

1 **Supporting information**

2

3 **Section S1**

4 - **Details on oven program and MS setting**

5 Three oven programs were set.

6 • (GC run I) For DDTs, HCB and HCHs the oven program was the following: starting temperature  
7 of 80 °C, 15 °C/min to 160 °C, 5 °C/min to 200 °C, hold for 1 min, 5 °C/min to 240 °C, 10 °C/min  
8 to 270 °C, 10 °C/min to 280 °C, hold for 3,33 min.

9 • (GC run II) For ECs the oven program was the following: starting temperature of 50 °C, 15  
10 °C/min to 160 °C, 4 °C/min to 200 °C, hold for 0.80 min, 1 °C/min to 205 °C, 30 °C/min to 280  
11 °C, hold for 2.37 min.

12 • (GC run III) For PCBs the oven program was the following: starting temperature of 90 °C, 20  
13 °C/min to 160 °C, 1.5 °C/min to 220 °C, hold for 6 min, 30 °C/min to 280 °C, hold for 3 min.

14 The MS was set in selected ion monitoring with SIM mode and retention time (min), identification  
15 and quantification ions of analytes are shown in the Table SI-1.

16 The detection limit of analyzed was from 2.1 to 6.3 pg/L for POPs considered, terbuthylazine, HHCB  
17 and AHTN, and from 5.2 to 15.6 pg/L for chlorpyrifos and pendimethalin.

18

1 Table SI-1: Analyzed chemicals retention time and characteristic fragments

Chemical name	Retention time (min)	Characteristic fragments	Specific mass-to-charge ratio
<b>GC run I</b>			
$\alpha$ -HCH	12.04	181-219	181/219 = 0.9
HCB	12.18	284-286	284/286 = 1.2
$\gamma$ -HCH	13.10	181-219	181/291 = 0.9
o,p'-DDE	19.64	246-318	246/318 = 2
p,p'-DDE	20.89	246-318	246/318 = 0.8
o,p'-DDD	21.12	235-237	235/237 = 1.5
p,p'-DDD	22.47	235-237	235/237 = 1.5
o,p'-DDT	22.57	235-237	235/237 = 1.5
p,p'-DDT	23.80	235-237	235/237 = 1.5
<b>GC run II</b>			
TBZ	15.87	214-229	214/229 = 2.80
HHCB	17.38	243-258	243/258 = 4.30
AHTN	17.38	243-258	243/258 = 4.30
CPF	20.32	314-197	314/197 = 1.30
PEN	22.26	252-281	252/281 = 7.05
<b>GC run III</b>			
PCB- 28	18.83	256-258	256/258 = 1.03
PCB -52	21.62	292-294	292/294 = 2.03
PCB-101	29.49	326-328	326/328 = 1.54
PCB-153	38.05	360-362	360/362 = 1.24
PCB-180	48.50	394-396	394/396 = 1.04

2  
3  
4  
5

1        -    **Details on quality control**

2    Table SI-2: Recovery rates for the analyzed chemicals (st. deviation in brackets).

Chemical	Recovery rate in water (%)	Recovery rate in suspended solids (%)
$\alpha$ -HCH	83 ( $\pm$ 3.7)	108 ( $\pm$ 6.6)
$\gamma$ -HCH	86 ( $\pm$ 6.9)	115 ( $\pm$ 6.1)
HCB	87 ( $\pm$ 11.2)	80 ( $\pm$ 2.1)
o,p'-DDE	78 ( $\pm$ 9.3)	114 ( $\pm$ 1.9)
p,p'-DDE	92 ( $\pm$ 14.3)	120 ( $\pm$ 0.9)
o,p'-DDD	94 ( $\pm$ 10.9)	109 ( $\pm$ 11)
p,p'-DDD	100 ( $\pm$ 14.5)	119 ( $\pm$ 0.3)
o,p'-DDT	106 ( $\pm$ 13.6)	118 ( $\pm$ 15.6)
p,p'-DDT	111 ( $\pm$ 16.4)	108 ( $\pm$ 8.1)
PCB 28	92 ( $\pm$ 8.2)	102 ( $\pm$ 6.0)
PCB 52	85 ( $\pm$ 3.0)	101 ( $\pm$ 15)
PCB 101	85.4 ( $\pm$ 6.0)	113 ( $\pm$ 16)
PCB 118	93 ( $\pm$ 3.0)	103 ( $\pm$ 8.9)
PCB 138	94 ( $\pm$ 4.1)	108 ( $\pm$ 7.8)
PCB 153	97.8 ( $\pm$ 11)	119 ( $\pm$ 15)
PCB 180	98 ( $\pm$ 7.5)	119 ( $\pm$ 15)
PEN	83 ( $\pm$ 5.4)	82 ( $\pm$ 4.1)
TBZ	96 ( $\pm$ 6.0)	87 ( $\pm$ 11)
CPF	101 ( $\pm$ 8.3)	113 ( $\pm$ 14)
AHTN	94 ( $\pm$ 4.1)	98 ( $\pm$ 4.3)
HHCB	93 ( $\pm$ 2.8)	102 ( $\pm$ 3.5)

