Spatial differentiation of chemical removal rates from air in Life Cycle Impact Assessment

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10   ABSTRACT

11   *Background, aim and scope* Spatial differentiation is a topic of increasing interest within Life Cycle Assessment
12   (LCA). For chemical related impacts, in this paper we evaluate the relative influence of substance properties and of
13   environmental characteristics on the variability in the environmental fate of chemicals using an advanced, spatially
14   resolved model. The goal of this study is to explore spatial distribution and spatial variability of organic chemicals,
15   assessing the variability of the removal rate from air with a multimedia spatially explicit model (MAPPE Global)
16   with a resolution of $1°*1°$ degree. This provides basis to help identify chemicals for which spatial differentiation
17   will be important in life cycle assessments, including whether differentiation will have added benefits over the use
18   of global generic default values, such as those provided by the USEtox model.

19   *Methodology* A methodology was developed to explore spatial distribution and spatial variability of the fate of
20   organic chemicals. Firstly, guidelines were developed to assign a hypothetical spatial distribution to chemicals
21   which were clustered on the basis of their physical-chemical properties and persistence. Secondly, a test set of 34
22   representative organic chemicals was used to run MAPPE Global and USEtox model. The results of MAPPE Global
23   were used to highlight spatial variability of removal rate from air amongst different chemicals and their related
24   patterns of variability. A comparison between USEtox and MAPPE Global removal rates from air was performed for
25   each chemical in order to highlight whether spatial differentiation is relevant for the assessment or not.

26   *Results and Discussion*, Hypothetical spatial distribution of chemical fate was assigned to each combination of
27   physical-chemical properties and persistence. Besides, spatial variability of removal rates from air was assessed
28   running MAPPE model for the test set of 34 chemicals. The variability of results spans from less than one to over 4
29   orders of magnitude, showing differences in variability for each cluster of chemicals. Furthermore, different patterns
30   of spatial variability are associated to each cluster of chemical as the spatial pattern is driven by a specific
31   component of the overall removal rate. The comparison between MAPPE and USEtox removal rates from air shows
32   that for 14 out of 34 chemicals within the test set USEtox values are close to the median of the results of MAPPE.
33   For 11 out of 34, USEtox underestimates the removal rate from air and the results are close to the 5th percentile of
34   MAPPE ones. This is mainly related to how wet/dry deposition and gas exchange are accounted in the two models.

35   *Conclusion and outlook* This work has made further progress towards understanding and implementing how to
36   develop a tailored-made guidance for assessing spatial differentiation in LCA. Results on spatial distribution and
37   spatial variability of chemical are presented as a basis for defining patterns of variability and supporting further
38   development of spatial scenarios and archetypes to be used for Life Cycle Impact Assessment. This provides
39   insights into whether using generic global default factors is likely to result in high uncertainty depending on the
40   type of chemical, as well as whether pattern-specific factors would reduce the uncertainty. Uncertainties related to
41   spatial differentiation are presented and discussed.

42

43   *Keywords: Spatial differentiation, spatial variability, chemicals fate, life cycle impact*
44   *assessment of chemicals, removal rates, USEtox, MAPPE model*

Background, aim and scope

There is continual debate whether the exclusion of spatial information in applications such as Life Cycle Assessment (LCA) may lead to misleading results, influencing the decision on products environmental performance (Finnveden et al 2009).

Traditionally, LCA has been applied in a site-independent manner as emissions and resource consumption data are often not spatially and temporarily resolved. Many adopted impact assessment models provided generic results, as often is the case in screening chemical risk assessments performed e.g. for policy support. Reasons can include political motives to e.g. not distinguish between chemical risks in such assessments due to where an emission occurs. Equally, providing more spatial resolution can complicate assessments and may not reduce the uncertainty of the results.

In recent years, several research activities have been focused on identifying whether or not spatially detailed assessment is fundamental for decision support (e.g. Hauschild and Potting 2005, Pennington et al 2005). In the context of Life Cycle Impact Assessment (LCIA), site dependent characterization factors have been calculated for different impact categories, including for acidification and eutrophication (Seppälä et al 2006, Gallego et al 2010), photochemical ozone formation (van Zelm et al 2008), ecotoxicity and human toxicity (Wegener Sleeswijk and Heijungs 2010).

Toxicity related impacts are argued to present high variability among different models (Huijbregts et al 2003, Geisler et al 2005) and results are sometimes expected to be highly sensitive to spatial differentiation; depending on emissions patterns, chemical properties, location, and various other parameters.

68 In particular, for toxicity related site dependent assessment, there is an increasing demand for a

69 balance between resolution required by models and complexity that can be handled given the

70 quality of available data, the computational resources, as well as issues related to the availability

71 of spatially/temporally resolved emissions data. No model can be a true representation of the real

72 system, and optimal model performance can be only achieved by balancing the model's level of

73 detail against the demand for input parameters that are always uncertain (MacLeod et al 2010).

74 Hence, it is necessary to further explore the uncertainties related to results derived from the

75 straightforward multimedia models without spatial resolution that are often used in applications

76 such as Chemical Risk and Life Cycle Assessments (where the variation in environmental

77 characteristics are usually ignored and the analysis is limited to modeling typical or average

78 environmental conditions) in comparison with spatially-resolved models at various resolutions.

79 Besides, Wania and Mackay (1999) highlighted that non-spatially resolved multimedia models

80 with low spatial and temporal resolution are appropriate for describing the behavior of persistent

81 contaminants in the environment. The behavior of chemicals can be predicted directly from the

82 physical-chemical properties, if this is the main purpose of the application. In other cases,

83 detailed models can be necessary to introduce spatial differentiation and for more detailed,

84 quantitative risk estimates. Several spatially resolved multimedia mass-balance models, at

85 various resolution, were developed for chemical assessment and adopted as decision-support

86 tools, such as Bert world (Toose et al 2004), Impact 2002 (Pennington et al 2005), Globox

87 (Wegener Sleeswijk and Heijungs 2010).

88 Furthermore, both in Chemical Risk Assessment and in LCA, the number of chemicals under

89 assessment can be huge. Many chemicals do not present characteristic of persistent or Long

90 Range Transport (LRT) pollutant but imply impact at local scale (e.g. the emission in urban air

91 of a chemical with a very low half life in air is foreseen to exert local effect)

92 To understand whether substance properties or environmental parameters are the key factors,

93 several studies have explored (Hertwich and McKone 2001, Pennington et al 2005, Hollander et

94 al 2009, Pistocchi et al 2010) the relative influence of substance properties and environmental

95 characteristic on the results of spatially explicit fate models. Substance properties such as

96 partitioning between environmental phases (that define the chemical space of a chemical) and

97 susceptibility to degradation are two major factors determining the fate and bioaccumulation of

98 organic chemicals in the environment (Brown and Wania 2009; Wania 2006).

99 The study of Hollander et al (2009), amongst others, showed that fate of chemicals in the

100 environment depends mainly on these substance-specific partition coefficient and degradation

101 rates. Nevertheless, the relative influence of environmental characteristics increases if models are

102 run at a more detailed spatial scale. This was confirmed by e.g. a case study on Canada,

103 performed by Manneh et al 2010 at three resolution scales, in which variability of the results

104 decrease significantly at higher resolution.

