Supplementary Material

Sources of organochlorine pesticides in air in an urban Mediterranean environment: Volatilisation from soil

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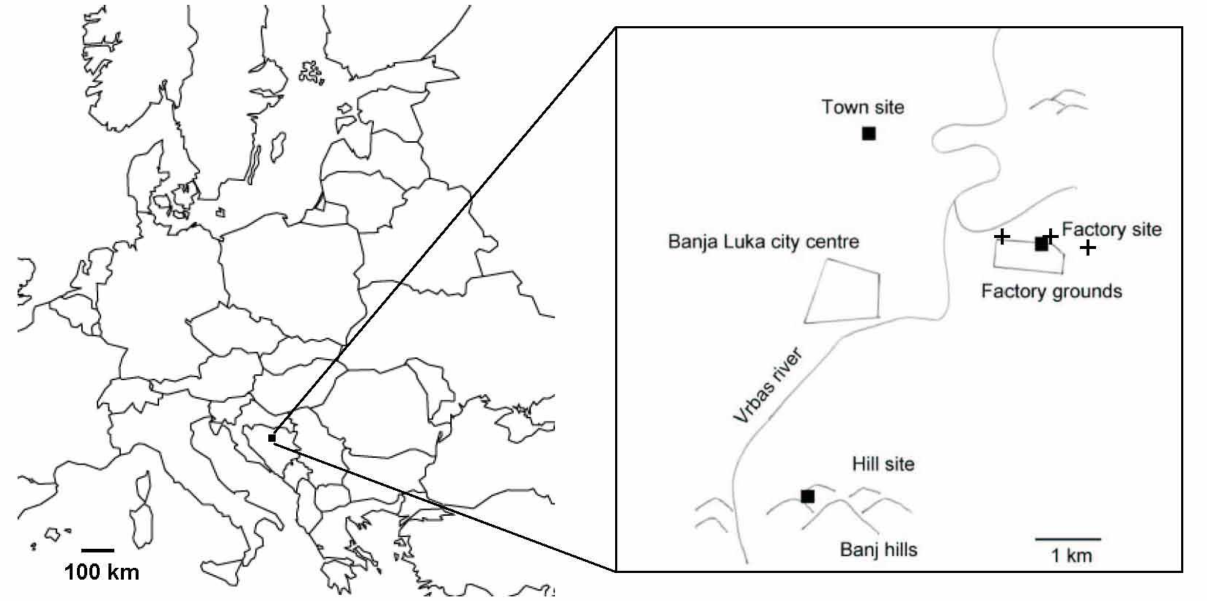
1. Sites

Fig. S1. Geography and location of sites and soil sampling locations (+)

