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

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Supporting information

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S1. List of chemical and chemical properties used in running the MAPPE Model

The data provided below were taken from the USEtox database. For comparison in few cases the Omniitox project (Molander et al 2004) data were also presented (indicated at the top of the columns)

Table S1. Test set of chemicals and related properties used in MAPPE runs

Chemicals	**Clusters**	**CAS**	**MW**	**Kow**	**Kaw**	**Kh25C**	**Air decay rate**	**Air decay rate**	**Soil decay rate**	**Ssoil decay rate**	**Water decay rate**
			[g/mol]	[-]	[-]	[Pa.m3.mol^{-1}]	[1/s]	[1/hour]	alpha_s [1/s]	[1/hour]	[1/s]
								Omniitox database		Omniitox database	
Tetrachloroethylene	1a	127-18-4	166	7,59E+02	7,15E-01	1,77E+03	3,50E-07	1,26E-03	1,13E-07	4,08E-04	1,10E-07
Carbon tetrachloride	1a	56-23-5	154	4,37E+02	1,11E+00	2,76E+03	1,13E-08		3,19E-08	1,15E-04	1,13E-07
Butadiene	1a	106-99-0	54	9,77E+01	2,97E+00	7,36E+03	1,13E-08		3,50E-07	1,26E-03	1,13E-07
Methomyl	2a	16752-77-5	162	3,98E+00	7,43E-09	1,84E-05	3,32E-06		3,83E-07	1,38E-03	3,49E-08
Acephate	2a	30560-19-1	183	1,41E-01	2,02E-11	5,01E-08	5,59E-06	9,18E-02	3,64E-06	1,31E-02	1,50E-07
Formaldehyde	2b	50-00-0	30	2,24E+00	1,36E-05	3,37E-02	5,31E-05	1,60E-02	3,50E-06	1,26E-02	2,01E-06
PCBs	3a	1336-36-3	292	1,26E+07	1,68E-02	4,15E+01	4,07E-07		2,14E-07	7,70E-04	5,70E-07
Phthalate, di(n-octyl)	3a	117-84-0	391	1,26E+08	1,04E-04	2,57E-01	1,03E-05		5,72E-07	2,06E-03	5,73E-07
Benzene, hexabromo-	3a	87-82-1	551	1,17E+06	1,13E-03	2,81E+00	5,73E-09		1,34E-07	4,81E-04	1,34E-07
Cypermethrin	3a	52315-07-8	416	3,98E+06	7,75E-06	1,92E-02	1,07E-05		1,54E-07	5,56E-04	1,60E-06
Mirex	3a	2385-85-5	546	7,94E+06	3,27E-02	8,11E+01	1,13E-06		3,50E-09	1,26E-05	1,13E-06
Dicofol	3b	115-32-2	370	1,05E+05	9,77E-06	2,42E-02	1,72E-06		1,32E-07	4,75E-04	2,14E-07
Heptachlor epoxide	3b	1024-57-3	389	9,55E+04	8,48E-04	2,10E+00	2,59E-06		2,74E-08	9,87E-05	2,74E-08
p-Dichlorobenzene	4a	106-46-7	147	2,51E+03	9,73E-02	2,41E+02	3,50E-07		3,50E-08	1,26E-04	1,13E-07
Aldrin	4a	309-00-2	365	1,02E+03	1,78E-03	4,40E+00	3,86E-05	1,39E-01	1,13E-08	4,08E-05	1,10E-08
1,1,2,2-Tetrachloroethane	4a	79-34-5	168	2,45E+02	1,48E-02	3,67E+01	1,13E-08		3,50E-08	1,26E-04	1,13E-07
Anthracene	4b	120-12-7	178	3,47E+04	2,25E-03	5,56E+00	3,50E-06		3,50E-08	1,26E-04	3,50E-07
gamma-HCH	4b	58-89-9	291	5,01E+03	2,08E-04	5,14E-01	1,85E-07		1,13E-08	4,08E-05	1,13E-08

Methanol	5a	67-56-1	32	1,70E-01	1,84E-04	4,55E-01	4,91E-07	1,70E-03	3,50E-06	1,26E-02	3,50E-06
1,2-Dichloroethane	5a	107-06-2	99	3,02E+01	4,77E-02	1,18E+02	1,13E-07		3,50E-08	1,26E-04	1,13E-07
Ethyl acetate	5a	141-78-6	88	5,37E+00	5,41E-03	1,34E+01	9,92E-07		1,13E-06	4,08E-03	2,01E-06
N-Nitrosodiethylamine	5a	55-18-5	102	3,02E+00	1,47E-04	3,63E-01	3,21E-05	3,19E-02	1,13E-07	4,08E-04	3,21E-05
Dimethyl phthalate	6a	131-11-3	194	1,32E+02	4,24E-06	1,05E-02	1,13E-06		3,50E-07	1,26E-03	1,13E-06
Thioperoxydicarbonic diamide, tetramethyl-	6a	137-26-8	240	5,37E+01	1,23E-05	3,04E-02	1,13E-06	4,08E-03	3,50E-07	1,26E-03	1,13E-06
Propoxur	6b	114-26-1	209	3,16E+01	5,77E-08	1,43E-04	3,85E-05	1,63E-01	3,50E-07	1,26E-03	3,50E-07
Captan	6c	133-06-2	301	2,00E+02	2,62E-07	6,48E-04	1,13E-05		3,50E-07	1,26E-03	1,13E-05
Pronamide	6c	23950-58-5	256	2,69E+03	3,95E-07	9,77E-04	6,62E-06		9,97E-08	3,59E-04	1,97E-07
1H-Isoindole-1,3(2H)-dione, 2-(trichloromethyl)thio -	6c	133-07-3	297	7,08E+02	3,09E-06	7,66E-03	7,87E-06		1,40E-08	5,04E-05	1,40E-08
Benomyl	6c	17804-35-2	290	2,00E+02	1,99E-10	4,93E-07	3,86E-05	1,39E-01	1,13E-07	4,08E-04	1,13E-06
Hexachlorobutadiene	7a	87-68-3	261	6,03E+04	4,16E-01	1,03E+03	1,50E-08	4,03E-05	1,13E-07	4,07E-04	1,10E-07
Hexachlorocyclopentadiene	7a	77-47-4	273	1,10E+05	1,09E+00	2,70E+03	1,97E-07		4,58E-07	1,65E-03	2,23E-06
Trifluralin	7b	1582-09-8	336	2,19E+05	4,16E-03	1,03E+01	1,13E-06	7,77E-02	1,13E-07	4,08E-04	1,13E-07
Hexachlorobenzene	7b	118-74-1	285	3,16E+05	6,86E-02	1,70E+02	2,62E-08		3,50E-09	1,26E-05	3,50E-09
Heptachlor	7b	76-44-8	373	1,86E+05	1,19E-02	2,94E+01	3,50E-06		1,13E-07	4,08E-04	3,50E-07

Explanation of abbreviations:

MW: Molecular weight

Kow: octanol-water partition coefficient

Kaw: air-water partition coefficient

Kh: Henry constant

S2 Description of the MAPPE model

MAPPE Global model is a GIS based model that grounds on concepts of the MAPPE model and computes the removal rates of a substance with given physico-chemical properties in an evaluative environment, composed of atmospheric boundary layer, soil, inland and seawater, for the whole world, with a resolution of 1ox1o (except for some parameters, which are defined at finer resolution (Zulian et al, 2011).

It is a spatialized steady state box model that computes chemical mass (M_x) for a certain grid cell as a algebraic combination of the maps of emissions (E_x) and removal rates (K_x) for each medium:

$$M_x = \frac{E_x}{K_x}$$

where x indicates air, soil, or ocean.

In a similar way, the mass fluxes (L_x) of chemicals originated from a cell and available for long range transport (“loads”) are computed as:

$$L_x = M_x K_{adv,x}$$

where $K_{adv,\ x}$ is the map of advection removal rates, associated to wind, ocean currents, runoff and erosion from soils.