3

4

5

## 1 Section S2

### 2 The OECD $P_{ov}$ and LRTP screening tool model

3 This model is currently used as a screening tool for making comparative assessments of  
4 environmental hazard properties of non ionizing chemicals, using metrics of overall persistence ( $P_{OV}$ )  
5 and long-range transport potential (LRTP) (Öberg and Iqbal, 2012; Mostrag et al., 2010). It  
6 incorporates a steady-state fugacity-based model (Mackay, 2001) in which troposphere, soil surface  
7 layer and seawater surface layer are considered as the three main environmental compartments;  
8 furthermore, equilibrium partitioning is assumed between sub-compartments belonging to the same  
9 main compartment. Further details on the characteristics of the chemical fate model incorporated in  
10 the software can be found in Wegmann and coworkers (2009). As substance-specific inputs, the  
11 software requires the air-water partition coefficient ( $K_{AW}$ ) and the octanol-water partition coefficient  
12 ( $K_{OW}$ ), as well as the degradation half-lives ( $DT_{50}$ ) in soil, water and air. For the compounds  
13 considered in this paper, data are listed in Table SI-2.

14 From these inputs,  $P_{OV}$  and two LRTP indicator values (CTD: characteristic travel distance and TE%:  
15 transfer efficiency) are calculated. The values of these three indicators are dependent on the mode of  
16 emission (into air, water or soil); the software calculates their values for each of the three possible  
17 emission scenarios and selects the highest values found. The  $P_{OV}$  (days) gives a measure of  
18 degradation time of a chemical in the whole environment; it is calculated for each mode of emission  
19 according to Eq. (1) (Wegmann et al., 2009):

$$20 \quad P_{OV,i} = \frac{M_{i,TOT}}{F_{DEG,i,A} + F_{DEG,i,W} + F_{DEG,i,S}} \quad (1)$$

21  
22  
23 where  $M_{i,TOT}$  (kg) is the total amount of contaminant at steady-state and  $F_{DEG,i,A}$ ,  $F_{DEG,i,W}$ , and  $F_{DEG,i,S}$   
24 are the degradation mass fluxes in air (A), water (W) and soil (S) (kg/h), respectively.

25 The CTD (unit in km) is the distance at which the chemical's concentration has fallen to about 37%  
26 of its initial value (at the point of release), assuming that the chemical is transported by a constant  
27 flow of air (wind speed = 4 m/s) or water (0.02 m/s). It represents the potential of a chemical to be  
28 transported over long distances in air or water and is calculated using Eq. (2) (Wegmann et al., 2009):

$$29 \quad CTD_i = \frac{M_{i,TOT}}{F_{i,E}} \times \frac{M_{i,i}}{M_{i,TOT}} \times v_i \quad (2)$$

30

1 The first term in the equation is the overall residence time in the multimedia environment (h), which  
 2 is the ratio of the total mass at steady-state for the given mode of emission ( $M_{i,TOT}$ , kg) divided by the  
 3 emission mass flux,  $F_{i,E}$ , that enters medium  $i$ . The second term in Eq. (2) is the dimensionless mass  
 4 fraction in the mobile medium, which is the same as the medium that receives the emissions ( $M_{i,i}$ ,  
 5 kg) divided by the total mass at steady-state for the given mode of emission ( $M_{i,TOT}$ , kg). Finally,  $v_i$   
 6 (km/h) is the assumed transport velocity in the mobile medium.