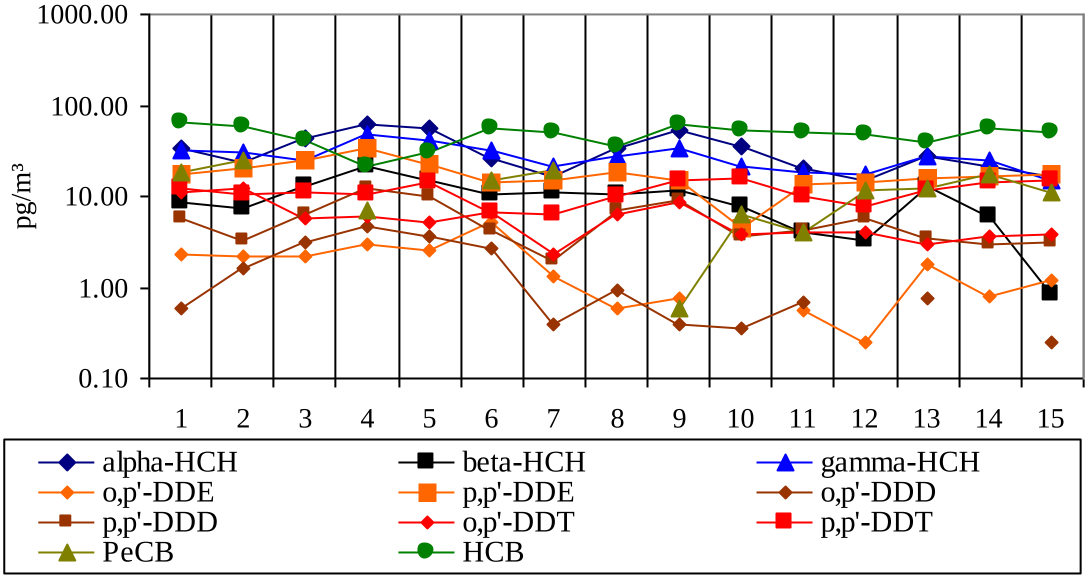


2. Results

2.1 Organochlorine pesticide time series

Fig. S2. Time series of 4-h samples (5 per 24 hours) of 11 OCPs at the (a) factory, (b) town and (c) hill site. Day-time samples are no. 3-5, 8-10 and 13-15. Values < LOQ were replaced by LOQ/2.

a.



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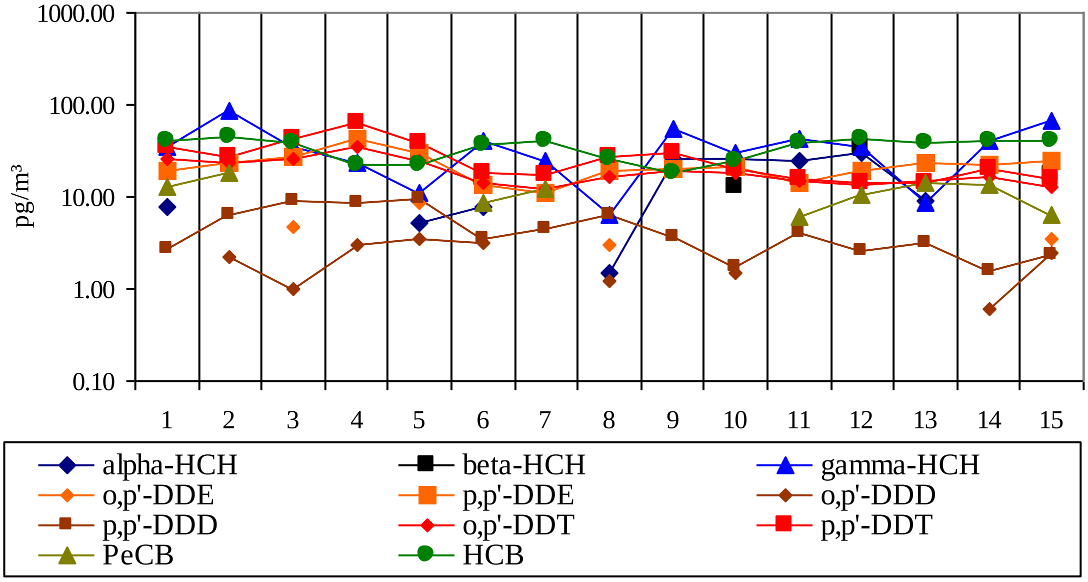

