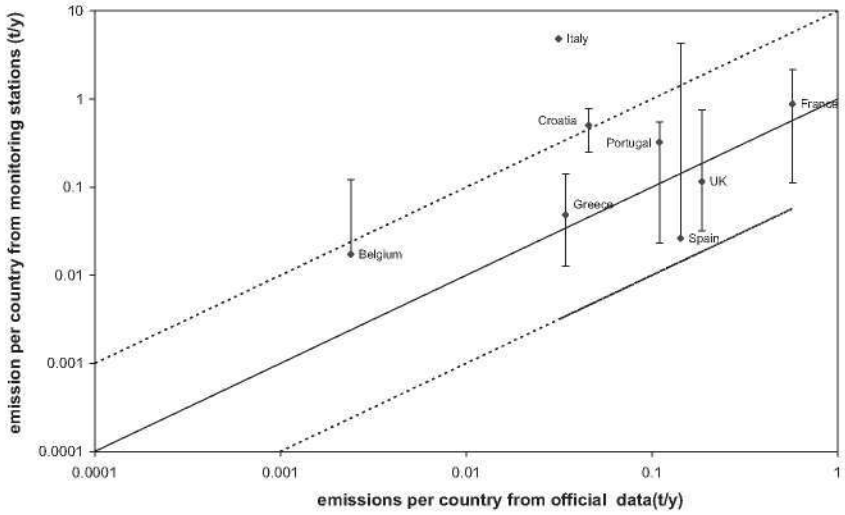

Fig. 7. Comparison of total emissions of γ-HCH to water per country (t/y) estimated from data of concentration in monitoring stations and total emission to water per country (t/y), estimated from data of total emissions in 2005 (Table 1 in Supporting information). 1:1 and a factor 10 lines are displayed.

(405 sampling points distributed throughout Europe) as shown in Fig. 5B, which are at least one order of magnitude higher.

As in 1995 the model was predicting reasonable concentrations, and in 2005 there is agreement with the MSCE-POP model for soil and atmospheric concentration, the underestimation in modelled results in 2005 was thought to owe to an underestimation and wrong distribution of emissions more than to model limitations.

In order to test this hypothesis, we used a very simple inverse modelling approach starting from data of concentrations in monitoring stations. By multiplying the value of water discharge used in our model (Pistocchi and Pennington, 2006), at each monitoring point by the corresponding measured concentration, we obtained an estimate of the mass flow of chemical through the measurement point. It is reasonable to treat γ-HCH as a conservative chemical as a first approximation since γ-HCH degrades in water within years (Table 1), whereas the residence time of water within the basin is often of the order of days. Consequently, we assigned mass flow through the measurement point to the whole contributing catchment upstream the corresponding point, and estimated overall emission in the catchment (Fig. 6). In order to derive, values of total emission to water per country, we divided each value of overall emission to catchments by the effective area, (where direct emissions to water occur) of the corresponding catchment within the country, assuming direct emissions to water occur only related to agriculture, and then multiplied by total effective area in the country. This way we obtained a range of values of total emissions for each country. If we compare these ranges of emission with the emissions to water for 2005, estimated from the atmospheric emissions under the assumption that the ratio is still 2.5%: 17.5% as for 1995, we find a generally reasonable agreement (Fig. 7) though our algorithm tends to overestimate emissions by overestimating agricultural areas where lindane is still emitted. This supports the hypothesis that, in 2005, γ-HCH emissions are not purely atmospheric, and may occur in particular to the water compartment.

We used this scenario of emissions distributed among the different media as for the year 1995 and following agriculture intensity to recalculate soil and water concentrations. This is clearly an "extreme" scenario that assumes γ-HCH emissions to have been