7 The TE (%) is an indicator of potential for atmospheric transport and deposition of the parent  
 8 compound in a remote region and is calculated for emissions to air, water and soil according to Eq.  
 9 (3) (Wegmann et al., 2009):

$$TE_i = \frac{F'_{i,D}}{F_{i,E}} \times 100 \quad (3)$$

11 where  $F_{i,D}$  (mol/h) is the atmospheric deposition mass flux in a target region and  $F_{i,E}$  (mol/h) is the  
 12 emission mass flux in a source region.

13

14 Table SI- 3 CUPs sales data in Northern Italy and some their relevant properties

Chemical Name	Sales data in North Italy <sup>a</sup> (tons of a.i.)	Molar Mass (g/mol) <sup>b</sup>	log $K_{aw}$ <sup>c</sup>	log $K_{ow}$ <sup>b</sup>	DT <sub>50</sub> air (h)	DT <sub>50</sub> water (h)	DT <sub>50</sub> soil <sup>b</sup> (h)
glyphosate	937	169.10	-10.07	-3.20	38.40 <sup>e</sup>	1,656 <sup>e</sup>	288
metam-sodium	746	129.19	-8.47	-2.91	2 <sup>d</sup>	52.80 <sup>d</sup>	168
fosetyl-aluminium	392	354.10	-12.89	-2.10	46 <sup>d</sup>	103.20 <sup>d</sup>	2.40
S-metolachlor	334	283.80	-6.05	3.05	5 <sup>e</sup>	288 <sup>e</sup>	360
terbuthylazine	292	229.71	-5.78	3.40	35 <sup>d</sup>	4,704 <sup>f</sup>	1,802
chlorpyrifos	231	350.89	-3.55	4.70	24 <sup>e</sup>	720 <sup>e</sup>	1,776
dithianon	191	296.32	-10.26	3.20	6.30 <sup>d</sup>	12.12 <sup>d</sup>	252
captan	164	300.61	-6.92	2.50	1.50 <sup>d</sup>	4.90 <sup>d</sup>	19.20
metam-potassium	94	145.28	-8.47	-2.91	2 <sup>d</sup>	52.80 <sup>d</sup>	168.
pendimethalin	83	281.31	-5.92	5.20	12 <sup>e</sup>	504 <sup>e</sup>	2,160
oxadiazon	44	345.20	-4.81	5.33	5.28 <sup>d</sup>	3,048 <sup>d</sup>	5,040
MCPA	43	200.62	-7.65	-0.81	18.72 <sup>e</sup>	324 <sup>e</sup>	576

- 1 <sup>a</sup> APPA, 2012, referred to Piemonte, Lombardy, Trentino Alto Adige, Friuli Venezia-Giulia, Veneto  
2 Regions  
3 <sup>b</sup> PPBD Pesticide Properties Database  
4 <sup>c</sup> Calculated from Henry's law constant (25°C) from PPDB  
5 <sup>d</sup> EFSA Conclusion  
6 <sup>e</sup> European Commission EU Pesticides Database  
7 <sup>f</sup> Grenni, 2011  
8  
9  
10

## 11 **Results of the application of the OECD P<sub>ov</sub> and LRTP screening tool model for the selection of** 12 **CUPs to be included in the monitoring campaigns**

13 Although important Italian cities (e.g. Milan, Turin, Bergamo, Verona) and industrial activities are  
14 located in the Po River plain, this area is still characterized by the presence of an intensive agriculture  
15 (almost the 30% of the total cultivated lands in Italy) (ISTAT, 2010). The agricultural activities are  
16 mainly focused in the production of arable crops (particularly maize), vineyards and fruit trees (Figure  
17 1 in the paper). These farming activities are intensive in the use of pesticides, consuming a total of  
18 about 14,800 tons of active ingredients in 2012 (APPA, 2012). During their spray application, a  
19 fraction of the applied dose can be lost in atmosphere. In addition, post-application emissions,  
20 involving volatilization from soil and plants and wind erosion of soil particles containing sorbed  
21 pesticides represent further significant pesticide input into the troposphere for several days or weeks  
22 after application (Bedos et al., 2002; Voutsas et al., 2005). The capability of pesticides to travel short  
23 or long distances depends on the amount of time it resides in the atmosphere, which is related to their  
24 chemical-physical properties and persistence. In addition, meteorological factors can influence the  
25 movement of polluted air masses (Addo et al., 1999).