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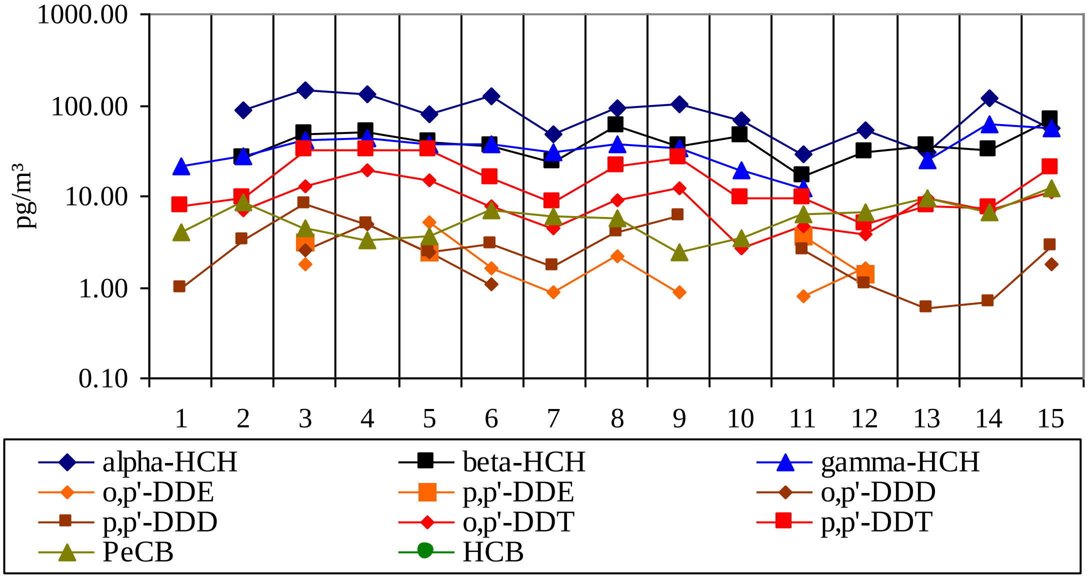


2.2 Vertical gradient measurements

Table S1: Number (#, out of 15) of significant negative vertical gaseous (left) and total (i.e. gaseous + particulate, right) concentration gradients by testing 2 criteria, i.e. number of replica air sample concentrations at z_1 which differed by less than the mean + 1 standard deviation (crit 1; i.e. $\Delta c_{z1} < (\mu_{\Delta c\ z1} + \sigma_{\Delta c\ z1}) \times c_{z1}$) and number of air sample concentrations at z_1 and z_2 which differed more than this much (crit 2; i.e. $|c_{z11} - c_{z12}| > (\mu_{\Delta c\ z1} + \sigma_{\Delta c\ z1}) \times c_{z1}$).

	# c_{z1} > LOQ	Gaseous			Total		
		$\mu_{\Delta c\ z1} \pm \sigma_{\Delta c\ z1}$ (%)	# crit 1 fulfilled	# crit 1 and crit 2 fulfilled	$\mu_{\Delta c\ z1} + \sigma_{\Delta c\ z1}$ (%)	# crit 1 fulfilled	# crit 1 and crit 2 fulfilled
α-HCH	15	8±8	13	13	8±8	13	13
β-HCH	14	10±9	13	13	47±63	11	11
γ-HCH	15	11±14	13	6	20±18	12	6
o,p′-DDE	8	33±25	6	2	62±61	7	3
p,p′-DDE	14	36±29	12	0	43±26	11	0
o,p′-DDD	5	85±91	5	5	111±102	4	4
p,p′-DDD	14	59±43	13	2	42±19	12	0
o,p′-DDT	14	65±27	13	0	70±24	13	0
p,p′-DDT	15	64±25	15	0	55±25	15	0
PeCB	9	34±26	8	4	35±25	8	4
HCB	15	17±16	12	1	17±19	12	2

Numerical examples for application of criteria 1 and 2 to *γ*-HCH:
γ-HCH gaseous concentrations were 14.0 and 21.0 pg m^{-3} at z_1 (mean of the replica samples $c_{z1} = (c_{z11} - c_{z12})/2 = 17.5$ pg m^{-3}) and 18.2 pg m^{-3} at z_2 for the sampling interval 01:20-05:20 h on 14 July, 27.2 and 28.1 pg m^{-3} at z_1 (mean $c_{z1} = 27.6$ pg m^{-3}) and 20.5 pg m^{-3} at z_2 for the subsequent sampling interval, 06:50-10:50 h, and 24.4 and 25.1 pg m^{-3} at z_1 (mean $c_{z1} = 24.7$

pg m^{-3}) and 22.2 pg m^{-3} at z_2 for the sampling interval 11:20-15:20 h on 14 July. I.e., for the subsequent sampling intervals Δc_{z1} was 7.0, 0.9 and 0.7 pg m^{-3}.