105 To ensure robustness in discussing the uncertainties and the variability related to the use of a

106 global default factors for risk/emission in applications such as LCA, instead of using spatially

107 defined ones, a detailed assessment has to be carried out considering uncertainties and variability

108 along the cause effect chain: fate, exposure and effect. In this study, we decided to focus on the

109 beginning of the environmental cause effect chain (removal rates) in order to assess the

110 variability associated with these factors.

111 The aim of this study is, firstly, to provide insight guidance into the drivers of spatial

112 differentiation and, secondly, to assess spatial variability of atmospheric chemical removal rates

113   using a global, spatially resolved multimedia model. The guidance on spatial differentiation and

114   distribution is based on physical and chemical properties, while spatial variability assessment

115   relays on the results of a complex and highly resolved global model MAPPE (Multimedia

116   Assessment of Pollutant Pathways in the Environment) Global Model (Pistocchi et al 2011b).

117   This allows identifying the pattern and extent of spatial differentiation and supports insights into

118   whether spatial details are necessary in the context of chemical impact assessment

119   A comparison between MAPPE Global and USEtox (Rosenbaum et al 2008) box model

120   parameters was performed at the level of air removal rates in order to discuss the uncertainties

121   related to the use of generic impact assessment factors and to highlight the potential relevance of

122   higher level of spatial detail in order to develop, in further steps, specific emission scenarios. The

123   model were run for a test set of 34 chemical covering various portions of chemical space in order

124   to assess the spatial variability associated with different physical-chemical properties.

125

Methodology

127   A complete assessment on spatial differentiation requires at least two levels of analysis:

128   • Assessment of spatial distribution (the range of potential environmental geographical

129   distribution) in order to understand at which scale a chemical is typically distributed

130   (local, regional, global etc) and

131   • Assessment of spatial variability (the variability of the distribution and fate of a chemical

132   among various scenarios, continents, countries).

133   The methodology to explore spatial distribution and spatial variability related to chemical fate in

134   the environment was organized as follows:

135   a. Spatial distribution. We propose a framework to assess the hypothetical spatial

136   distribution and optimal geographical resolution for the fate assessment of chemicals on

137   the basis of their physical chemical properties. Organic chemicals were clustered dividing

138   chemical space according to likely similar environmental behavior. A range of likely

139   geographical distribution was assigned to each chemical group.

140   b. Spatial variability. A representative test set of 34 chemicals was identified from previous

141   research that covers likely chemical fate behavior. For each chemical of the test set, the

142   spatially explicit multimedia model MAPPE was run to assess the variability of the

143   results and to identify specific geographical patterns of variability. The analysis of the

144   spatial variability was performed exploring variability in chemical removal rates from air.

145   c. Comparison of the results provided by MAPPE with the global default values provided

146   by USEtox in order to assess the related uncertainties.

147

Spatial distribution of chemicals based on LRTP metrics

Clusters of organic chemicals

150 Persistence (P), Long Range Transport Potential (LRTP), Bioaccumulation (B) and Toxicity (T)

151 are characteristics directly related to a chemical's environmental risk (Muir and Howard, 2006).

152 Since these characteristics are related to physical chemical properties, organic chemicals were

153 clustered on the basis of their physical chemical properties in order to define a general

154 framework for identifying groups of chemicals with likely similar fate–behavior in the

155 environment. This built on the previous work of the Omniitox project (Molander et al 2004).

156 The framework was based on chemicals' equilibrium partition coefficients between octanol and

157 water (Kow), air and water (Kaw) and octanol and air (Koa) and on chemical's persistence.

158 Firstly, the chemical space was divided in 16 sub-sections (1a, 2a etc) adapting the scheme

159 proposed by Gouin 2000, revised by Pennington et al (2005) for non-dissociating and non-

160 amphiphilics chemicals. Fig.1 presents the 16 subsections of the chemical space. The sub-

161 sections are based on Kow and Kaw partitioning coefficients according to similar environmental

162 partitioning behavior. The 45° diagonals represent constant values of Koa under the assumption

163 of LogKoa= LogKow – LogKaw.

164 The range of physical chemical properties of each subsection is defined in Table 1. The clusters

165 are organized also in order to distinguish: fliers, multiple hoppers, swimmers and single hopper

166 chemicals (Wania 2006). These definitions refer to the different behaviors of chemicals, based

167 on their own properties: "fliers" are transported by air, "swimmers" present a low Henry's

168 constant and are transported by water, "multiple hoppers" are semi volatile chemicals in dynamic

169 exchange between atmosphere and ocean, "single hoppers" generally present high Koa and when

170 they are deposited to soil there is no revolatilisation

171 *Test set of chemicals*

172 Within the chemical space, a so-called "test set" of 34 organic chemicals was adopted. The test

173 set takes into account chemicals having a large diversity of physical chemical properties in order

174 to be representative, as far as possible, of their potential differences in the environmental

175 behavior. Furthermore, these substances with these representative properties had already been

176 used to assess multimedia fate of chemicals by Pennington et al (2005) and for model cross

177 comparison in USEtox (Rosenbaum et al 2008). The representative test set of chemicals and the

178 associated physical chemical data used in running the MAPPE model are listed in S1 of the

179   supporting material. The position of each chemical within the chemical space is also plotted in

180   Fig.1

181

182   *Spatial distribution of chemicals based on physical chemical properties*

183   In defining guidance for spatial distribution, we considered how different chemical properties

184   could be used to identify when a local, regional or global assessment of chemical fate is needed.

185   The guidance was developed by defining the hypothetical spatial distribution of a chemical on

186   the basis of its physical chemical properties, such as Kow, Koa, Kaw and persistence.

187   The guidance on spatial distribution is based on a flow chart (Table 1) in which each cell

188   represents a combination of:

189   • One of the 16 subsections of the chemical space, derived from the clustering made on the

190   basis of specific chemical behavior and LRTP.

191   • One of the 4 classes of persistence (below 1 day, from 1 day up to 1 week, from 1 week

192   up to 1month, and more than 1 month). The classes were set taking into account that two

193   days of half life in air is considered a screening criteria for differentiating LRT chemicals

194   from others (UNEP, 2001). This might apply to substances emitted in parts of temperate

195   Europe, North America, or Asia, for example, and then traveling with some efficiency to

196   reach the Arctic (Scheringer et al 2009).

197   For each combination of chemical properties and persistence, the hypothetical spatial

198   distributions was assigned on the basis of the results of the OECD "Tool" (Wegmann et al 2009)

199   and of literature review on patterns of spatial distribution of LRT chemicals.

200

201 *"The Tool" by OECD and Spatial distribution of LRT chemicals*

202 "The Tool" is the overall environmental Persistence (Pov) and Long-Range Transport Potential

203 (LRTP) Screening Tool recently released by the Organization for Economic Cooperation and

204 Development (OECD 2010, Wegmann et al 2009). This is a harmonized approach for assessment

205 of overall persistence (Pov) and Long Range Transport Potential (LRTP) on the basis of physical

206 chemical properties of chemicals. The Tool represents the consensus of current multimedia

207 model assessment methods to calculate the overall environmental persistence (Pov) and

208 Characteristic Travel Distance (CTD) as described by Beyer et al (2000) and Transfer Efficiency

209 (TE) as described by Macleod and Mackay (2004), as metrics for LRTP (Wegmann et al., 2009).

210 The Tools came from the study of Fenner et al 2005 in which nine different multimedia models

211 were assessed. Significant differences among the nine models assessed by Fenner et al 2005 have

212 been shown to be restricted to a certain region of the chemical space. This suggests that for the

213 other areas of the chemical space the models predict similar behavior of chemicals in term of Pov

214 and LRTP.