For example in the atmospheric compartment we consider:

Air-aerosol partitioning

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

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

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

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

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

Wet deposition

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

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

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

Particle dry deposition

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

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

Gas absorption

The absorption velocity of atmospheric chemicals in gas phase depends on the type of ground surface. The following categories of ground surface are presently described in the model:

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

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

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

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

The absorption velocity on forests, $K_{gas,\ forest}$ (m s^{-1}) is therefore:

$$\mathrm{K_{gas,forest}} = \left(0.036\frac{\mathrm{Dec}}{100} + 0.0078\ \frac{\mathrm{Eve}}{100}(1-\ \frac{\mathrm{Bro}}{100}) + 0.054\frac{\mathrm{Eve}}{100}\frac{\mathrm{Bro}}{100}\right)\left(\frac{300}{\mathrm{MW}}\right)^{0.5}$$

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

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

$$\mathrm{K_{gas,soil}} = \frac{D_a}{(\xi h + d_a)}$$

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

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

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

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

Under these assumptions,

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

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

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

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

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

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

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

Then, for each grid cell in the model, the gas absorption is calculated as:

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

where w being the percentage of the cell that is water, and Imp the percentage that is impervious surface.

Degradation

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

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

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

Total atmospheric removal rate

The total atmospheric removal rate (d^{-1}) is:

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

where the last term represents the air intramedium transport or dilution by advection. Here u_{10} (m s^{-1}) is the wind speed at *10*m height and *X* (m) is the size of the calculation cell (approximately *100000* m corresponding to 1 degree resolution). Then the term of advection rate quantifies the fraction of the air to be moved out through the lateral borders of computational cells with u_{10} speed.

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

The other extreme case is when emissions occur in a uniform (homogeneous) way in space, thus the advection may be neglected. In this case, one should consider:

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

Real situations should be in between these two extremes.

Deposition

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

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

Reference for this section

McLachlan M, Horstmann M (1998). Forests as filters of airborne organic pollutants: a model Env Sci Technol 32: 413-420

Pistocchi A (2005). Report on multimedia fate and exposure model with various spatial resolutions at the European level, NoMiracle IP D2.4.1 technical report, 62 pp

Schwarzenbach R P; Gschwend P M, Imboden D. M (1993). Environmental Organic Chemistry. Wiley: New York 681pp.

Zulian, G, Isoardi P, Pistocchi A (2010) Global atlas of environmental parameters for chemical fate and transport assessment, EC, EUR 24255 EN

S3. Chemical space of organic chemicals in the USEtox database

Fig.S1 Chemical space (Kow and Kaw) covered by the substances in USEtox ("database organics"). The box indicates the chemical space assessed in the paper and detailed in Fig S2.

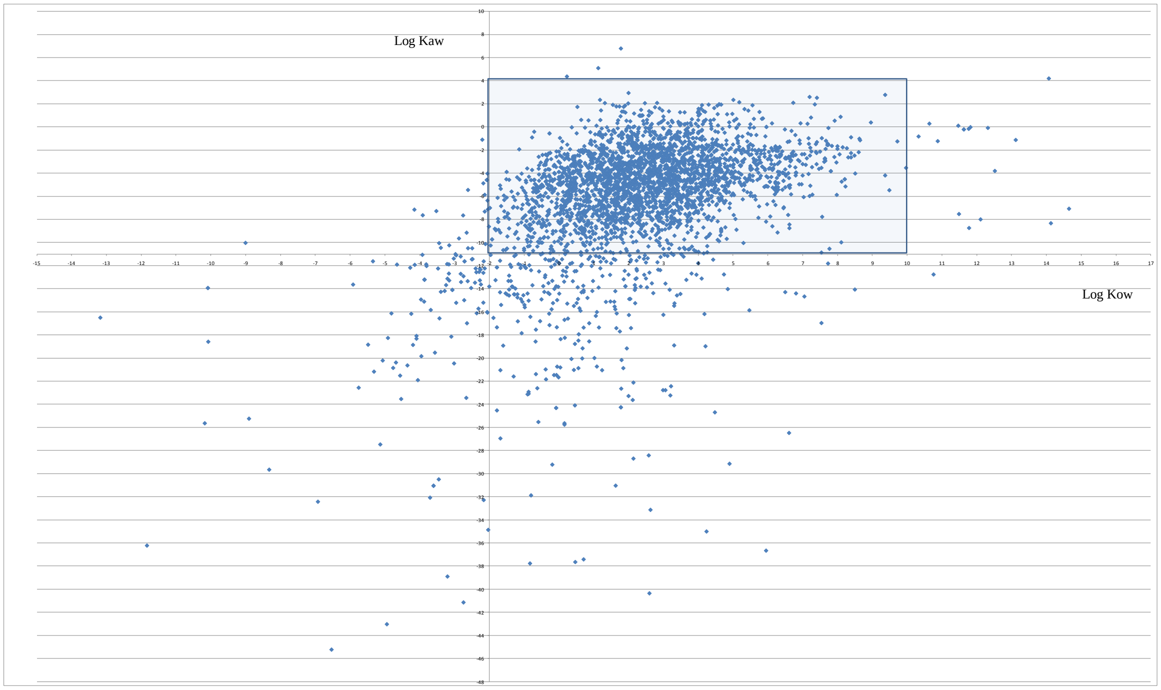


Figure S2. Chemicals within the chemical space defined to cluster chemicals in this paper

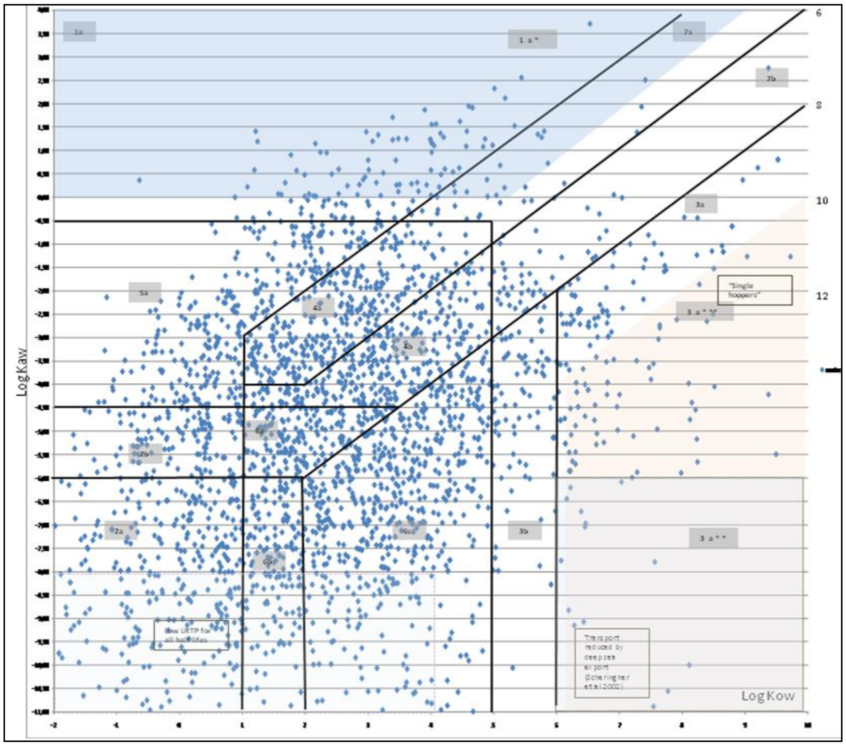
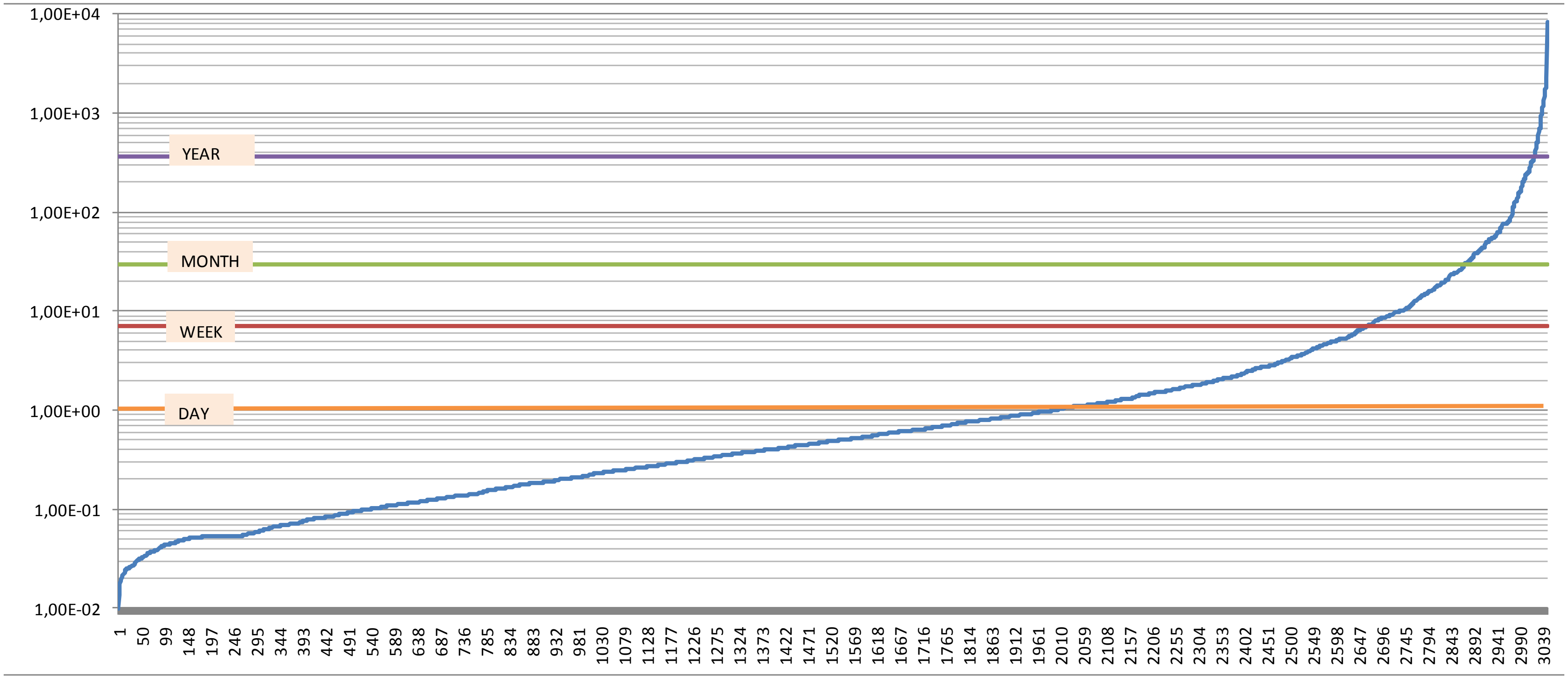