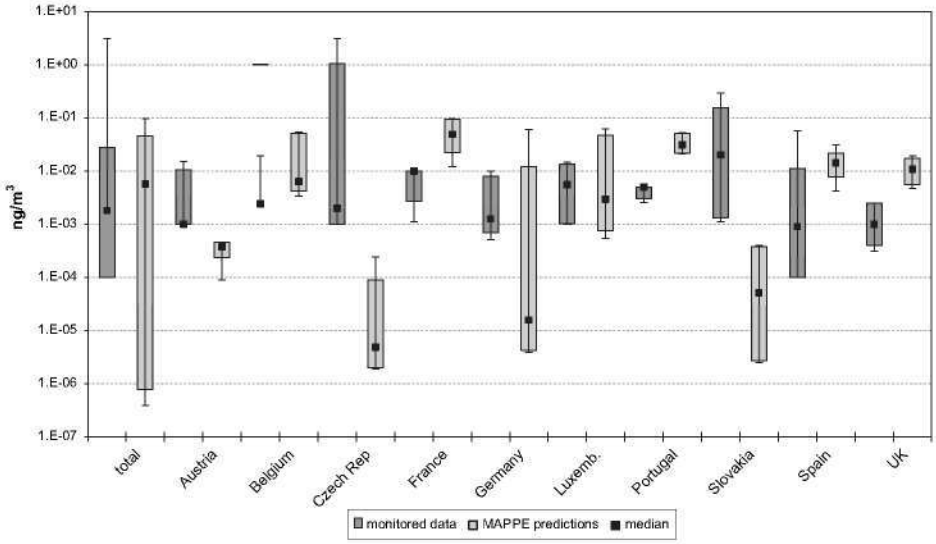

Fig. 8. Comparison of values of concentration in water (ng/m^3) predicted with the MAPPE model, according to the new values of emission estimated, and values of concentration measured in the monitoring stations.

reduced while maintaining the same modes of use, which should not the case thanks to the introduction of several restrictive measures in Europe. Synthesis of results of concentration in soils is included in the Supporting information (Fig. S8). In this way, we obtain higher values than in the scenario with emissions to the atmosphere only, and patterns of distribution similar to those derived in 1995. By comparing values of concentration in water predicted with the MAPPE model according to the new scenario of emission, and concentrations measured at the monitoring stations (Fig. 8), it seems that the model tends to underestimate concentrations in countries that report null emissions (Austria, Czech Republic, Germany Luxembourg, Slovakia), while overestimates in countries still declaring emissions (Belgium, France, Portugal, Spain, UK). These results observed also would show that concentrations in surface water in a specific place are dependent of to the basin better than the country where this place is located. Yet, the overestimated values are more in agreement with observations in terms of orders of magnitude and ranges of concentrations. In general, this better match supports the hypothesis that emissions of γ-HCH are not only to the atmosphere, despite the ban of the substance for agricultural use. A large uncertainty in the estimation of emissions still persists, which hampers further refinement of fate and transport models.

3.4. γ-HCH in seawater

Fig. 9 presents maps of seawater concentration computed as a consequence of atmospheric deposition only, neglecting riverine input to the sea, according to the algorithms used in (Pistocchi, 2008). Concentrations follow the pattern of atmospheric deposition presented in (Vizcaíno and Pistocchi, in preparation) with median values in the order of magnitude of 0.01 ng/l in 1995 and 0.001 ng/l in 2005, but high differences in ranges of concentrations between the different sea zones (as shown in Fig. S9 of Supporting information). Our predictions underestimate MSCE-POP predictions and existing monitoring data (Lakaschus et al., 2002; Ilyina et al., 2006) within one order of magnitude in 1995, and two orders of magnitude in 2005 (Fig. 10). MAPPE evaluates