215 Hence, the combination of LRTP (based on Kow, Kaw and Koa) and persistence (Gouin, 2010)

216 supports the identification of the hypothetical spatial distribution, for assessing the fate of

217 chemical as presented in Table 1 in accordance with The Tool results

218 A further cross checking with studies on LRTP patterns was performed to support assigning the

219 spatial distribution to each combination in Table 1.

220 E.g. the Artic Contamination Potential (Wania 2006) indicates that some LRTP chemicals are

221 subject to a specific pattern of distribution in the environment and for those substances the

222 preferred scale of assessment is the global one. This is confirmed also by monitoring campaigns,

223 such as the comprehensive study of patterns of distribution (Macdonal et al 2000) developed

224   under the Canadian Northern Contaminants Program (NCP) which has enhanced the

225   understanding of the pathways by which contaminants reach Arctic and move through terrestrial

226   and marine ecosystems. Other studies (Toose et al 2004) identified significant source-to-sink

227   pathways and processes in the long-range transport of chemical to Arctic regions. For substances

228   that degrade faster in water than in soil, but are quite persistent in the atmosphere, or that are

229   soluble and highly persistent in water, highest Arctic contamination is expected to occur if the

230   substances have intermediate volatility and high hydrophobicity.

231   *How to use the guidance on spatial distribution*

232   Ideally, a LCA practitioner has to identify the chemicals representing the major contributors to

233   the toxicity related impact, checking, then, where the chemicals are located in the chemical space

234   to easily identify the potential spatial distribution of the chemicals under assessment according to

235   Table 1.

236   Considering, e.g. carbon tetrachloride (CCl_4), for its physical-chemical properties it is in the

237   subsection 1a. As CCl_4 half life in air in the literature spans from 3 to 5 months, it can be

238   considered as a chemical with a high potential of being globally distributed. This is confirmed by

239   the result of the "The Tool", in which it presents both high CTD and high TE. Therefore, the

240   chemical should be considered as a global contaminant to be assessed at global scale. Indeed, the

241   place of emission and the place of the potential related impact may be very distant.

242   On the other hand, highly hydrophobic chemicals (like 3a) with low to moderate persistence are

243   expected to have a local/ regional spatial distribution. This may affect the result of the impact

244   assessment, especially for specific routes of exposures, such as implication for human intake

245   fraction via inhalation.

246   For chemicals distributing from continental to global scale, it is expected that the place of

247   emission and the place of impact may be distant and, therefore, global models at low resolution

248   can be suitable for the impact assessment. On the other hand, for chemicals distributing locally

249   or regionally, models at higher resolution are preferable, as the major contribution to impact is

250   related to local condition. In the latter case, as shown also by Hollander et al 2009, the role of

251   environmental parameters became more relevant than the mere physical-chemical properties.

252   **Spatial variability of removal rates for the test set of chemicals**

253   Knowing the hypothetical spatial distribution, a second relevant step is to assess the spatial

254   variability and whether or not to proceed with a site specific assessment. As mentioned above,

255   the choice is not only related to the hypothetical spatial distribution of a chemical, based on its

256   physical chemical properties, but also on specific environmental parameters that may influence

257   the final result.

258   Referring to Table 1, we may argue that for highly hydrophobic chemicals with low persistence

259   (although the scale of their spatial distribution is local) we may rely on global site-independent

260   approach. Irrespective of specific location of emission, they will present low spatial variability of

261   the fate. Indeed, fate of chemicals in the environment is much more affected by chemical

262   properties than by environmental conditions when the chemical present very extreme partitioning

263   properties. Wherever the emission takes place we can assume that the behavior is similar.

264   This assumption can be applied also for chemicals with LRTP that are subject to specific spatial

265   pattern (e.g. those that present a High Arctic Contamination Potential): in this case, highly

266   detailed information on the source of emission has a limited influence on the final fate

267   calculations.

268   Therefore, the need for spatial differentiation was further explored combining the assessment

269   based on physical chemical properties with the assessment of specific environmental parameters

270   leading to specific "patterns" of spatial distribution and variability.

271   The variability in the chemical behavior and the potential related patterns were identified with

272   the spatially resolved MAPPE Global model. The analysis of the variability of removal rates

273   from air (Kair) governing environmental fate of chemicals emitted in air was the starting point

274   for the assessment.

275   Kair total is the sum of 5 removal rate processes (1): Particle dry deposition (Kpart), Wet

276   deposition (Kwet), Gas absorption (Kgas), Degradation (Kdeg) and Advection (Kadv).

277   Kair = Kpart + Kwet + Kgas + Kdeg + Kadv   (1)

278   At equal emission rates (one unit of emission), the air removal rates are expected to be different

279   for different groups of chemicals and for different environmental conditions. Under this

280   assumption, MAPPE Global model was run in order to assess the spatial variability in the

281   removal rates for the test set of chemicals.

282   **The Global Multimedia Assessment of Pollutants pathways in the Environment -**
283   **MAPPE Global model**

284   MAPPE Global is a GIS based model that builds on the concept of the previous MAPPE Europe

285   version (Pistocchi 2008; Pistocchi et al 2010). MAPPE Global is a spatially-resolved steady state

286   multimedia model (i.e. the rate coefficients are not temporally resolved in current version). The

287   detailed model description, background parameters and input data are reported in Pistocchi et al

288   2011b (see also S2).

289   Currently, MAPPE computes only the removal rates of a substance with given physico-chemical

290   properties. It is composed of atmospheric boundary layer, soil, inland and seawater, for the

291   whole world, with a resolution of 1°x1^{o} (except for some parameters, which are defined at finer

292   resolution). Advection at the global scale between cells is not yet modeled. Hence, the influence

293   of distributing an emission over a region, which would reduce the maximum potential variability

294   for some types of chemical, is not modeled at the global scale.

295   The MAPPE Global computes, for each grid cell, mass fluxes of chemical that are available for

296   transport outside of the cell, and their global variability. MAPPE Global is developed

297   specifically to answer questions concerning the environmental fate of contaminants taking into

298   account the variability of environmental processes at the global scale and the variability of fate in

299   response to spatial variability of emissions and chemical fate processes, such as:

300   -   How will a chemical spread across different media in different climatic and landscape

301   settings?

302   -   How important is the variability of environmental processes in determining the fate of

303   chemicals across the globe?

304   -   How much of a chemical emitted to air will result in a load to soil or waters?

305   With respect to spatial differentiation, MAPPE Global allows: adopting several scales of

306   assessment by differentiating on the basis of grid cells (100x100 km), political boundaries

307   (countries) or geographical borders (river basins, continents, global); and identifying specific

308   patterns in the environmental behavior of chemicals.

309   **Comparison MAPPE versus USEtox**

310   Straightforward non-spatial multimedia models are widely used in LCIA for modeling chemical

311   fate and human exposure. USEtox reflects a latest consensus amongst LCA model developers for

312   the calculation human and eco toxicity characterization factors amongst associated multimedia

313   models. The aim of the comparison was to understand the maximum level of uncertainty

314 associated with the use of such a global default value provided by USEtox, by applying a

315 multimedia model with a spatial resolution of 1*1 degree, in this case MAPPE. To highlight the

316 variability of factors at the beginning of the environmental cause-effect chain, the comparison

317 was made at the level of the removal rates coefficients.

318 USEtox has been set up to model a global default continent, and it has a nested multimedia

319 model in which it is possible to consider global, continental (with six environmental

320 compartments) and urban scale differentiation.