Figure S3. Atmospheric half life in days for the organic chemicals in the USEtox database (plotted for all the chemicals presented in the database)



S4. Variability of removal rates from air for the 34 chemicals in the test set (with advection)

Fig. S4 Results of Kair total (1/d) including advection for the 34 chemicals in the test set

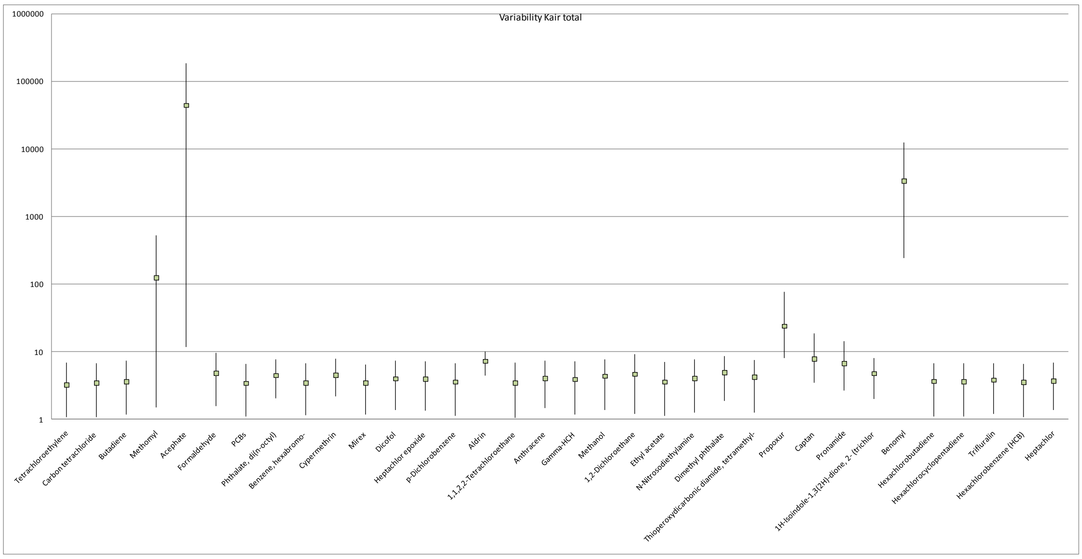


Table S2 Comparison of the MAPPE and USEtox results: MAPPE Median, 5% and 95% percentile, USEtox continental and global default for the total Kair (1/d) for the 34 chemicals in the case of no advection

	MAPPE			**USEtox**	
	95%ile	5%ile	median	USEtox-continental	USEtox-global
Tetrachloroethylene 1a	1.16E+01	3.02E-02	1.28E+00	1.11E-02	1.17E-02
Carbon tetrachloride 1a	1.20E+01	9.50E-04	1.30E+00	1.65E-04	5.86E-04
Butadiene 1a	2.03E+01	9.50E-04	2.18E+00	4.32E+00	4.32E+00
Methomyl 2a	5.29E+02	2.99E-01	1.22E+02	1.12E+00	1.27E+00
Acephate 2a	1.86E+05	7.19E+00	4.40E+04	1.39E+00	1.53E+00
Formaldehyde 2b	2.47E+01	3.84E-01	3.02E+00	9.54E-01	1.29E+00
PCBs 3a	8.76E+00	3.52E-02	9.73E-01	9.05E-02	1.22E-01
Phthalate, di(n-octyl) 3a	2.07E+00	8.64E-01	1.29E+00	1.09E+00	1.15E+00
Benzene, hexabromo- 3a	5.52E+00	4.94E-04	6.14E-01	1.84E-02	8.10E-02
Cypermethrin 3a	2.53E+00	9.51E-01	1.53E+00	1.55E+00	1.64E+00
Mirex 3a	6.48E+00	9.76E-02	7.84E-01	3.58E-02	2.40E-02
Dicofol 3b	5.07E+00	1.49E-01	9.69E-01	6.41E-01	7.46E-01
Heptachlor epoxide 3b	6.65E+00	2.24E-01	9.56E-01	3.84E-01	4.91E-01
p-Dichlorobenzene 4a	1.23E+01	3.02E-02	1.35E+00	2.22E-02	2.70E-02
Aldrin 4a	1.04E+01	3.34E+00	4.09E+00	4.24E+00	4.31E+00
1,1,2,2-Tetrachloroethane 4a	1.15E+01	9.76E-04	1.24E+00	2.30E-02	5.11E-02
Anthracene 4b	1.10E+01	3.02E-01	1.38E+00	2.64E+00	2.73E+00
Gamma-HCH 4b	6.52E+00	1.60E-02	9.59E-01	7.74E-02	2.32E-01
Methanol 5a	2.25E+01	4.08E-02	2.59E+00	1.62E-01	4.96E-01
1,2-Dichloroethane 5a	1.50E+01	9.76E-03	1.62E+00	1.88E-02	2.97E-02
Ethyl acetate 5a	1.60E+01	8.57E-02	1.80E+00	1.21E-01	1.96E-01
N-Nitrosodiethylamine 5a	1.27E+01	7.65E-01	2.19E+00	2.40E+01	2.41E+01
Dimethyl phthalate 6a	7.46E+00	9.77E-02	1.27E+00	5.13E-01	6.62E-01
Thioperoxydicarbonic diamide, tetramethyl- 6a	7.69E+00	9.76E-02	1.14E+00	2.40E+01	2.41E+01
Propoxur 6b	7.38E+01	3.92E+00	2.14E+01	2.71E+00	2.86E+00
Captan 6c	1.67E+01	9.77E-01	4.82E+00	6.48E+00	6.61E+00
Pronamide 6c	1.13E+01	5.72E-01	3.33E+00	1.50E+00	1.62E+00
1H-Isoindole-1,3(2H)-dione, 2-(trichlor) 6c	5.11E+00	6.80E-01	1.64E+00	1.57E+00	1.70E+00
Benomyl 6c	1.26E+04	2.41E+02	3.33E+03	1.16E+01	1.17E+01
Hexachlorobutadiene 7a	9.24E+00	9.68E-04	9.95E-01	2.30E-03	3.28E-03
Hexachlorocyclopentadiene 7a	9.05E+00	1.70E-02	9.89E-01	2.57E-02	2.60E-02
Trifluralin 7b	7.98E+00	9.76E-02	8.86E-01	1.58E+00	1.63E+00
Hexachlorobenzene (HCB) 7b	8.85E+00	2.26E-03	9.53E-01	1.95E-02	2.51E-02
Heptachlor 7b	8.03E+00	3.02E-01	1.13E+00	3.97E+00	4.00E+00