The mean relative deviation for 2 parallel samples of γ-HCH at the same level (n = 15) was $|c_{z11} - c_{z12}| / c_{z1} = 0.15$ and its relative standard deviation $\sigma_{\Delta c\ z1} = 124\%$. Hence, the uncertainty of γ-HCH measurements, defined as $(\mu_{\Delta c\ z1} + \sigma_{\Delta c\ z1})$ was (15 + 1.24*15) % = 34 %.

Test of criterion 1 (i.e. $\Delta c_{z1} < (\mu_{\Delta c\ z1} + \sigma_{\Delta c\ z1}) \times c_{z1}$?) delivers $\Delta c_{z1} = 7.0 > 0.34 \times 17.5$ pg m^{-3} (not passed), $\Delta c_{z1} = 0.9 < 0.34 \times 27.6$ pg m^{-3} (passed) and $\Delta c_{z1} = 0.7 < 0.34 \times 24.7$ pg m^{-3} (passed) for the 3 subsequent sampling intervals. Test of criterion 2 (i.e., $|c_{z1} - c_{z12}| > (\mu_{\Delta c\ z1} + \sigma_{\Delta c\ z1}) \times c_{z1}$?) delivers $|c_{z1} - c_{z12}| = 7.1 < 0.34 \times 27.6$ pg m^{-3} (not passed) and $|c_{z1} - c_{z12}| = 2.5 < 0.34 \times 24.7$ pg m^{-3} (not passed) for the 2 subsequent sampling intervals which passed criterion 1, sampling times 06:50-10:50 h and 11:20-15:20 h.

3. Data interpretation - Tests on phase equilibrium

3.1 Inter-site variability of concentrations in air

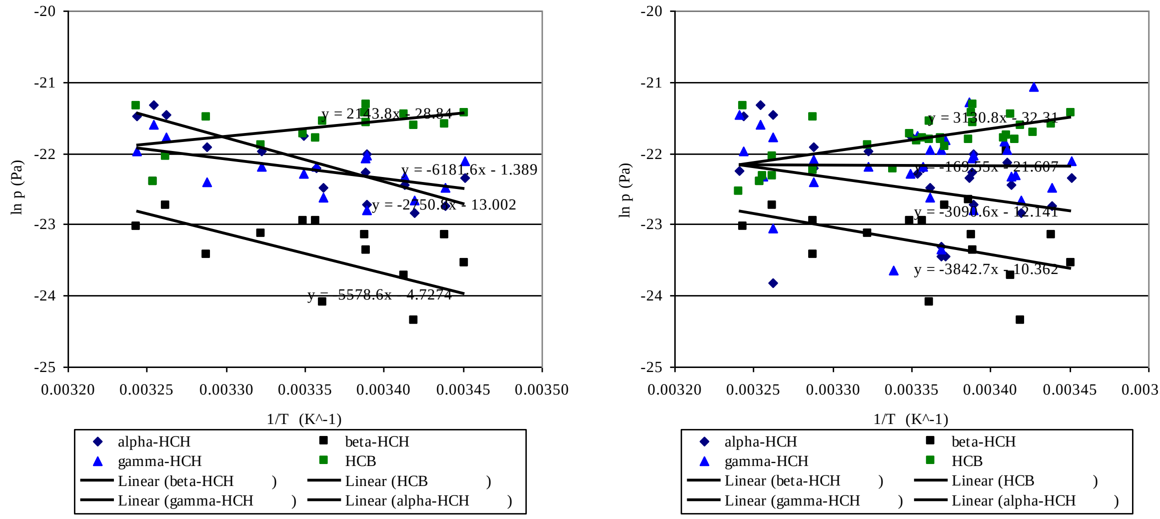
Table S2: Inter-site variability of total (gaseous + particulate) concentrations of OCPs quantified by the correlation coefficient, r^2. Significant correlations are marked * ($p < 0.05$) or ** ($p < 0.01$).