321 In Fig.S1, all the organic chemicals presented in the USEtox database are plotted. Most of the

322 chemicals are within the chemical space of Fig.1. Few other substances, with extreme

323 partitioning properties are outside. These will have extreme behavior in partitioning either in air,

324 in soil or in water. In Fig.S2 the position of chemicals within the chemical space defined in this

325 paper is shown and for them the guidance on spatial distribution can be applied. Furthermore, it

326 is relevant to note that over a half of the chemicals in the USEtox database (Fig.S3) have half

327 lives in air less than 1 day. Following the indication in Table 1, for many of those chemicals a

328 local spatial distribution is foreseen to be relevant.

Results and discussion

330 The MAPPE Global model was run in order to highlight the maximum spatial variability of the

331 removal rate coefficients considering emissions in air of one unit of chemical in each cell of

332 1°x1° degree in which the globe is divided, in order to:

333 • assess the global variability of removal rates from air for the test set of 34 chemicals,

334   identifying associated patterns of spatial variability for chemical's clusters

335 • compare of the results of MAPPE and USEtox

Global variability of removal rates from air and associated patterns

In a first screening calculation, we ran MAPPE for the 34 chemicals considering all the 5 removal processes from air: particle dry deposition (Kpart) and wet deposition (Kwet), gas exchange (Kgas), degradation (Kdeg) and advection (Kadv). The results (see Fig. S4) evidenced that 30 out of 34 chemicals have variability in global values below one order of magnitude if we consider the total Kair, including the advection. In the case of Aldrin, the variability is even less than one order. Propoxur and Benomyl are over one order of magnitude but below two. Two chemicals, representative of the 2a class, present a high variability: Methomyl almost three orders of magnitude while Acephate over four orders of magnitude.

Secondly, as we want to focus the assessment on the variability at local scale, the analysis was performed without advection and considering only the other four removal processes: (Kpart, Kwet, Kgas, and Kdeg). The results of the variability (median, 5% and 95% quantiles) are presented in the Fig.2, clustered by order of magnitude of variability in Table 2. Background data are reported in Table S2.

In general, the variability of the chemicals spans from less than one up to more than four orders of magnitude. These results support the need of assessing separately the potential spatial distribution of a chemical (local, regional, at country level etc) and its spatial variability.

The comparison of the variability of results with and without advection (Fig.S4 and Fig.2) implies that for persistent chemicals the advection will be more important compared to the other removal processes. It is worth to highlight that the variability of removal rates as a function of location will thus be reduced, due to an averaging over space associated with dispersion.

Besides, chemicals in the same classes (e.g. 3a) don't present the same variability of the removal rates. Chemicals such as di(n-octyl)phthalate and Cypermetrin show a very low variability (less

359   than one order of magnitude) whereas Hexabromobenzene shows a variability of more than four

360   orders of magnitude, PCB's and Mirex over two orders

361   For almost all the chemical in the test set, the extended ranges of variability are observed in the

362   area below median values, while for all chemicals the variability over the medians is up to one

363   order of magnitude.

364   Hence, for chemicals that present high variability of Kair, it is necessary to explore the sources

365   of this variability in order to identify main related drivers and geographical patterns.

366   Aiming at identifying reasons for variability and at specifying whether the variability follows

367   similar spatial patterns for different chemicals, maps of distribution of values at global scale

368   were calculated. Actually, maps could be used not only to visualize but also to analyze the spatial

369   nature of pollutants (Lahr and Kooistra, 2010). Analyzing the spatial patterns in the maps of the

370   chemicals (all available in SI), the variability of the results in Fig. 2 could be explained as

371   follows:

372   For chemicals in the group 1a, the dominant compartment is air. The variability could be driven

373   by gas exchange in the atmosphere that basically depends on the variability of land cover. See

374   for example, for Butadiene, the map removal rate from air without advection (Fig S5).

375   Comparing the spatial pattern of the Kair with the pattern of Kgas, it is confirmed that there is a

376   dependence of the final result on the variability of the gas exchange and the differences in the

377   global distribution of land cover influence the variability of the results (Fig.S6).

378   The environmental partitioning of 2a chemicals is mainly related to water. The high variability in

379   the Kair values could be explained by the difference in the precipitation among countries.

380   Comparing the total removal rate of a highly hydrophilic chemical, such as the acephate

381   (Fig.S7), with the pattern of the map of the wet deposition removal rate (Fig.S8) and the pattern

382   of the annual average precipitation map (Fig.S9), it is clear that the foremost removal rate

383   process is the wet deposition. The same explanation may describe the spatial variability of

384   Methomyl, also in the 2a group but less hydrophilic (Fig.S10).

385   In the case of hydrophobic chemicals with a low affinity for air, such as PCBs in the 3a group,

386   the pattern of variability may be explained considering those chemicals emitted to air, with gas

387   absorption (Fig. S11 and S12). However the additional patterns map (Fig. S13-14) shows that a

388   certain influence of Kpart could be accounted for the total variability, as the highest values in the

389   total removal rate are in the same areas where particle dry deposition is uppermost.

390   Furthermore, for explaining the different variability amongst chemicals within 3a (e.g.

391   Cypermethrin and Hexabromobenzene), a combination of the role of degradation rate and the

392   variability of the Kgas has to be taken into account. The variability of gas exchange drives (Fig

393   S15 and S17) the overall variability of the Kair when the degradation rate is low (as in the case

394   of Hexacromobenzene – 4.9 10^{-4} 1/d) and the persistence is high (over 1000 days of half live in

395   air). In the opposite case, where the degradation rate is higher (as Cypermethrin – 0.92 1/d or

396   di(n-octyl)phthalate – 0.89 1/d) and the persistence is low (respectively 0.75 and 0.78 days of

397   half life in air) the overall variability is very low (Fig. S18). Then, the degradation, as an

398   elimination process from atmosphere, reduces the range of variability of total air removal rates,

399   which potentially express a large variability due to the wide spatial fluctuations of gas exchange

400   or wet/dry deposition. This means that it is not possible to assign spatial variability to a certain

401   group of chemicals based only on the partitioning properties without accounting for the role of

402   degradation.

403   For multimedia chemicals, like those in 4b, the pattern of variability is related to the interplay of

404   different removal rates (see Fig S19-S23) even if substantial contribution is still related to gas

405   exchange since the Kgas is the prevailing removal rate compared to the others. In Fig S24, an

406   example for Lindane is presented, showing variability of removal rates across countries where

407   Kgas and Kwet present variability over 3 orders of magnitude, whilst Kdeg and Kpart around

408   one order.

409

410   **Comparison of removal rates from air: MAPPE versus USEtox**

411   The comparison MAPPE versus USEtox was performed in order to assess the total air removal

412   rates (Kair) calculated by running a multimedia model with default environmental parameters

413   and no spatial resolution against MAPPE with a spatial resolution of 1x1 degree.

414   Since we are exploring the variability at the very beginning of the environmental cause effect

415   chain, the comparison covered only contrasting removal rate coefficients from air to assess the

416   uncertainties related to a site generic approach, such as the one proposed by USEtox.

417   The USEtox results were calculated keeping as they are the default environmental parameters

418   provided by the model. The removal rates for continental and global scale were calculated

419   specifying the values of removal to stratosphere, degradation, wet and dry deposition and gas

420   adsorption.