S5. Patterns of variability

Series of maps of removal rates for selected chemical used to illustrate pattern of variability. The maps were calculated with MAPPE global at a spatial resolution of 1x1 degree

Butadiene

Fig S5. Map of the air removal rate of Butadiene (no advection case). Resolution of the map is 1°*1° degree. The pattern of variability is dominated by the variability of Kgas (removal rate due to gas exchange)

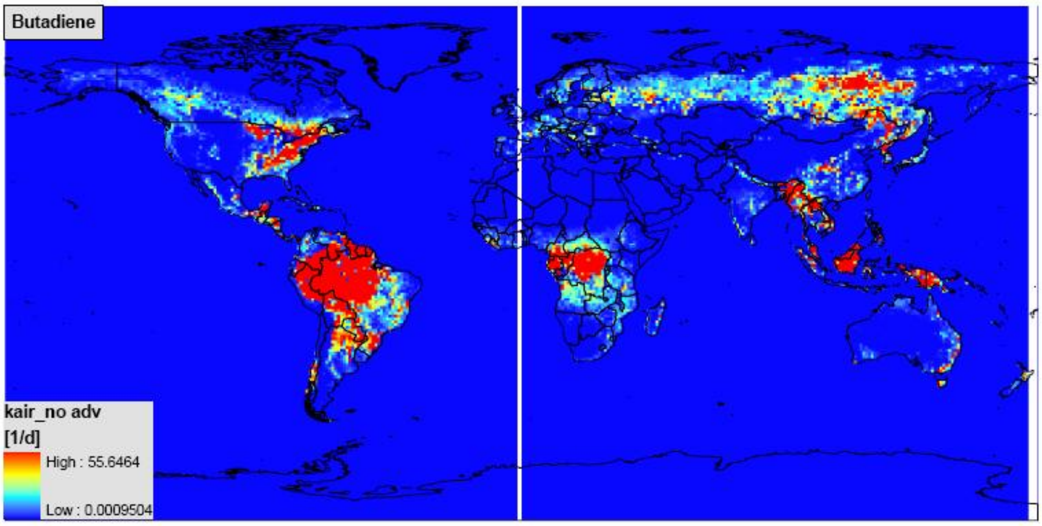
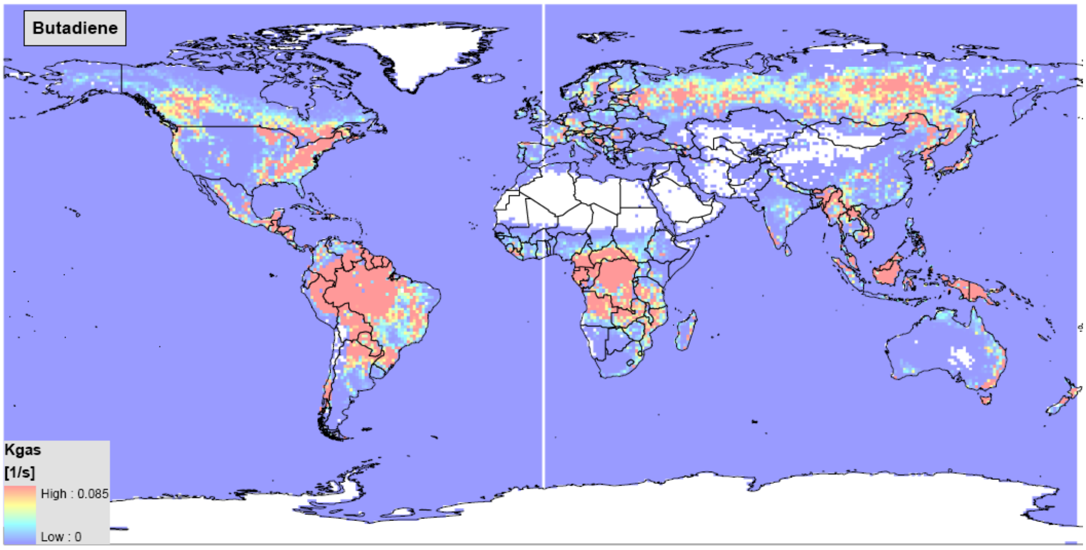


Fig.S6 Map of the removal rate due to gas exchange of Butadiene



Acephate

Fig. S7 Map of the air removal rate of Acephate (no advection case). Resolution of the map is 1°*1° degree .The pattern of variability is dominated by the variability of Kwet (removal rate due to wet deposition)