	urban-urban	urban[(1)]-rural
α-HCH	-0.21	+0.45
β-HCH	-0.51	+0.13
γ-HCH	-0.25	+0.24
o,p'-DDE	+0.11	+0.20
p,p'-DDE	+0.76**	+0.12
o,p'-DDD	+0.72**	+0.86**
p,p'-DDD	+0.65**	+0.51
o,p'-DDT	+0.50	-0.04
p,p'-DDT	+0.13	+0.23
PeCB	+0.91**	+0.48
HCB	+0.43	±0.00

(1) factory site

3.2 Clausius-Clapeyron plots

Fig. S3: Clausius-Clapeyron plots of HCH isomers and HCB at the factory site based on the local total concentrations (sum of gaseous and particulate fractions, mean of 2 samplers at level z_1) (a) without or (b) with correction for background concentrations (given by c_a measured at the hill site). Day-time samples correspond to $1/T \leq 0.00338$) and night-time samples correspond to $1/T \geq 0.00337$.



a. b.

Table S3: Observed values (slopes of linear regressions) of the enthalpy of the surface-air exchange, ΔH_{exp}, based on 4h-means, and literature values of the enthalpy of volatilization from the liquid phase, ΔH_{vap}, and of octanol-air partitioning ΔH_{oa} (kJ mol^{-1}).

	ΔH_{exp}			ΔH_{vap}	ΔH_{oa}
	Factory site	Town site	Hill site		
α-HCH	+51.4	- 4.7	+21.5	+67.0[a]	+61.8[c]
β-HCH	+46.4	n.d.	+19.5	+68.2[a]	+94.5[c]
γ-HCH	+22.9	-25.5	+ 1.9	+74.7[a]	+65.3[c]
HCB	-17.8	-34.3	n.d.	+67.6[b]	+55.8[c]

[a] Xiao et al., 2004; [b] Shen and Wania, 2005; [c] Shoeib and Harner, 2002

3.3 Fugacity estimates

Fugacities of OCPs in soil (f_s) and air (f_a) were calculated as (Harner et al., 2001):

$$f_s = c_s\, H(T) / (0.411\ \phi_{OM}\ K_{OW}) \quad (1)$$

$$f_a = c_a\, R\, T \quad (2)$$

with c is the concentration in the medium (mol m^{-3}), H(T) is the temperature dependent Henry's law constant (Pa m^3 mol^{-1}), ϕ_{OM} is the mass fraction of the organic matter in soil, K_{OW} is the octanol–water partitioning coefficient, R is the gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature (K). The factor 0.411 improves the correlation between the soil-air partitioning coefficient and K_{OW} (Hippelein and McLachlan, 1998; Meijer et al., 2003c). H(T) was obtained using the integrated van't Hoff equation:

$$\ln(H_1/H_2) = -\Delta H_{vap}(1/T_1 - 1/T_2)/R \quad (3)$$

with H_1 and H_2 are Henry's law constants at two temperatures, T_1 and T_2 are temperatures (K), and ΔH_{vap} is the enthalpy of vaporisation (J mol^{-1}). The fugacity fraction (ff) is calculated as the fugacity in soil divided by the sum of fugacities in soil and air and gives an indication of the net direction of air-soil exchange.