421   In Fig.2 and Table S2, and Fig S25, the results of USEtox also are reported.

422   The model comparison shows that for 14 (such as Formaldehyde 2b, Cypermethrin 3a, Aldrin 4a

423   and N-Nitrosodiethylamine 5a) out of 34 representative substances the median of the total air

424   removal rates calculated with MAPPE is within one order of magnitude of difference with

425   USEtox. For almost all the tested substances, the USEtox values are below the median values

426   calculated by MAPPE. The only exceptions are: Butadiene, Anthracene, N- Nitrosodiethylamine,

427   Tetramethyl- thioperoxydicarbonic diamide (Thiram), Trifluralin and Heptachlor. In general,

428   USEtox tends to underestimate MAPPE Global estimates for the removal rates between 1 and 4

429   orders of magnitude and the USEtox values are close to the 5th percentile of the MAPPE results

430   for 7 out of 34 chemicals.

431   Moreover, for the groups of flyers (1a) or hydrophilic substances (2a, 7a) the underrating is

432   higher and varies from 2 up to almost 4orders (maximum deviation observed for Acephate 2a)

433   It is worthy to highlight that in case of low variability of the MAPPE results worldwide (as for

434   di(n-octyl)phthalate, Cypermethrin, Aldrin and Folpet) the USEtox value is very close to the

435   median. At higher variability, the uncertainties (difference of global default value from the

436   median of the spatially resolved one) associated to the global default values increase.

437   Assuming equal chemical properties, two main factors may lead to the discrepancies: different

438   algorithms to calculate the removal rates; variability of environmental parameters in MAPPE

439   compared to the environmental parameters in the default setting of USEtox.

440   Analyzing the results in Fig 2 and in Fig S25, the following conclusions can be drawn:

441   For chemical for which the removal rate is dominated by wet and dry deposition (as e.g. 2a),

442   MAPPE results show a higher variability due to a broader range of average rain rate across the

443   globe (fixed value in USEtox: 700 mm yr-1; values in MAPPE: 600-3600 mm yr-1).

444   Furthermore, MAPPE doesn't consider intermittent rain conditions whereas USEtox accounts for

445   that. This may explain the different estimation of Kwet.

446   For chemical for which the removal rate from air is dominated by gas exchange (as e.g 1a),

447   MAPPE results present a variability associated with different land coverage. As explained in the

448   S.I., MAPPE accounts for different gas exchange for various land coverage, assuming broad

449   differences in gas absorption velocity and in related coefficient. Specifically, MAPPE assigns

450   higher gas exchange coefficient to different forested areas compared to USEtox.

451 For chemical for which the degradation rate in air is much higher than the other removal rates

452 (e.g Butadiene, N-Nithrosodiethylamine, tetramethyl-Thioperoxydicarbonic diamide,

453 heptachlor), USEtox tends to overestimate the MAPPE results (e.g. N- Nitrosodiethylamine and

454 Thiram).

455 Further research is needed to give a better insight on the reason behind the spatial variability and

456 the associated discrepancies in the results. Once the full documentation of the algorithms behind

457 USEtox will be available, a comprehensive sensitivity analysis of the parameters of the two

458 models may help in identifying further differences and drivers of uncertainties. Anyway this was

459 beyond the scope of this study.

460

461 **Conclusions and Outlook**

462 This study is based on a comparison of the result of a detailed spatially resolved model,

463 computational intensive but useful to understand better specific patterns in spatial differentiation,

464 against a simplified approach to the assessment of chemicals, provided by model such as

465 USEtox, in order to identify key drivers of variability/ uncertainties. The main results show the

466 importance of assessing both spatial distribution and spatial variability to provide guidance on

467 spatial differentiation for the specific purpose of LCA. Summarizing, the key findings are the

468 following:

469 • Spatial distribution of chemicals could be identified through a guidance based on physical

470 chemical properties and persistence of chemicals, following the results of the OECD Tool

471 (Wegmann et al 2010) and literature review.

472 • Spatial variability in removal rate from air is different for various clusters of chemicals
473   due to the interplay of physical-chemical properties and degradation rates. The variability
474   increases especially for chemical with low air degradation rate. This means that it is not
475   possible to assign spatial variability to a certain group of chemicals based only on the
476   partitioning properties without accounting for the role of degradation.

477 • Spatial variability is associated to different spatial patterns, due to the influence of
478   specific removal rate for each cluster of chemicals. In this paper, relevant patterns
479   affecting variability of removal rates were identified, supporting the need of considering
480   both physical chemical properties and environmental parameters in assessing chemicals
481   fate.

482 • The comparison of the USEtox model and the spatially resolved model MAPPE for the
483   removal rate coefficient from air-revealed discrepancies that span from 1 up to 4 orders of
484   magnitude. The differences are mainly due to the removal rates related to wet/dry
485   deposition and gas exchange. A comprehensive sensitivity analysis may give further
486   insight in order to address uncertainties related to specific differences in the algorithms
487   and in the default model setting of USEtox.

488

489 **Outlook and recommendations**

490 This work has made further progress towards understanding and implementing how to develop a

491 tailored-made guidance for the specific purpose of assessing spatial differentiation in LCA.

492 Nevertheless, some issues need to be addressed in further research activities. Nowadays, the real

493   challenge for spatial differentiation is a transition from theoretical framework towards feasible

494   and reliable approaches, tackling some relevant issues:

495   **Role of advection.**

496   Although this issue was beyond the scope of this study, the advection represents the major

497   process contributing to the transport of LRT chemicals among countries and spatial variability

498   analysis have to be conducted at various scale of resolution.

499   **Not only LRT chemicals.**

500   So far, research efforts were mainly dedicated in identifying LRT chemical that can act as global

501   chemical. Nevertheless, an effort is required also for identifying suitable scale for the impact

502   assessment of others chemicals. Although this substances are not POP or LRTP, they may locally

503   affect human health and ecosystems due to their high local concentration or to their high toxicity.

504   **Sensitivity analysis.**

505   Sensitivity analysis (study of impact of input parameters on the value of outputs) has to be

506   carried out to identify the key parameters affecting variability and patterns. This is particularly

507   useful in supporting the definition of relevant scenarios and archetypes as well as understanding

508   which data are the key input data for each chemical cluster and the key removal mechanisms.

509   This is crucial also to better understand the key parameters affecting the discrepancies found

510   between USEtox and MAPPE results. The environmental parameters to be considered may be

511   classified into geometric parameters (e.g., atmospheric mixing height), process parameters (e.g.,

512   dry deposition velocity), and compartment property data.

513   **Framework for assessing uncertainties and variability**

514   A common framework for assessing uncertainties and variability to be adopted in LCA is

515   required and has to be conducted step by step along the environmental cause effect chain.

516   According to Meyer et al 2005, the study of uncertainty has to be distinguished in: the study of

517   the uncertainty of the input parameters on the uncertainty of output parameters, highlighting

518   variability (spatial and temporal variation in the environmental parameters) and true uncertainty

519   (deficiencies in knowledge). Therefore, further comparison and assessment have to be conducted

520   not only on the final results (e.g. variability in characterization factors) but also in the

521   intermediate steps, considering: parameter uncertainties, model uncertainties and temporal

522   variability.

523   Parameter uncertainty: the main source of uncertainties is related to physico-chemicals properties

524   of chemicals in the environment (degradation half-lives and partition coefficients) and they needs

525   to be characterized and taken into account from the very beginning of any chemicals assessment

526   (Boethling et al 2009 and Rosenbaum et al 2008). Indeed, MAPPE requires the input of at least 2

527   partition coefficients (Kow, Kaw or Koa) and 3 or 4 degradation rate constants or half-lives for

528   air, water, soil, and sometimes sediment.