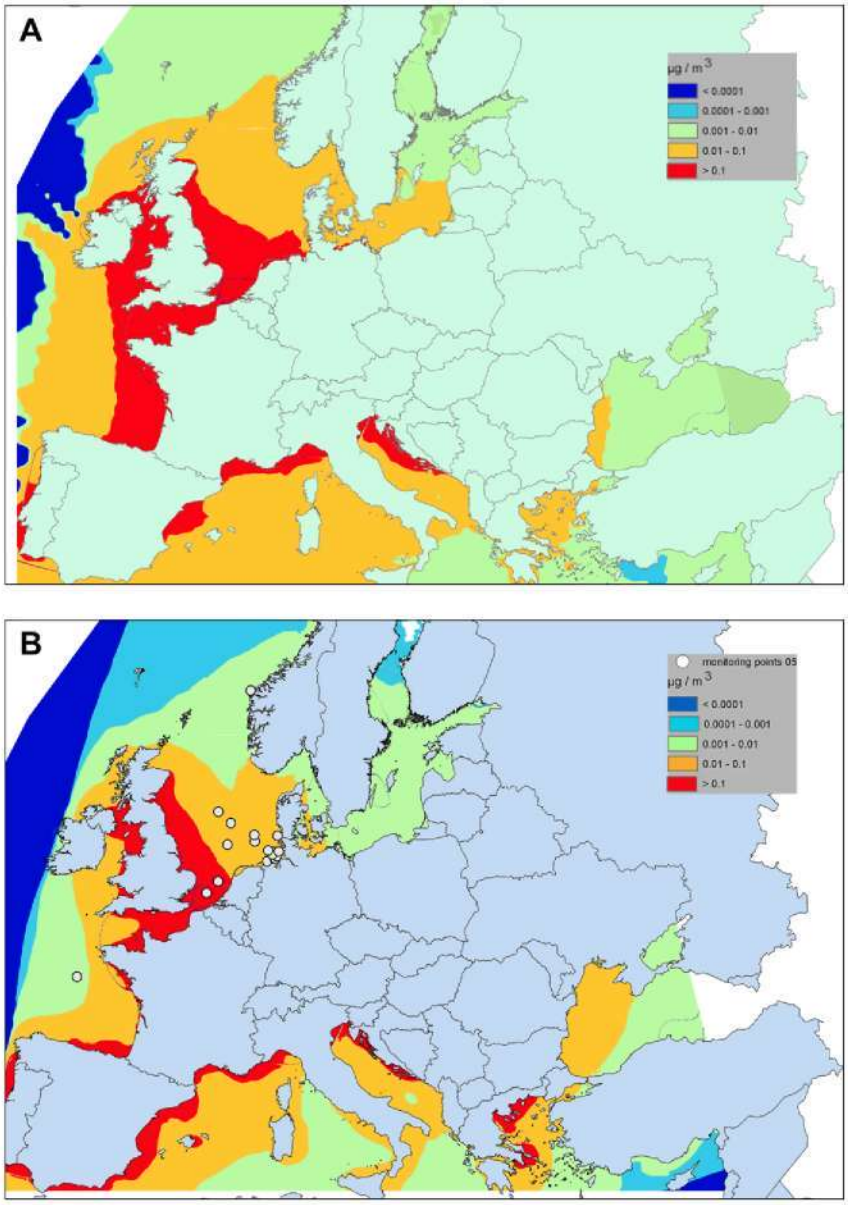

Fig. 9. Estimated concentrations of γ-HCH in ocean waters for the year 1995 (A) in (µg/m^3) and 2005 (B) in (µg/m^3).

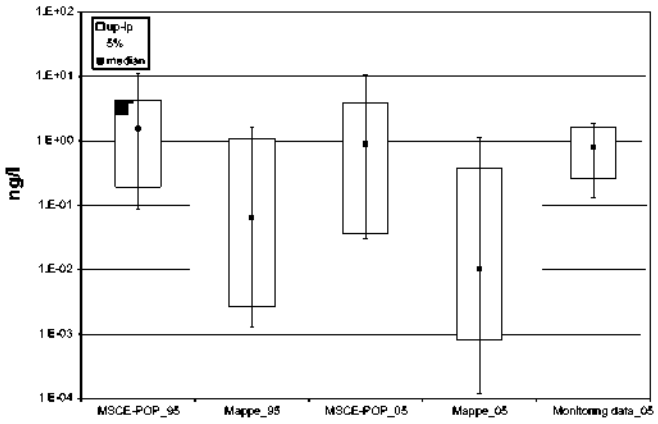

Fig. 10. Ranges of values of concentration of γ-HCH in ocean, from values predicted by MSCE-POP, Mappe models and monitoring data, in 1995 (left) and 2005 (right).

concentration in the sea mixing depth with average values of 60 m, whereas monitoring data were sampled out at 11 m (Lakaschus et al., 2002) and 5 m (Ilyina et al., 2006) depth (no information about MSCE-POP model parameterization was available), which would explain up to one order of magnitude in the underestimation. On the other hand, from the comparison of estimated deposition data for the two models available for year 2005, underestimation can be partly explained by the observed underestimation in MAPPE calculations (Pistocchi and Galmarini, 2008) of atmospheric dry deposition, the dominant removal pathway above sea surfaces (Van Jaarsveld et al., 1997), with respect to MSCE-POP calculations. This underestimation is more evident in areas where wet deposition is negligible, due to lower values of precipitation, as it is the case of Mediterranean, Baltic and Black Seas (see Fig. S9 of Supporting information). Also, our calculation does not take into account the transport of POPs with ocean currents, which may be important in remote areas. Finally, background values of contaminant due to past emissions or coming from remote sources were not considered in MAPPE calculations, although that would not explain the misestimating since total decay rate of γ-HCH in sea presents average values lower than one year (total decay rate is controlled by settling and volatilization, more than by degradation).