26 In table SI-2, the most widely used pesticides in North Italy are reported. From the available data,  
27 there are at least 12 CUPs that are used in quantities exceeding 10 tons of a.i. per year (many of them  
28 are used in quantities exceeding the 100 tons a.i. per year). This information can be useful as a  
29 preliminary step to identify those compounds that could have the potential of contaminating the  
30 investigated areas (the greater is the use, the higher the potential of contamination). However, as  
31 previously described, the capability of these compounds to be transported away from the area of  
32 emission is mainly depending by their properties. Based on this consideration, as a further screening,  
33 to identify among the 12 compounds those having the highest potential to reach the Alpine glaciers,  
34 "The OECD Tool" model was applied. In this way, a selection of CUPs to be included into the  
35 monitoring campaigns was made.

1 The results of “The OECD Tool” application are reported in Figure S1. The thin black line in each  
2 plot defines the maximum LRTP that is possible for a given  $P_{ov}$ . In addition, in both plots vertical and  
3 horizontal reference lines are present. According to the classification scheme proposed by Klasmeier  
4 et al., 2006, the vertical line separates high and low persistent substances, whereas the horizontal line  
5 forms boundary between those chemicals with POP-like potential for long range transport from those  
6 substances that are expected to be less mobile in the environment. In both plots, the majority of the  
7 investigated CUPs is located in the bottom left quadrant.

8 Based on the calculated values of CTD and  $P_{ov}$ , pesticides are subdivided in two categories:

- 9 • in the first group are included glyphosate, oxadiazon, pendimethalin (PEN), chlorpyrifos  
10 (CPF) and terbuthylazine (TBZ) which have a  $P_{ov}$  higher than 100 days and a CTD above 150  
11 km, value potentially sufficient to cover the distance from Po river plain to alpine cold remote  
12 sites;
- 13 • the second group comprises MCPA, captan, dithianon, fosetyl- aluminium, metam-sodium,  
14 metam –potassium and S-metolachlor and has a  $P_{ov}$  of about 1-26 days and a CTD shorter  
15 than 100 km. These substances can be classified not harmful for the alpine cold ecosystem  
16 due to their low persistence and low travel potential.

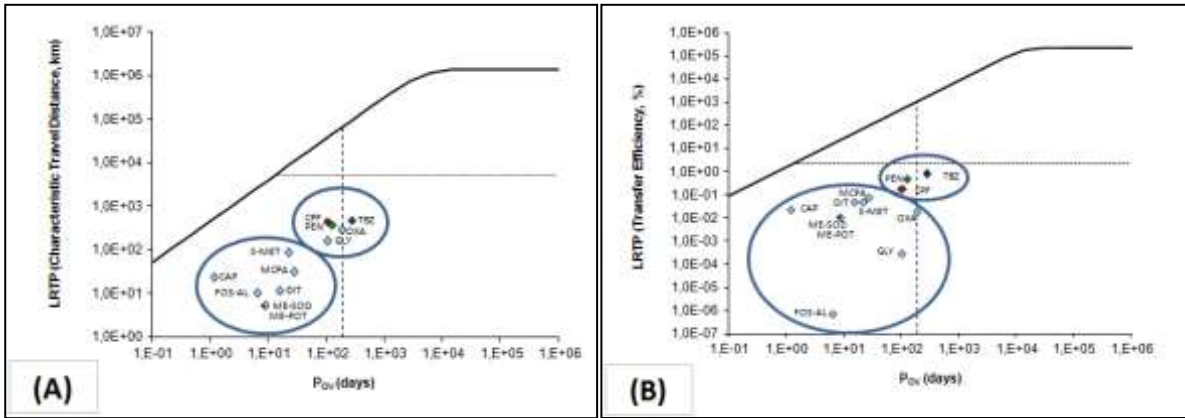
17 The second indicator used to describe LRTP is the estimation of how much contaminant can reach a  
18 certain distance. The majority of the selected CUPs exhibits a TE values below 0.1%, while only  
19 PEN, CPF and TBZ reached 0.2%, 0.5% and 0.8% respectively. Moreover, TBZ is the only substance  
20 falling in the bottom right quadrant.

21 Based on the considerations presented, PEN ( $P_{ov}$  of 129 days, CTD of 377 km), CPF ( $P_{ov}$  of 106 days,  
22 CTD of 457 km) and TBZ ( $P_{ov}$  of 282 days, CTD of 483 km) were selected for the analytical  
23 determinations in glacial melt water samples.