529   Model uncertainty: The set-up of the model involves uncertainties because the model structure

530   and the selection of environmental processes always give an incomplete representation of reality

531   based on knowledge and objectives of the model developer (Scheringer et al 2009). MAPPE is a

532   steady state model with first-order removal process. As other similar model, this implies model's

533   uncertainty as e.g., in the model, the feedback effect is not considered as its importance is limited

534   for most organic chemical (Margni et al 2004). Furthermore, for the specific purpose of spatial

535   models evaluation, Monte Carlo simulations are among the methods most commonly applied for

536   the analysis of parameter's uncertainty. We didn't use it for assessing variability/uncertainties in

537   this study since Montecarlo simulation of spatial parameters in box models can significantly

538   overestimate the realistic effect of spatial variation (Hollader et al 2009). A promising method to

539   assess uncertainty and uncertainty propagation was presented by Hong et al 2010. Besides, for a

540   comprehensive uncertainty assessment there is the need of comparing models results at various

541   resolutions; under different background parameter assumption; and also with measured real data.

542   At the actual stage of site-specific model's development, the model validation is often limited to

543   local situation and rarely validated at wider scale (continental or even global).

544   Temporal variability: All the calculations are based on average annual values of input

545   parameters. Therefore, temporal/seasonal variation is not taken into account but may affect the

546   final result of the removal rates. (e.g. when discrete events such as precipitation are temporally

547   averaged)

548   **Patterns of spatial variability**

549   Recently, a discussion on the state of art and perspectives in spatially explicit multimedia fate

550   models (Pistocchi et al 2010 and 2011a) has highlighted that the key question to be addressed is

551   not anymore "how to compute" (numerical methods, spatial temporal discretization, quantitative

552   uncertainty and sensitivity analysis) but "what to compute". This suggests concentrating the

553   effort in understanding spatial patterns of both emission and environmental key drivers.

554   **Substance or space: not only a matter of resolution**

555   We may conclude that whether site-dependent factors reduce uncertainty compared to using

556   generic defaults depends on the physical chemical properties of the chemical under assessment

557   and the environmental scenario in which the emission occur. A further development of guidance

558   on spatial differentiation has to be chemical-specific and scenario-dependent.

559   **Use of map for communicating**

560 The potential benefit for communicating LCIA results in the form of maps has to be further

561 explored. Nevertheless, it is important to help LCA practitioners to easily identify situations for

562 which spatial differentiation in the LCIA of chemicals should be considered relevant.

563

566

567

568 References

569 Beyer A, Mackay D, Matthies M, Wania F, Webster E, (2000) Assessing long-range transport potential of persistent

570 organic pollutants. Environ Sci Technol 34(4):699–703

571 Boethling RS, Fenner K, Howard P, Klecˇka G, Madsen T, Snape JR, Whelan MJ (2009). Environmental persistence

572 of organic pollutants: Guidance for development and review of POP risk profiles. Integr Environ Assess Manage

573 5:539–556.

574 Brown TN, Wania F (2009) Development and exploration of an organic contaminant fate model using poly-

575 parameter linear free energy relationships. Environ Sci Technol 43:6676–83

576 Fenner K, Scheringer M, MacLeod M, Matthies M, McKone T, Stroebe M, Beyer A, Bonnell M, Le Gall AC,

577 Klasmeier J, Mackay D, van de Meent D, Pennington D, Scharenberg B, Suzuki N, Wania F (2005) Comparing

578 Estimates of Persistence and Long-Range Transport Potential among Multimedia Models. Environ Sci Technol

579 39(7):1932-1942

580 Finnveden G, Hauschild MZ, Ekvall T, Guine´e J, Heijungs R, Hellweg S, Koehler A, Pennington D, Suh S (2009)

581 Recent developments in life cycle assessment, J Environ Manag , 91: 1–21

582 Gallego A, Rodriguez L, Hospido A, MoreiraMT, Feijoo G (2010). Development of regional characterisation

583 factors for aquatic eutrophication. Int J Life Cycle Assess 15:32-43

584 Geisler G, Hellweg S, Hungerbühler K (2004) Uncertainty analysis in life cycle assessment (LCA). Case study on

585 plant-protection products and implications for decision making. Int J Life Cycle Assess 10:184–192

586 Gouin T, Mackay D, Webster E, Wania F. (2000) Screening Chemicals for Persistence in the Environment. Environ

587 Sci Technol 34(5):881-884

588 Gouin T (2010) The precautionary principle and environmental persistence: prioritizing the decision-making

589 process. Environ Sci Policy 13(3):175-184.

590 Hauschild M, Potting J (2005) Spatial differentiation in life cycle impact assessment – the EDIP2003 methodology.

591 Environmental News no. 80. The Danish Ministry of the Environment, Environmental Protection Agency,

592 Copenhagen.

593   Hertwich EG, McKone TE (2001). Pollutant-specific scale of multimedia models and its implications for the

594   potential dose. Environ Sci Technol 35: 142–148.

595   Hollander A, Pistocchi A, Huijbregts M A J, Ragas A M J, Meent D V D (2009) Substance or space ? The relative

596   importance of substance properties and environmental characteristics in modeling the fate of chemicals in Europe.

597   Environ Tox Chem 28(1):44-51.

598   Hong J, Shaked S, Rosenbaum R, Jolliet O (2010) Analytical uncertainty propagation in life cycle inventory and

599   impact assessment: Application to an Automobile Front Panel. Int J Life Cycle Assess 15(5):499–510

600   Huijbregts MAJ, Gilijamse W, Ragas AMJ, Reijnders L (2003). Evaluating uncertainty in environmental life-cycle

601   assessment a case study comparing two insulation options for a Dutch one-family dwelling. Environ Sci Technol

602   37(11):2600–2608.

603   Lahr J, Kooistra L (2010). Environmental risk mapping of pollutants: state of the art and communication aspects. Sci

604   Total Environ 408:3899-3907.

605   Macdonal R W, Barrie L A, Bidleman TF, Diamond ML, Gregor DJ, Semkin RG, Strachan WM, Li YF, Wania F,

606   Alaee M, Alexeeva LB, Backus S M, Bailey R, Bewers JM, Gobeil C, Halsall CJ, Harner T, Hoff JT, Jantunen LM,

607   Lockhart WL, Mackay D, Muir DC, Pudykiewicz J, Reimer KJ, Smith JN, Stern GA (2000) Contaminants in the

608   Canadian Arctic: 5 years of progress in understanding sources, occurrence and pathways. Sci Total Environ *254*: 93-

609   234.

610   Macleod M, Mackay D (2004) Modeling transport and deposition of contaminants to ecosystems of concern: a case

611   study for the Laurentian Great Lakes. Environ Pollut 128 (1–2):241–250

612   Macleod M, Scheringer M, McKone T E, Hungerbuhler K (2010) The state of multimedia mass-balance modeling in

613   environmental science and decision-making. Environ Sci Technol 44(22):8360-4.

614   Manneh R, Margni,M, Deschênes L (2010). Spatial variability of intake fractions for Canadian emission scenarios: a

615   comparison between three resolution scales. Environ Sci Technol 44: 4217-4224.