Another reason for the mismatch between predicted concentrations in seawater and monitoring data can be in neglecting riverine input, as is the case of both the MSCE-POP model, and MAPPE. To assess the importance of riverine loads, we converted the values of loads computed by MAPPE into concentrations in coastal waters according to the European Technical Guidance Document on risk assessment (European Commission, 2003) as explained above. Values of concentrations computed are up to 10–100 $\mu g/m^3$ for 1995, and 1–10 $\mu g/m^3$ for 2005 (Fig. S10 of Supporting information for details). The magnitude of these values, especially significant for confined seas, show the importance of considering loads from rivers in total concentration in oceans.

4. Conclusions

A spatially-explicit chemical fate model MAPPE is presented, which enables estimating the spatial distribution of γ-HCH in Europe with reference to a given emission scenario. It only uses simple GIS calculations based on the knowledge of the physico-chemical properties of the contaminant, and climate and landscape parameters maps, but results are comparable with those produced through complex simulation models such as MSCE-POP. The MAPPE model demonstrates the potential of GIS calculations to support chemical fate and transport assessment in a simplified way and with spatial detail as high as allowed by the input data available. The model is extremely flexible and can be easily adjusted to reflect better understanding of chemical properties such as partitioning and degradation, and better representations of landscape and climate variables. Nowadays more and more frequently updated by remote sensing acquisitions and sectoral studies. Moreover, with respect to existing models, it is capable of estimating the spatial distribution of γ-HCH in continental surface waters, which is, to our knowledge, the first attempt in this direction at pan-European level, and a useful effort considering that lindane is listed as a priority substance under the WFD (Directive, 2000/60/EC). The results for 1995 seem fairly realistic; the assumption of full implementation of the ban of lindane in 2005, leaving residual usages of this chemical with atmospheric emissions only, does not provide realistic soil and water concentrations. An emission scenario similar to 1995 for what concerns the distribution of the modes of entry, but with reduced emissions, appears more realistic and compares favorably with observed concentrations in orders of magnitude, although with large discrepancies concerning the regional distribution of emissions. These seem to be the largest source of error in producing regional estimates of γ-HCH distribution. We attempted a back-analysis of monitored concentrations, yielding reasonable estimates of emissions over monitored catchments and suggesting that further research in this direction may lead to a better characterization of γ-HCH emissions in Europe.

In the case of ocean concentrations, predictions with the MAPPE approach are comparable in accuracy with the ones of MSCE-POP for open seas as North Sea or Atlantic Ocean, and provide a lower and upper range of values through considering direct atmospheric deposition and riverine inputs, respectively, which overall encompass the observed ranges of concentrations. Accurately predicting concentration patterns in seawater entails the consideration of background values of contaminant and river inputs, and the development of a more sophisticated seawater transport model, as successfully developed e.g. for the North Sea (Ilyina et al., 2006). Nevertheless, presented approach provides a quick and flexible estimate capturing general trends in the phenomena. In general, spatially-explicit models such as the MAPPE approach may be useful and of practical interest in the assessment of policies at continental scale such as the European WFD (Directive, 2000/60/EC), since they provide a quick, flexible, simple and inexpensive calculation of spatial patterns and orders of magnitude of concentrations in different emission scenarios. Future research on will consider potentials for its synergic use with remote sensing and GIS data sets to assess spatial distributions of chemical risk for human health and ecosystems These calculations enable checking the consistency between observations, emission inventories and model assumptions, in an iterative process aimed at gradually refining our understanding of the fate of chemicals of concern.

In view of these results, it is essential to improve the quality of chemical emission estimates, seeking accurate information in terms of quantities emitted, and their mode of release to the environment. We advocate that improved emission estimates, rather than refinements in model calculations, are expected to provide substantial improvements in the understanding of chemical fate of pollutants.

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Appendix. Supporting information

Supporting information associated with this article can be found in the online version at doi:10.1016/j.envpol.2010.07.018.

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