(4) $\quad \mathrm{ff} = f_s / (f_s + f_a)$

Physico-chemical data were taken from literature (Li et al., 2003; Xiao et al., 2004; Shen and Wania, 2005; Jantunen and Bidleman, 2006). Soil temperatures from 2 and 5 cm depth, which had been measured at 7:00, 14:00 and 21:00 h at the town site were equally weighted and linearly interpolated to derive mean day-time and mean night-time temperatures representative for the analysed topsoil. For consistency, also air temperatures were taken from the town site. Soil concentration data were taken as measured at l_1 (Table 1). Three and two values of c_a were averaged to obtain mean day-time and mean night-time concentrations in air, respectively. It is assumed that OM mass equals 1.7 times organic carbon mass. The soil density, ρ_s, needed to calculate c_s (mol m^{-3}) from measured values (in ng g^{-1}), is unknown and estimated to be in the range 1.4-1.8 g cm^{-3}. Results for ff are listed in Table S4.

Table S4: Ranges of OCP fugacity fractions, $\mathrm{ff} = f_s / (f_s + f_a)$, estimated for subsequent day-time and night-time periods, 11-14 July 2008, at the factory site, l_1, together with differences between air and soil temperatures, ΔT (K). Ranges reflect the uncertainty of $\rho_s = 1.4\text{-}1.8$ g cm^{-3} (see text). Observed $\Delta c / \Delta z < 0$ (suggesting ff > 0.5) are marked bold.

	N 11-12 July	D 12 July	N 12-13 July	D 13 July	N 13-14 July	D 14 July
ΔT	-4.1	0.1	-4.6	2.2	-2.8	-1.4
α-HCH	**0.78-0.82**	**0.73-0.78**	**0.84-0.87**	**0.76-0.80**	**0.85-0.88**	**0.80-0.84**
β-HCH	<0.005	**<0.005**	**<0.005**	**<0.005**	**<0.005**	**<0.005**
γ-HCH	0.58-0.64	**0.63-0.69**	0.64-0.70	**0.67-0.72**	0.71-0.76	0.63-0.68
p,p'-DDT	0.02	0.03	0.03-0.04	0.02-0.03	0.02-0.03	0.01
p,p'-DDE	0.01	0.01	0.01-0.02	0.02	0.02	0.01-0.02
p,p'-DDD	0.02	0.02	0.03-0.04	**0.02**	0.02	0.02-0.03
HCB	0.90-0.92	0.96-0.97	0.92-0.94	0.94-0.956	0.91-0.94	0.91-0.93

The fugacity fractions; ff, near 0.5 indicate equilibrium; fractions >0.5 indicate net volatilization, whereas values <0.5 indicate net deposition. However, due to uncertainties and the propagation of errors in the calculation, fugacity fractions between 0.3 and 0.7 are not considered to differ significantly from equilibrium (Harner et al., 2001; Meijer et al., 2003b). Hence, significant upward fluxes are predicted for α-HCH (all nights and days), γ-HCH (one night) and HCB (all nights and days), significant downward fluxes for β–HCH and the DDX compounds (all nights and days). Volatilisation is predicted but not observed in seven cases, for γ-HCH (one night) and HCB (all nights and days). The latter discrepancy can be explained by the measurement uncertainties, i.e. small negative gradients (stated above, section Vertical concentration gradients). Volatilisation is observed but not predicted for β–HCH (three days and two nights) and *p,p'*-DDD (one day). The discrepancies for β–HCH could eventually be explained by spatial variability of the soil concentration, which is particularly large for β–HCH (the value of the relative standard deviation doubles the one of the other OCPs): ff = 0.53-0.77 would result were the predictions based on the highest soil concentration measured (at l_3, see Table 1). The discrepancy for *p,p'*-DDD cannot be explained analogously, as ff = 0.16 would be predicted based on the highest soil concentration measured (at l_2, see Table 1) and $c_s \geq 0.80$ ng g^{-1} would be needed to predict ff $\geq$ 0.50. However, the spatial variability of the soil concentration may well have been larger than covered by sampling at the three locations.

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