616   Margni M, Pennington DW, Bennet DH, Jolliet O (2004) Cyclic Exchanges and Level of coupling between

617   environmental media:intermedia feedback in multimedia fate models. Environ Sci Technol 38: 5450–5457.

618   Meyer T, Wania F, Breivik K (2005) Illustrating sensitivity and uncertainty in environmental fate models using

619   partitioning maps. Environ Sci Technol 39:3186–3196.

620   Molander S, Lidholm P, Schowanek D, Recasens M, Fullana P, Christensen FM, Guinee J B, Hauschild M, Jolliet

621   O, Carlson R, Pennington D W, Bachmann TM (2004) OMNIITOX-operational life-cycle impact assessment

622   models and information tools for practitioners. Int J Life Cycle Assess 9:(5)282–288.

623   Muir DCG, Howard PH (2006) Are there other persistent organic pollutants? A challenge for environmental

624   chemists. Environ Sci Technol 40:7157–66.

625   OECD (2010) THE OECD Pov and LRTP Screening Tool

626   http://www.oecd.org/document/17/0,3343,en_2649_34373_40754961_1_1_1_1,00.html (accessed December 2010)

627   Pennington DW, Margni M, Ammann C, Jolliet O (2005) Multimedia fate and human intake modeling: Spatial

628   versus nonspatial insights for chemical emissions in Western Europe. Environ Sci Technol 39(4):1119-1128.

629   Pistocchi A (2008) A GIS-based approach for modeling the fate and transport of pollutants in Europe. Environ Sci

630   Technol 42:3640-3647.

631   Pistocchi A, Sarigiannis DA, Vizcaino P (2010) Spatially explicit multimedia fate models for pollutants in Europe:

632   State of the art and perspectives. Sci Total Environ 40(18):3817-3830

633   Pistocchi A, Groenwold J, Lahr J, Loos M, Mujica M, Ragas A, Rallo R, Sala S, Schlink U, Strebel K, Vighi M,

634   Vizcaino P (2011a) Mapping cumulative environmental risks from chemical pollution. Environ Model Assess.

635   16:119-133

636   Pistocchi A, Marinov D, Pontes S, Zulian G (2011b) Multimedia assessment of pollutant pathways in the

637   environment - Global scale model (MAPPE Global). EU Report (in preparation)

638   Rosenbaum RK, Bachmann TM, Gold LS, Huijbregts MAJ, Jolliet O, Juraske R, Köhler A, Larsen HF, MacLeod

639   M, Margni M, McKone TE, Payet J, Schuhmacher M, van de Meent D, Hauschild MZ (2008) USEtox - The UNEP-

640   SETAC toxicity model: recommended characterization factors for human toxicity and freshwater ecotoxicity in Life

641   Cycle Impact Assessment. Int J LCA 13(7):532-546

642   Scheringer M, Stroebe M, Held H (2002) Chemrange 2.1 - A Multimedia Transport Model for Calculating

643   Persistence and Spatial Range of Organic Chemicals. ETH Zurich, www.sust-

644   chem.ethz.ch/research/groups/prod_assessment/Projects/chemrange/index

645   Scheringer M, Jones K C, Matthies M, Simonich S, Meent D V D (2009) Multimedia Partitioning , Overall

646   Persistence , and Long-Range Transport Potential in the Context of POPs and PBT Chemical Assessments. Integr

647   Environ Assess Manage 5(4): 557-576.

648   Seppälä J, Posch M, Johansson M, Hettelingh JP (2006). Country-dependent Characterisation Factors for

649   Acidification and Terrestrial Eutrophication Based on Accumulated Exceedance as an Impact Category Indicator.

650   Int J LCA 11(6): 403-416.

651   Toose L, Woodfine DG, Macleod M, Mackay D, Gouin J (2004) BETR-World: a geographically explicit model of

652   chemical fate: application to transport of α-HCH to the Arctic. Environ Pollut 128: 223-240

653   UNEP (2001). Stockholm Convention on Persistent Organic Pollutants. United Nations Environment Programme.

654   Geneva, Switzerland. http://chm.pops.int (accessed December 2010)

655   Van Zelm R, Huijbregts MAJ, Den Hollander HA, Van Jaarsveld HA, Sauter FJ, Struijs J, Van Wijnen HJ, Van de

656   Meent D (2008) European characterization factors for human health damage of PM10 and ozone in life cycle impact

657   assessment. Atmos Environ 42:441-453.

658   Wania F (2006) Potential of degradable organic chemicals for absolute and relative enrichment in the arctic. Environ

659   Sci Technol 40:569–77

660   Wania F., Mackay D (1999) The evolution of mass balance models of persistent pollutant fate in the environment.

661   Environ. Pollut 100 (1):223–240.

662   Wegener Sleeswijk A, Heijungs R (2010). GLOBOX: A spatially differentiated global fate, intake and effect model

663   for toxicity assessment in LCA. Sci Total Environ 408:2817-2832

664   Wegmann F, Cavin L, Macleod M, Scheringer M, Hungerbuhler K (2009) The OECD software tool for screening

665   chemicals for persistence and long-range transport potential. Environ Modell Softw 24(2):228–237.

666

667 Table 1 Guidance on spatial distribution of the chemicals based on LRT metrics (physical chemical properties and

668 persistence) for emissions in air

Subsections	Log Kow	Log Kaw	Log Koa	<1 day	1day>x>1 week	1 week >x< 1 months	>1 month	Main fate compartment
1a		> -0.5	<4	L	R/C	Co/G	Co/G	air
1a*		>0	<6.5	R/C	G	Co/G	Co/G	Air (fliers)
2a	<1	<-6		L	R/C	Co/G	Co/G	water
2b	<1	-4.5<x<-6		L	R/C	Co/G	Co/G	water
3a	>6		>8	L	L	R/C	Co/G	solid
3a**	>6	<-6		L	L	R/C	R/C	Solid
3a***			>10	L	L	R/C	R/C	Solid
3b	5<x<6		>8	L	L	Co/G	Co/G	solid
4a	1<x<5	-4.5<x<-0.5	4<x<6	L	R/C	Co/G	Co/G	Multimedia
4b	1<x<5	-4.5<x<-0.5	6<x<8	L	R/C	Co/G	Co/G	Multimedia
5a		-4.5<x<-0.5	<4	L	R/C	Co/G	Co/G	air-water
6a	1<X<4	-4.5<X<-6	6<X<8	L	L	Co/G	Co/G	water-solid
6b	1<x<2	<-6		L	L	R/C	Co/G	water-solid
6c	2<x<5	<-4.5	>8	L	L	R/C	Co/G	water-solid
7a		>-0.5	4<x<6	L	R/C	Co/G	Co/G	air-solid
7b	>5		6<x<8	L	R/C	Co/G	Co/G	air-solid

669 L= local scale (up to 10^1 Km); R= regional scale; C= country scale (up to 10^3 Km); Co/G=
670 continental/global scale (10^4 -10^5 Km)

671   * So volatile that they don't deposit to the Earth's surface, even under the condition of the Artic
672   Environment (Wania 2006)
673   ** Transport reduced by deep sea export (Scheringer et al 2002)
674   *** Single hoppers, tending to be associated with particles in the atmosphere, usually deposited
675   irreversibly to the Earth's surface (Wania 2006)
676

677 Table 2 Variability of the removal rates from air for the 34 chemicals in the test set. .Orders of magnitude of

678 difference between 5th and 95th percentile are presented.