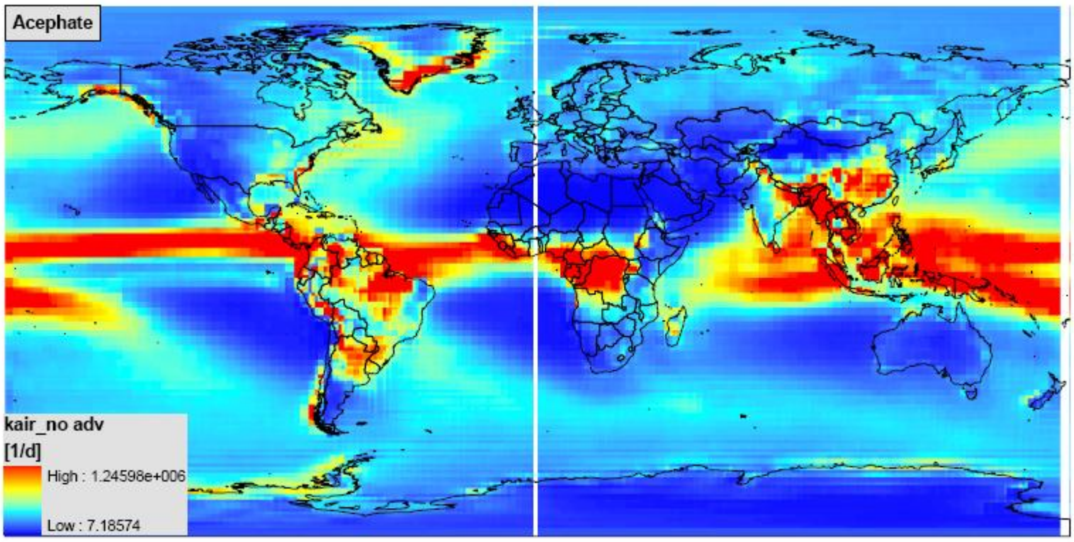


Fig. S8 Map of the air Acephate: removal rate due to wet deposition

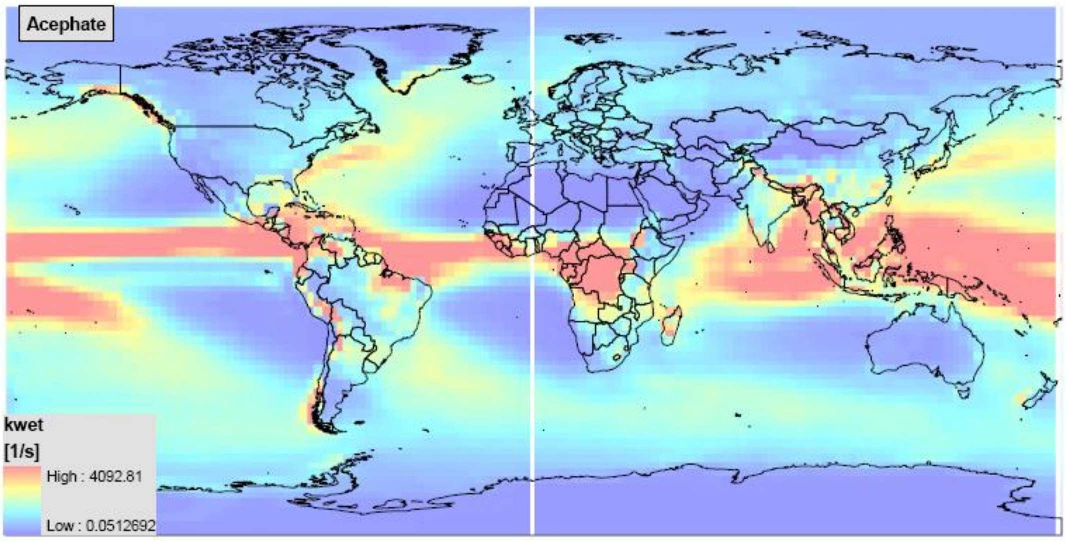
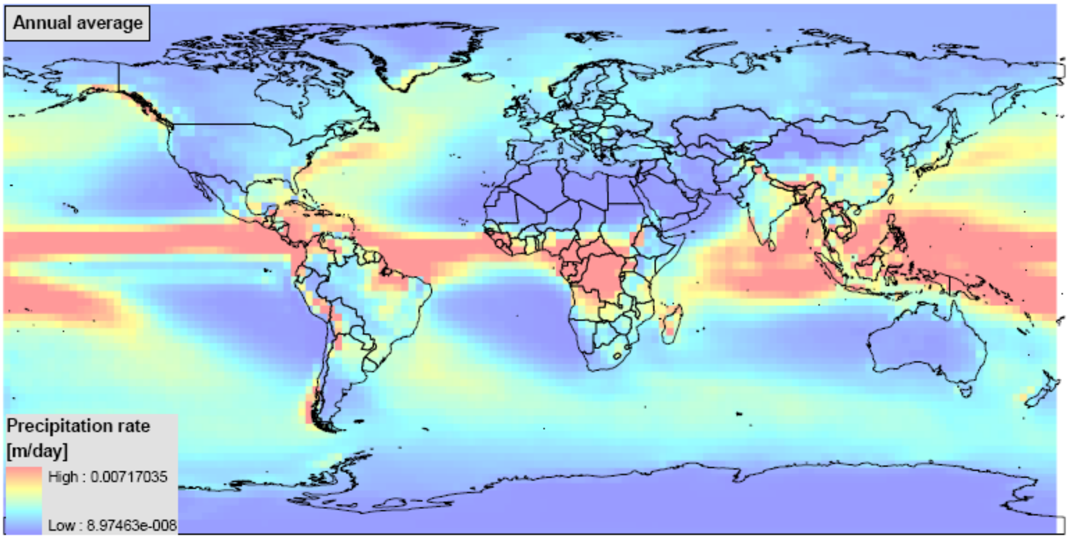
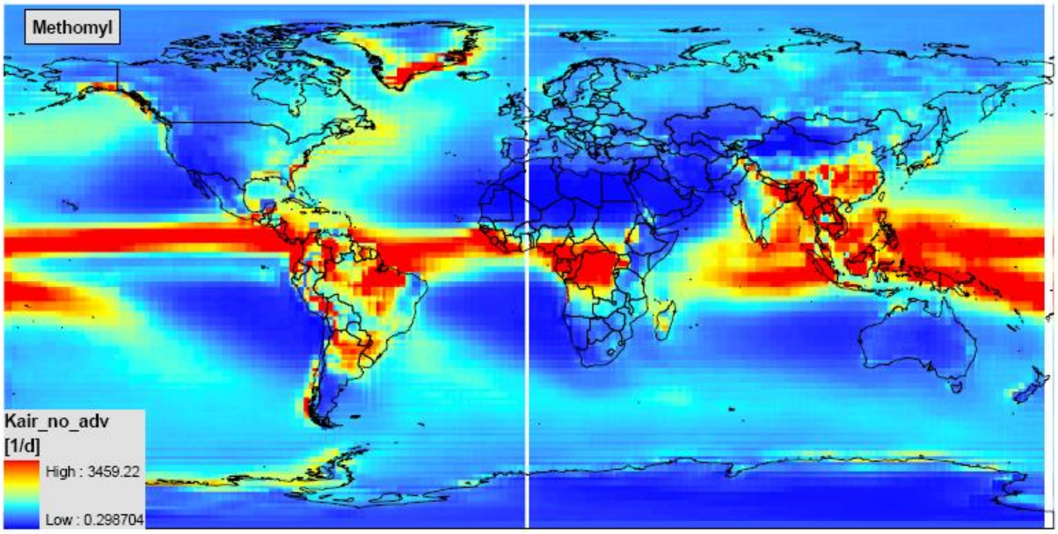


Fig.S9 Map of the average annual precipitation



Methomyl

Fig. S10 Map of the air removal rate of Methomyl (no advection case)



PCB’s

Fig. S11 Map of the air removal rate of PCB’s (no advection case)