24 In literature, different CTDs, ranging from 62 to 430 km, are reported for CPF (Hoferkamp et al.,  
25 2010; Mackay et al., 2014; Muir et al., 2004). The variability of  $DT_{50}$  in air, from 3 to 24 hrs,  
26 determines the differences in CTD values. The long-range transport potential depends strongly by  
27 half-life in air which is influenced by  $\bullet OH$  radical concentration. Mackay and coworkers (2014)  
28 reported that conservative value assumed lesser concentration of  $\bullet OH$  and therefore higher  $DT_{50}$  in  
29 air, while minor levels of  $\bullet OH$  are more appropriate for conditions in remote regions and at higher  
30 latitudes. The selection of the proper model input data is a crucial point in order to have reliable  
31 information on LRAT, but it has to be considered that all the three investigated alpine peaks are much  
32 closed to agricultural areas. In particular, apple and wine crops, where CPF is mostly used, are 70, 40

1 and 10 km far from Lys, Forni and Giogo Alto Glacier, respectively. In such situation, a shorter  $DT_{50}$   
 2 value is not relevant, as the distance is not sufficient to prevent CPF to reach the glaciers.

3



4

5 Figure S1 - The calculated  $P_{ov}$ , CTD and TE of the most sold CUPs in Northern Italy . (A):  $P_{ov}$  vs  
 6 CTD and (B)  $P_{ov}$  vs TE. CAP= captan, CPF=chlorpyrifos, DIT= dithionon, FOS-AL= fosetyl-  
 7 aluminium, GLY= glyphosate, ME-POT=metam-potassium, ME-SOD = metam-sodium, OXA=  
 8 oxadiazon, PEN= pendimethalin, S-MET= S-metolachlor, TBZ= terbuthylazine

9



1 Table SI-4: Chemicals concentrations (ng/L) in glacial meltwater samples (nd= not detected)

	<b>LYS July</b>	<b>LYS October</b>	<b>FORNI July</b>	<b>FORNI Sept</b>	<b>GIOGO July</b>	<b>GIOGO Sept</b>
$\alpha$ -HCH	0.62	0.74	nd	nd	nd	nd
$\gamma$ -HCH	0.34	0.44	nd	nd	nd	nd
<b>□HCHs</b>	<b>0.96</b>	<b>1.18</b>	<b>nd</b>	<b>nd</b>	<b>nd</b>	<b>nd</b>
HCB	0.03	0.03	nd	0.04	nd	0.02
o,p' -DDE	nd	nd	nd	nd	nd	nd
p,p' -DDE	0.04	nd	nd	0.27	nd	0.10
o,p' -DDD	nd	nd	nd	nd	nd	nd
p,p' -DDD	nd	nd	nd	nd	nd	nd
o,p'-DDT	nd	nd	nd	nd	nd	nd
p,p'-DDT	0.23	0.33	0.46	0.23	nd	0.10
<b>□DDTs</b>	<b>0.27</b>	<b>0.33</b>	<b>0.46</b>	<b>0.50</b>	<b>nd</b>	<b>0.20</b>
PCB 28	0,45	nd	0,20	nd	nd	nd
PCB 52	0,30	0,24	0,14	0,28	0,43	0,58
PCB 101	0,01	nd	nd	nd	nd	0,01
PCB 153	nd	nd	nd	nd	nd	nd
PCB 180	nd	nd	nd	nd	nd	nd
<b>□PCBs</b>	<b>0,76</b>	<b>0,24</b>	<b>0,35</b>	<b>0,28</b>	<b>0,43</b>	<b>0,60</b>
terbutylazine	1.98	1.23	0.29	0.13	nd	nd
chlorpyrifos	0.43	0.21	1.06	0.50	1.02	0.37
pendimethalin	nd	nd	nd	nd	nd	nd
<b>□CUPs</b>	<b>□□□□</b>	<b>□□□□</b>	<b>□□□□</b>	<b>□□□□</b>	<b>□□□□</b>	<b>□□□□</b>
AHTN	1.69	1.15	1.79	0.87	0.95	1.18
HHCB	1.15	1.28	1.57	1.06	0.99	1.46
<b>□Musks</b>	<b>2.84</b>	<b>2.43</b>	<b>3.36</b>	<b>1.93</b>	<b>1.94</b>	<b>2.64</b>