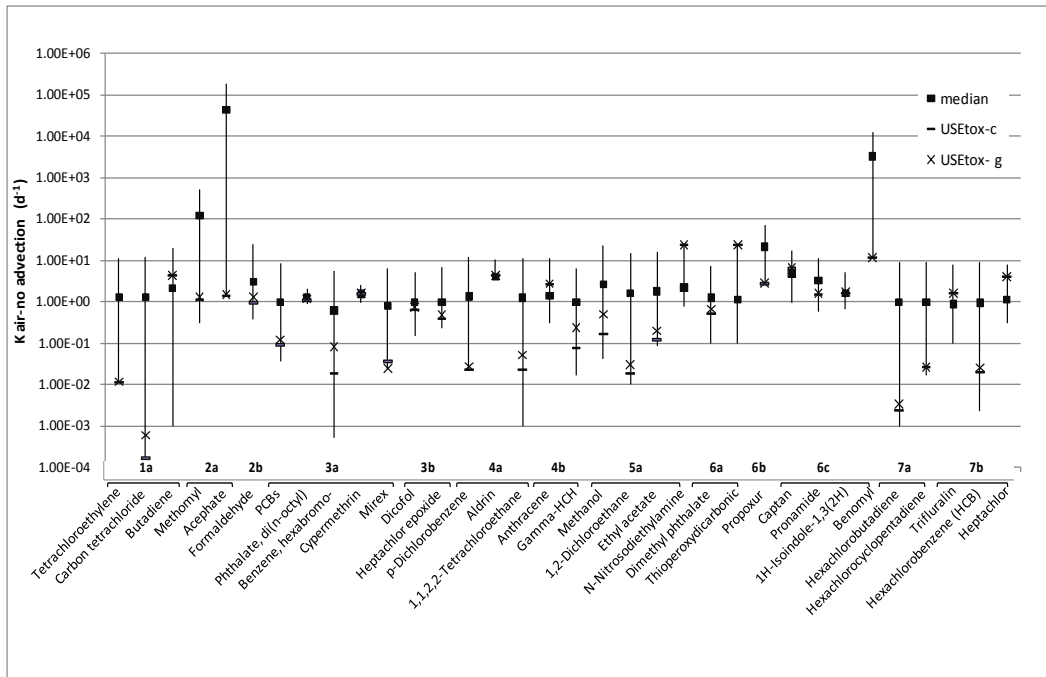|	<1 order of magnitude	1<x<2	2<x<3	3<x<4	x>4
1a			Tetrachloroethylene 1a	Carbon tetrachloride 1a	Butadiene 1a
2a			Methomyl 2a		Acephate 2a
2b		Formaldehyde 2b			
3a	Phthalate, di(n-octyl) 3a Cypermethrin 3a	Mirex 3a	PCBs 3a		Benzene, hexabromo- 3a
3b		Dicofol 3b Heptachlor epoxide 3b			
4a	Aldrin 4a		p-Dichlorobenzene 4a		1,1,2,2-Tetrachloroeth ane 4a
4b		Anthracene 4b Dimethyl phthalate 4b	Gamma-HCH 4b		
5a		N-Nitrosodiethylamine 5a	Methanol 5a Ethyl acetate 5a	1,2-Dichloroethane 5a	
6a		Thioperoxydicarbonic diamide, tetramethyl-6a			
6b		Propoxur 6b			
6c	1H-Isoindole-1,3(2H)-dione, 2-(trichlor) 6c	Pronamide 6c Captan 6c Benomyl 6c			
7a			Hexachlorocyclopenta diene 7a	Hexachlorobuta diene 7a	
7b		Trifluralin 7b Heptachlor 7b		Hexachlorobenz ene (HCB) 7b	

679

680

681

682 Fig. 1 Sub-sections of the chemical space (1a, 2a …) with similar environmental behavior and location of the 34

683 representative chemicals in the test set
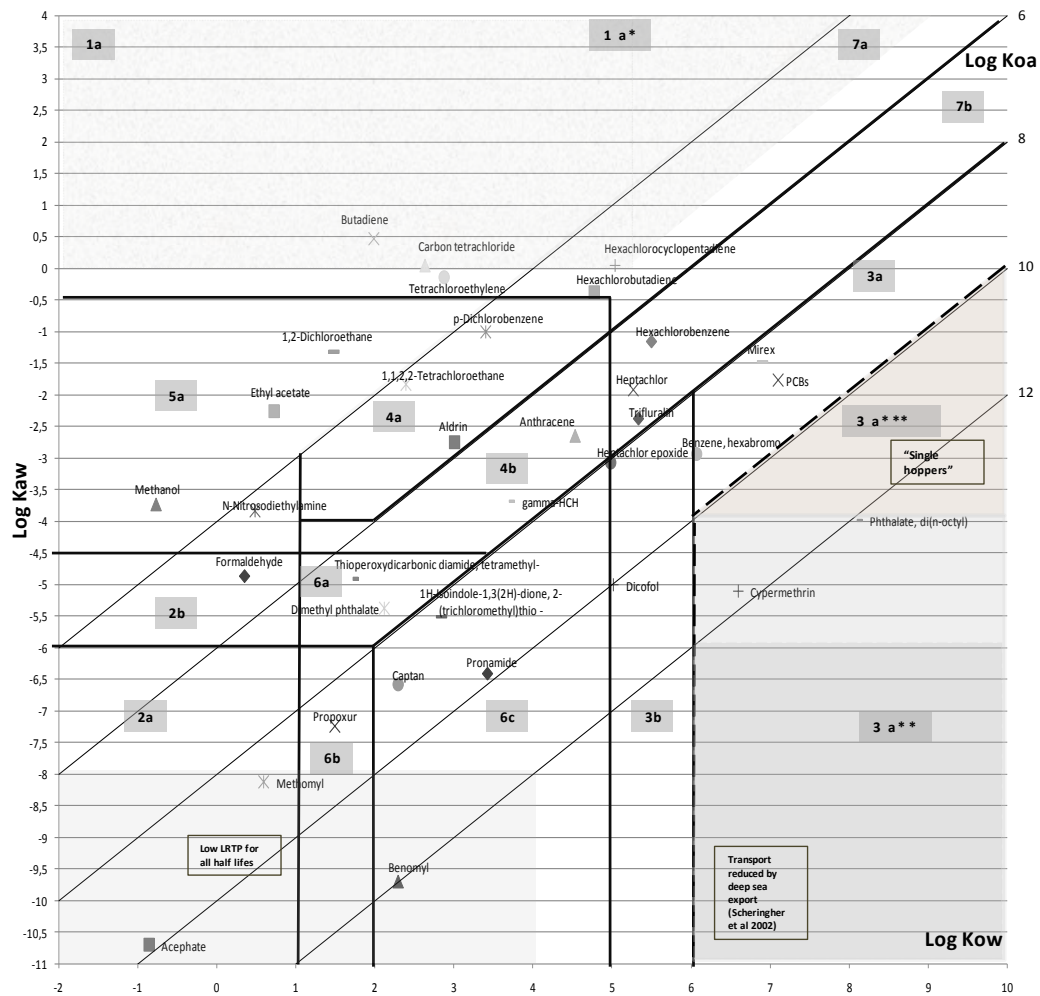
684
685

686 Fig. 2 Variability of removal rate from air (Kair total in 1/d) for the test set of 34 representative chemicals (no

687 advection case). Results plotted: MAPPE median (■), 5th and 95th percentile values at 1*1 degree of resolution;

688 USEtox (-) continental and (X) global default values

689

690

691