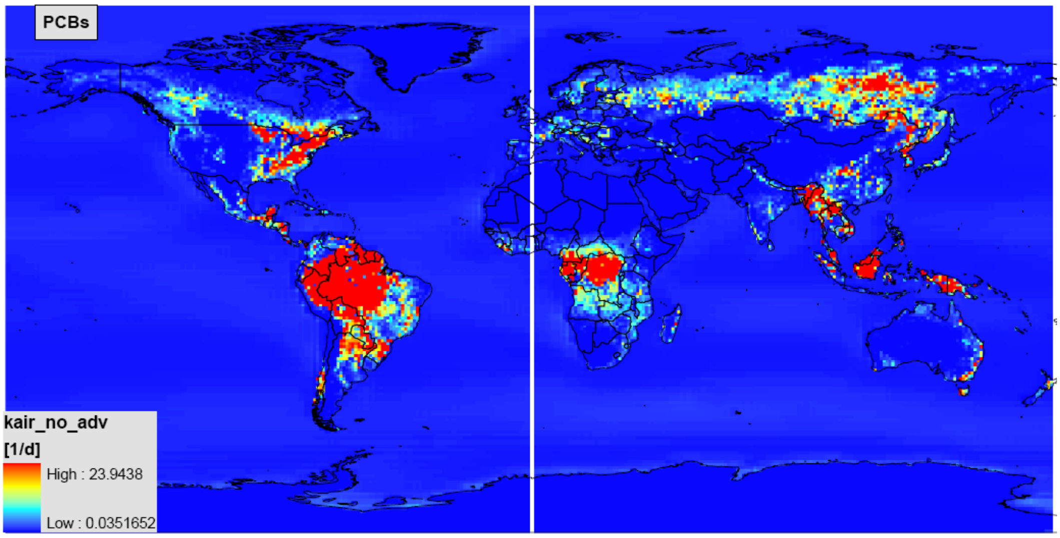


Fig. S12 Map of air removal rate due to gas exchange of PCB’s

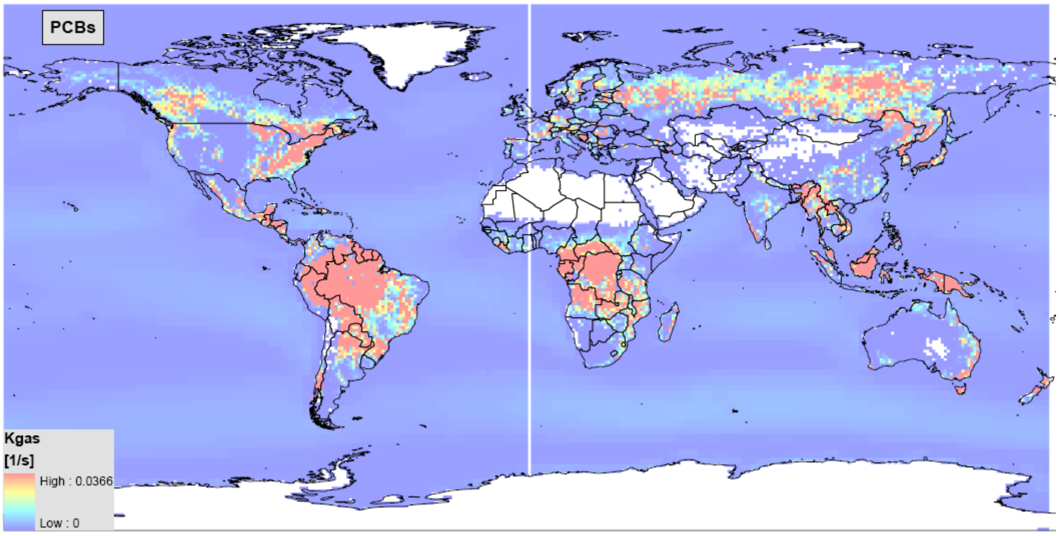


Fig. S13 Map of air removal rate due to wet deposition of PCB's

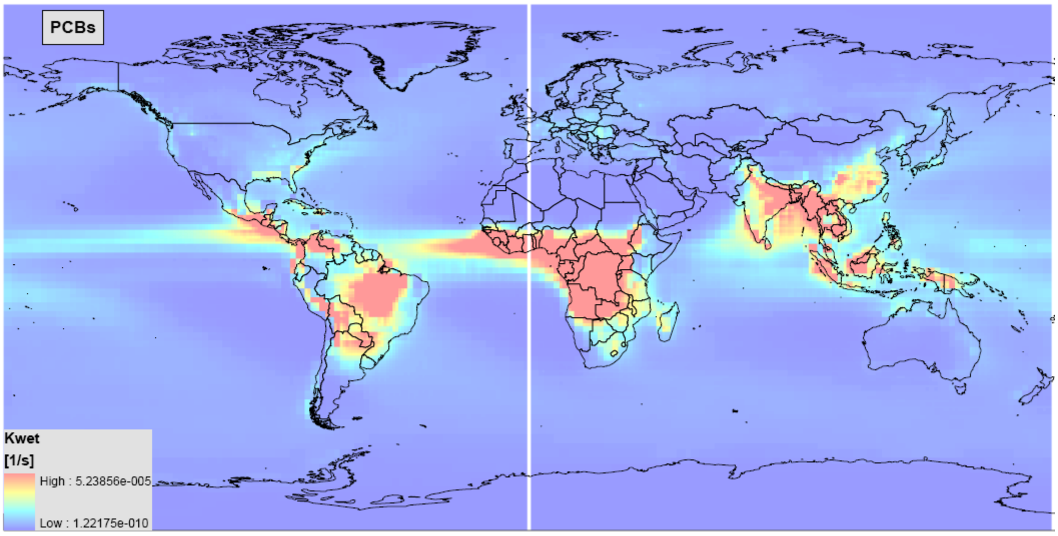
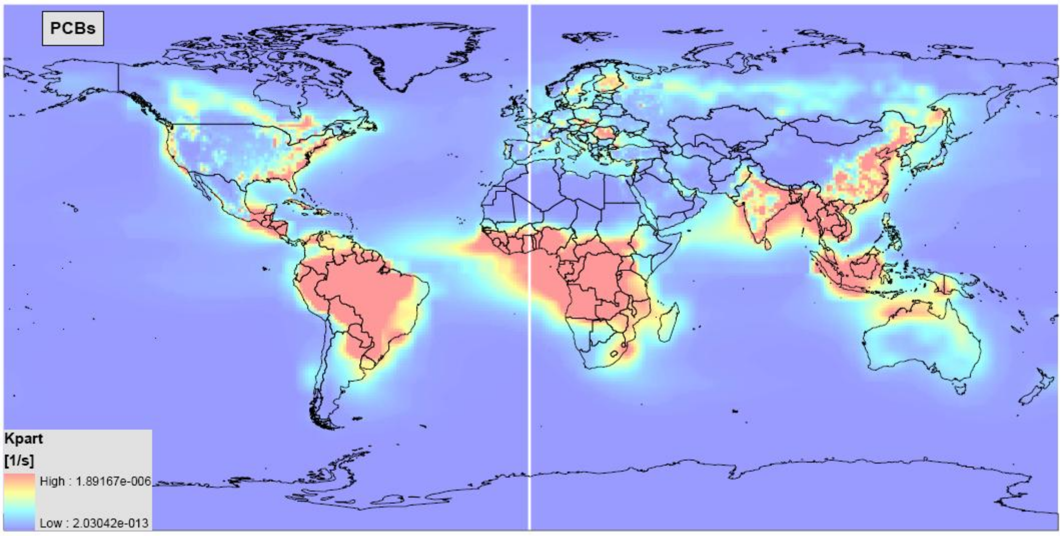


Fig. S14 Map of air removal rate due to particle dry deposition of PCB's



Hexabromobenzene

Fig. S15 Map of total air removal rate of Hexabromobenzene (no advection case)