2

3

1 **References**

- 2 Addo, W., Van Pul, J., Bidleman, T.F., Brorström-Lunden, E., Builtjes, P.J.H., Dutchak, S., Duyzer,  
3 J.H., Gryning, S., Jones, K.C., Van Dijk, H.F.G., Van Jaarsveld, J.A., 1999. Atmospheric  
4 transport and deposition of pesticides: an assessment of current knowledge. *Water. Air. Soil*  
5 *Pollut.* 115, 245–256.
- 6 APPA (Agenzia Provinciale per la Protezione dell’Ambiente), 2012. Dati vendita (pesticide sales  
7 data) elaborati dal gruppo AAAF - anno 2012.
- 8 Bedos, C., Cellier, P., Calvet, R., Barriuso, E., Gabrielle, B., 2002. Mass transfer of pesticides into  
9 the atmosphere by volatilization from soils and plants: overview. *Agronomie* 22, 21–33.  
10 doi:10.1051/agro
- 11 EFSA (European Food and Safety Authority), 2012. Conclusion on the peer review of the pesticide  
12 risk assessment of the active substance metam. doi:10.2903/j.efsa.2011.2334.
- 13 EFSA (European Food and Safety Authority), 2011. Conclusion on the peer review of the pesticide  
14 risk assessment of the active substance terbuthylazine. doi:10.2903/j.efsa.2011.1969.
- 15 EFSA (European Food and Safety Authority), 2010. Conclusion on the peer review of the pesticide  
16 risk assessment of the active substance dithianon. doi:10.2903/j.efsa.2010.1904.
- 17 EFSA (European Food and Safety Authority), 2009. Conclusion on the peer review of the pesticide  
18 risk assessment of the active substance captan.
- 19 EFSA (European Food and Safety Authority), 2005. Conclusion on the peer review of the pesticide  
20 risk assessment of the active substance fosetyl. doi:10.2903/j.efsa.2010.1445.
- 21 European Commission, n.d. EU Pesticides Database.
- 22 Grenni, P., 2011. Effects of Pesticides on Soil and Water Fauna and Microflora. Ph.D. thesis.
- 23 Hoferkamp, L., Hermanson, M.H., Muir, D.C.G., 2010. Current use pesticides in Arctic media; 2000-  
24 2007. *Sci. Total Environ.* 408, 2985–2994. doi:10.1016/j.scitotenv.2009.11.038
- 25 ISTAT (Istituto nazionale di statistica), 2010. Censimento agricoltura 2010.
- 26 Klasmeier, J., Matthies, M., Macleod, M., Fenner, K., Scheringer, M., Stroebe, M., Le Gall, A.C.,  
27 Mckone, T., Van De Meent, D., Wania, F., 2006. Application of multimedia models for  
28 screening assessment of long-range transport potential and overall persistence. *Environ. Sci.*

- 1 Technol. 40, 53–60. doi:10.1021/es0512024
- 2 Mackay, D., Giesy, J.P., Solomon, K.R., 2014. Fate in the Environment and Long-Range  
3 Atmospheric Transport of the Organophosphorus Insecticide, Chlorpyrifos and Its Oxon, in:  
4 Reviews of Environmental Contamination and Toxicology. pp. 35–76.
- 5 Mostrag, A., Puzyn, T., Haranczyk, M., 2010. Modeling the overall persistence and environmental  
6 mobility of sulfur-containing polychlorinated organic compounds. Environ. Sci. Pollut. Res. 17,  
7 470–477.
- 8 Muir, D.C.G., Teixeira, C., Wania, F., 2004. Empirical and modeling evidence of regional  
9 atmospheric transport of current-use pesticides. Environ. Toxicol. Chem. 23, 2421–2432.
- 10 Öberg, T., Iqbal, M.S., 2012. The chemical and environmental property space of REACH chemicals.  
11 Chemosphere 87, 975–981. doi:10.1016/j.chemosphere.2012.02.034
- 12 PPBD, n.d. Pesticide Properties Database.
- 13 Voutsas, E., Vavva, C., Magoulas, K., Tassios, D., 2005. Estimation of the volatilization of organic  
14 compounds from soil surfaces. Chemosphere 58, 751–758.  
15 doi:10.1016/j.chemosphere.2004.09.057
- 16 Wegmann, F., Cavin, L., MacLeod, M., Scheringer, M., Hungerbühler, K., 2009. The OECD software  
17 tool for screening chemicals for persistence and long-range transport potential. Environ. Model.  
18 Softw. 24, 228–237. doi:10.1016/j.envsoft.2008.06.014
- 19