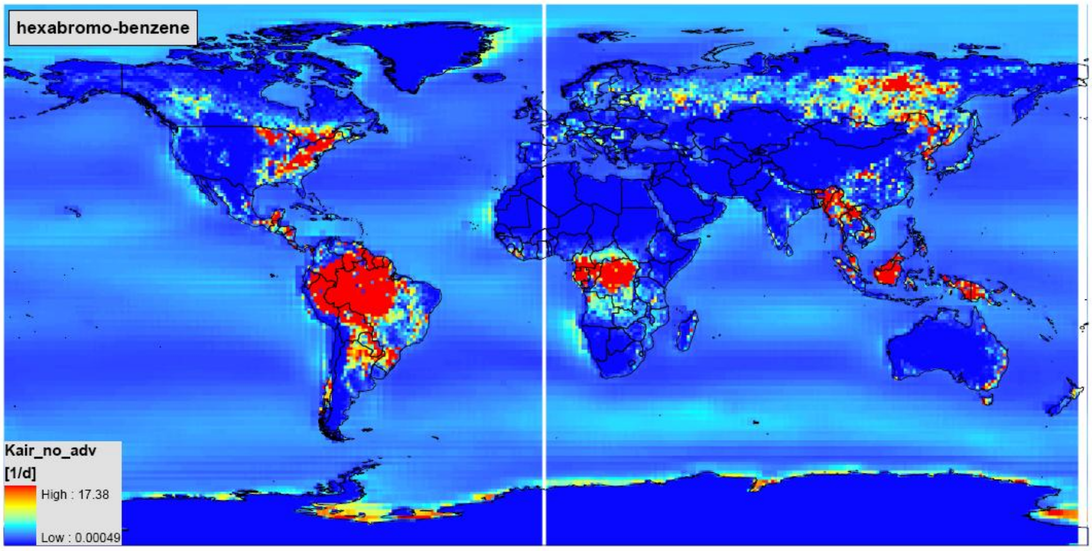


Fig. S16 Map of air removal rate due to gas exchange of Hexabromobenzene

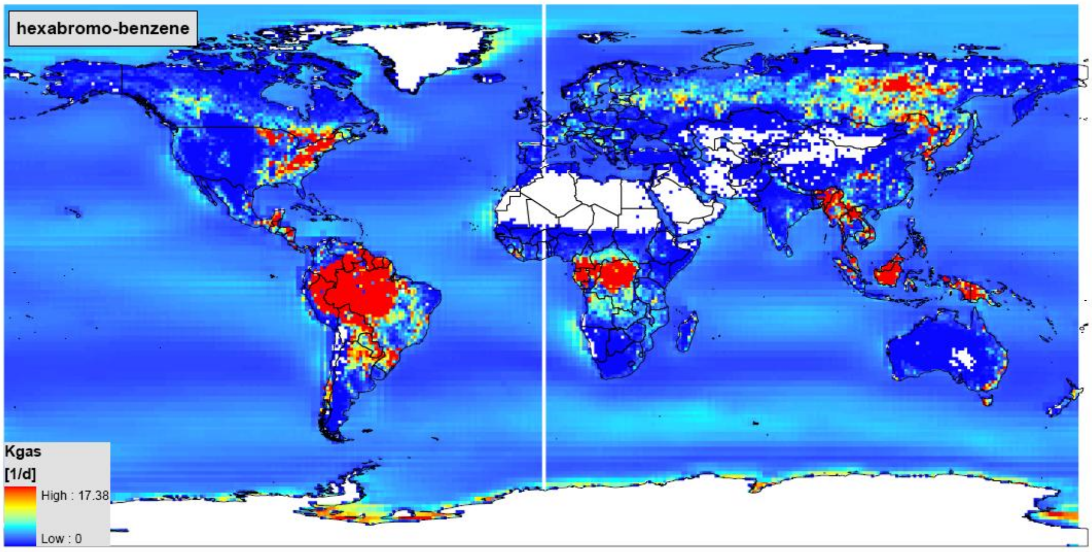
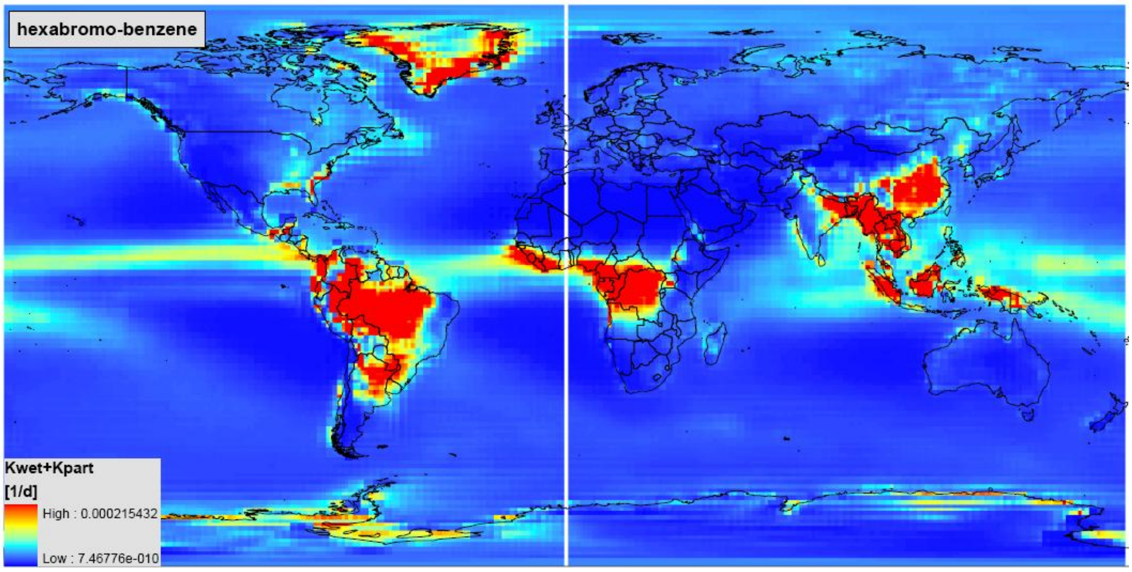
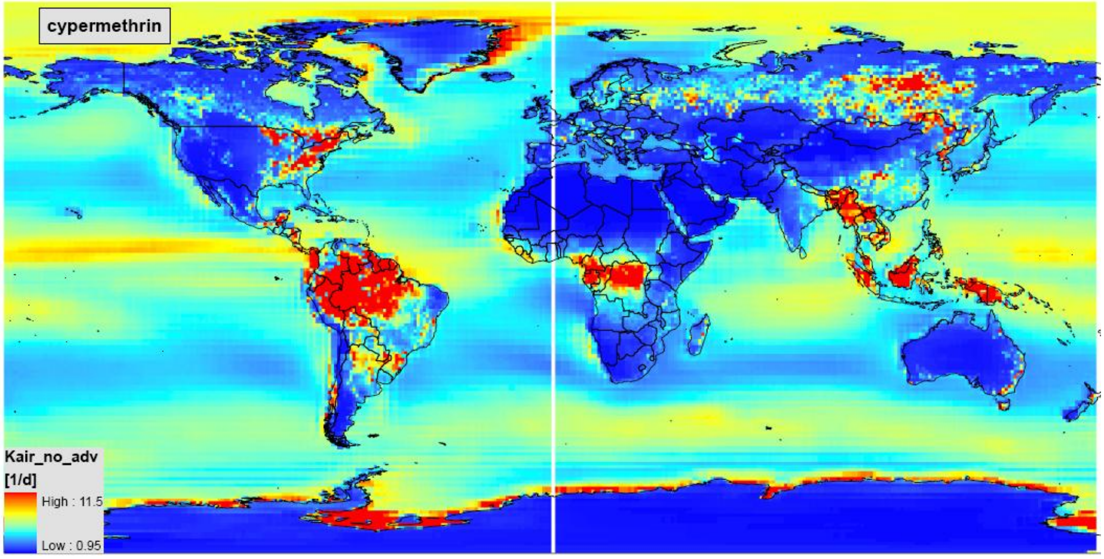


Fig. S17 Map of air removal rate due to wet and dry deposition of Hexabromobenzene



Cypermethrin

Fig. S18 Map of total air removal rate of Cypermethrin (no advection case)



Lindane

Fig. S19 Map of total air removal rate of Lindane (no advection case)

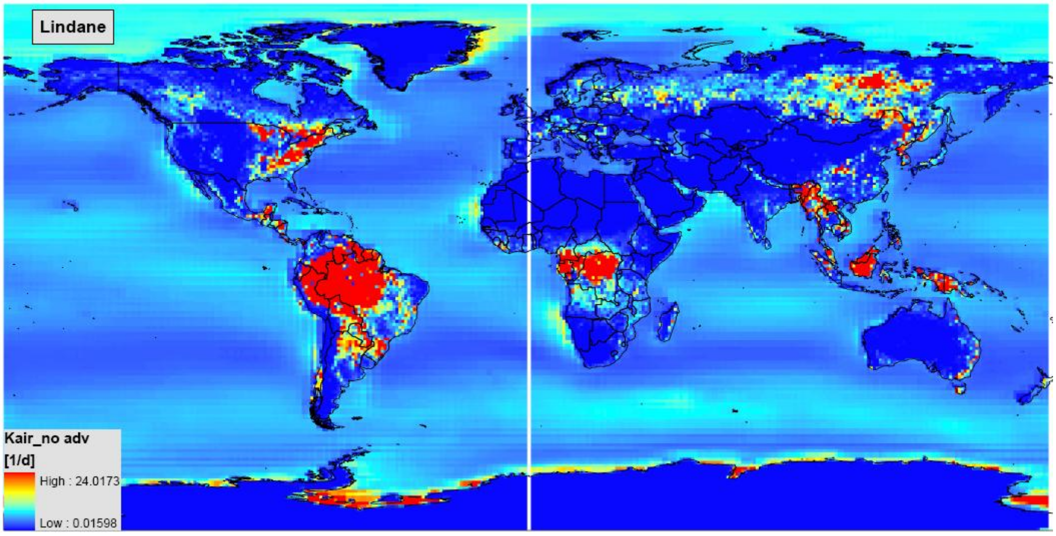


Fig. S20 Ratio of removal rate from air due to particle dry deposition to Kair (no advection) for Lindane

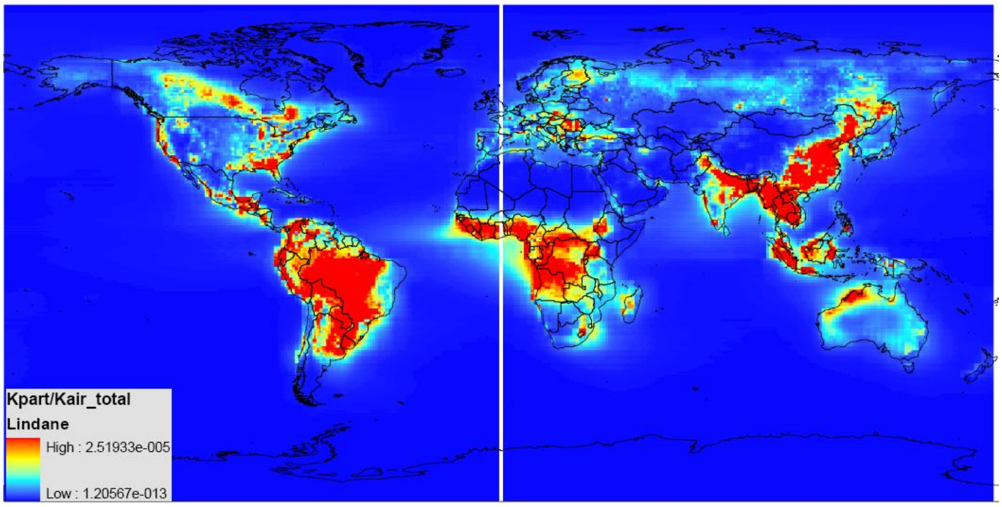


Fig. S21 Ratio of removal rate from air due to wet deposition to Kair (no advection) for Lindane

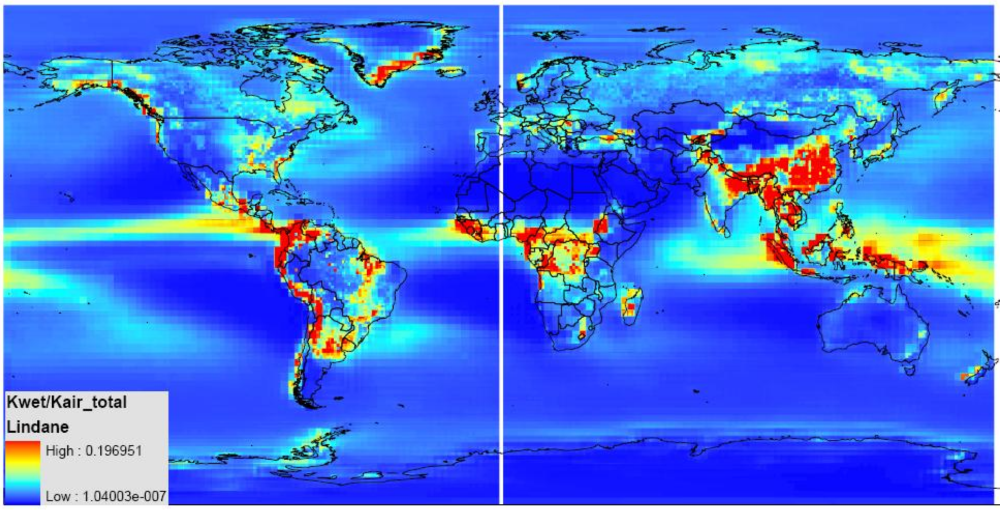


Fig. S22 Ratio of removal rate from air due to gas exchange to Kair (no advection) for Lindane

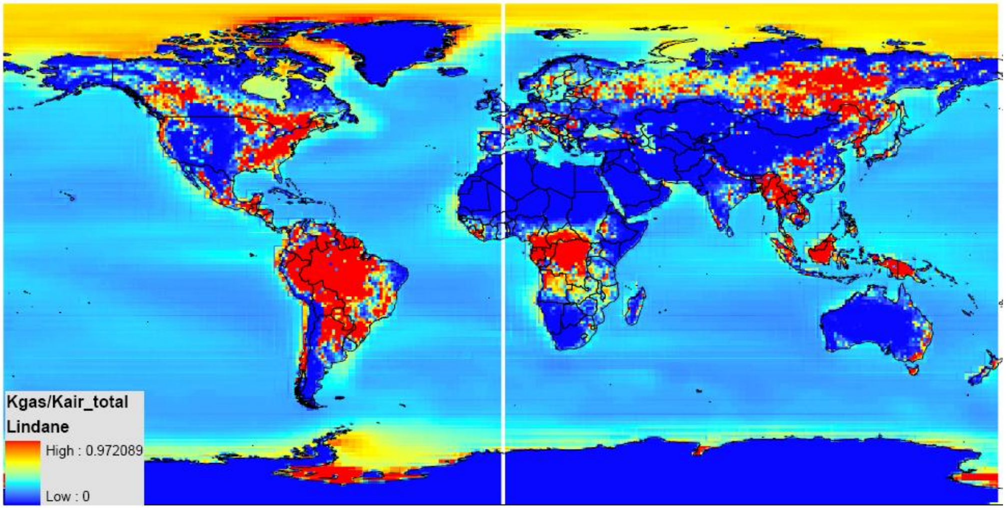
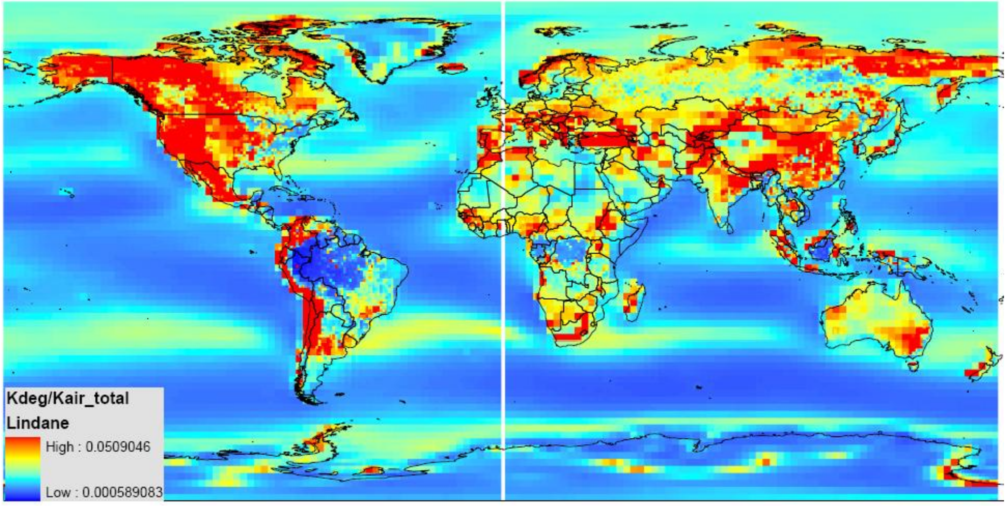


Fig. S23 Ratio of removal rate from air due to degradation to Kair (no advection) for Lindane. In this case Kdeg is dependant by temperature



S6. Relative importance of removal rates

Fig. S24 Relative importance of various removal processes in air at country level for Lindane

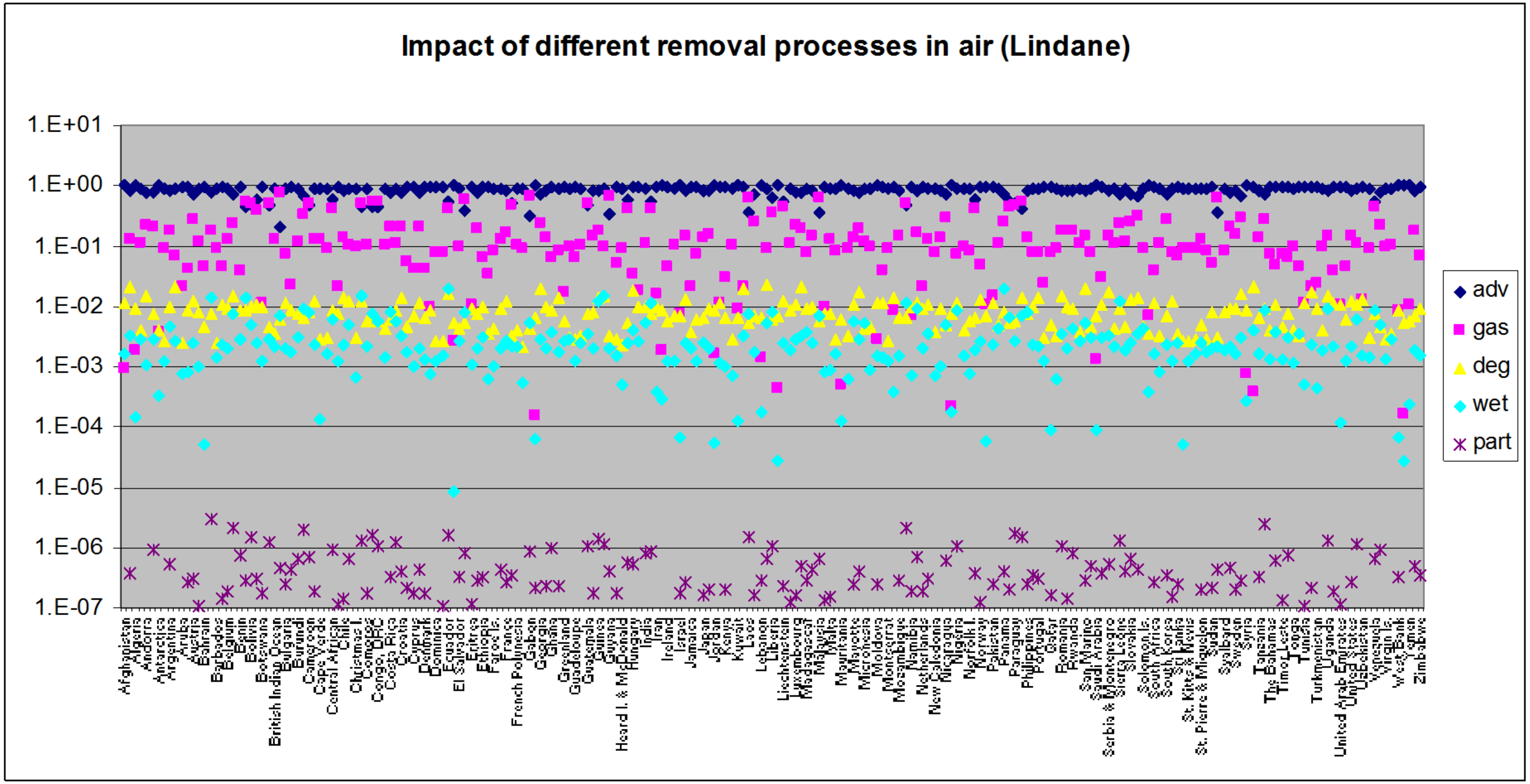


Fig. S25 Relative importance of the removal rates of the chemical in the test set. Removal rates from USEtox (removal to stratosphere, degradation, wet and dry deposition, gas adsorption) are plotted. MAPPE median and USEtox global results are also presented.