Atmos. Chem. Phys. Discuss., 15, 23651–23681, 2015
www.atmos-chem-phys-discuss.net/15/23651/2015/
doi:10.5194/acpd-15-23651-2015

Atmospheric Chemistry and Physics Discussions
Open Access

Pesticides in the atmosphere: a comparison of gas-particle partitioning and particle size distribution of legacy and current-use pesticides

C. Degrendele[1,2], K. Okonski[1], L. Melymuk[1], L. Landlová[1], P. Kukučka[1], O. Audy[1], J. Kohoutek[1], P. Čupr[1], and J. Klánová[1]

[1]Masaryk University, RECETOX (Research Centre for Toxic Compounds in the Environment), Faculty of Science, Kamenice 753/5, 62500 Brno, Czech Republic
[2]Max Planck Institute for Chemistry, Multiphase Chemistry Department, Hahn-Meitner-Weg 1, 55128 Mainz, Germany

Received: 14 July 2015 – Accepted: 6 August 2015 – Published: 2 September 2015

Correspondence to: J. Klánová (klanova@recetox.muni.cz) and L. Melymuk (melymuk@recetox.muni.cz)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

This study presents a comparison of seasonal variation, gas-particle partitioning and particle-phase size distribution of organochlorine pesticides (OCPs) and current-use pesticides (CUPs) in air. Two years (2012/2013) of weekly air samples were collected at a background site in the Czech Republic using a high-volume air sampler. To study the particle-phase size distribution, air samples were also collected at an urban and rural site in the area of Brno, Czech Republic, using a cascade impactor separating atmospheric particulates according to six size fractions. The timing and frequencies of detection of CUPs related to their legal status, usage amounts and their environmental persistence, while OCPs were consistently detected throughout the year. Two different seasonal trends were noted: certain compounds had higher concentrations only during the growing season (April–September) and other compounds showed two peaks, first in the growing season and second in plowing season (October–November). In general, gas-particle partitioning of pesticides was governed by physicochemical properties, with higher vapor pressure leading to higher gas phase fractions, and associated seasonality in gas-particle partitioning was observed in nine pesticides. However, some anomalous partitioning was observed for fenpropimorph and chlorpyrifos suggesting the influence of current pesticide application on gas-particle distributions. Nine pesticides had highest particle phase concentrations on fine particles ($< 0.95\,\mu$m) and four pesticides on coarser ($> 1.5\,\mu$m) particles.

1 Introduction

In 1939, dichlorodiphenyltrichloroethane (DDT) was discovered to have insecticidal properties. Since that time, synthetic pesticides have been widely used around the world to control pests in agricultural production (Li and Macdonald, 2005). Legacy organochlorine pesticides (OCPs) are banned for agricultural purposes in most countries, including the Czech Republic, and have been replaced by what are often termed “current-use pesticides” (CUPs). CUPs generally have lower persistence and bioaccumulative potential and higher water solubility, which should result in reduced negative environmental impacts (Kannan et al., 2006). However, given their detection in multiple environmental media, including in remote locations (Koblizková et al., 2012; Zhang et al., 2013), and the relative lack of information regarding their toxic effects, the potential environmental and human risks cannot be neglected. The atmospheric transport of OCPs has been well studied over the last decades (Lammel et al., 2009; Růžičková et al., 2008; Shen et al., 2004), but there is a lack of information on the seasonal trends and partitioning of CUPs which is needed to understand their environmental fate.

There are three main processes leading to the presence of pesticides in the air. First, pesticides can enter the atmosphere during application. For example, during spray application, up to 30 % of the dosage directly enters the atmosphere (Van den Berg et al., 1999). Another primary emission is wind erosion of soil particles containing sorbed pesticides, which can occur days or weeks after application. Finally, pesticides can volatilize from soils, plants and from old industrial sites. In the case of pesticides that are not currently authorized for agricultural use (e.g., OCPs), volatilization and wind erosion of soil particles should be the only relevant emission pathways.

Once pesticides enter the air, they partition between gas and particle phases according to their physicochemical properties (vapor pressure, octanol-air partition coefficient), the concentration of total suspended particulate matter (TSP) and meteorological parameters (ambient temperature, relative humidity) (Pankow, 1987). Knowledge of this gas-particle partitioning is necessary to understand atmospheric residence times, the significance of removal pathways from air (deposition, gas absorption, photodegradation) and the potential for long range atmospheric transport (LRAT) (Bidleman et al., 1986; Eisenreich et al., 1981; Scheyer et al., 2008). Additionally, the atmospheric residence times of particles vary with particle size (Vecchi et al., 2007), further influencing wet/dry deposition and LRAT (Götz et al., 2008). Particle size distribution is also an important factor for human risks from inhalation exposure, as smaller particles penetrate deeper into the respiratory system (Englert, 2004).

The gas-particle partitioning of OCPs has been well documented (Cindoruk, 2011; Scheyer et al., 2008; Sofuoglu et al., 2004) and most OCPs are predominantly found in the gas phase. Gas-particle partitioning has been also reported for a range of CUPs (Borras et al., 2011; Sadiki and Poissant, 2008; Sanusi et al., 1999; Sauret et al., 2008; Yao et al., 2008), 12 of which are also included in this study, and vapor pressure, which is influenced by temperature, has been identified as the main factor governing CUP partitioning. However, the seasonal variation of this partitioning has only been investigated for chlorpyrifos (Li et al., 2014) and alachlor (Scheyer et al., 2008). Similarly, knowledge of how CUPs are distributed among different particle sizes is very limited (Coscollà et al., 2013b), and the seasonality of this particle size distribution has never been investigated for CUPs. To fill these gaps, we assess the seasonal variation of a set of legacy and current-use pesticides (Table 1) in outdoor air, with a focus on the gas-particle partitioning and the particle size distribution. For many of these CUPs, this is the first time that their seasonal gas-particle partitioning and size distributions have been examined.

2 Methodology

2.1 Air sampling

Air samples were collected in two sampling campaigns. A map of the sampling sites is provided in Fig. S1 in the Supplement. Firstly, to study seasonal trends and gas-particle partitioning, air was sampled at the Košetice observatory (49°34′24″ N, 15°04′49″ E), which is an established background site of the European Monitoring and Evaluation Programme (EMEP) network (Holoubek et al., 2007). The site is located in an agricultural region in central Czech Republic. While the site is located in an agricultural region, it is not directly on cultivated land, therefore the air sampled should not reflect direct emissions from pesticide application (e.g., spray application droplets) but rather the average conditions of a rural air mass. From January 2012 to December 2013, a high volume air sampler (Digitel DH77 with PM_{10} pre-separator) was used to collect weekly air samples. The sample volume was on average 4310 m^3 (∼ 25 $m^3\,h^{-1}$, 7 day sampling duration). Particles were collected on quartz fiber filters (QFFs) (QM-A, 150 mm, Whatman, UK) and gas phase on polyurethane foam (PUF) (two in series, T3037, 110 mm × 50 mm, 0.030 $g\,cm^{-3}$, Molitan a.s., Czech Republic). PUFs were pre-cleaned via Soxhlet-extraction with acetone and dichloromethane for 8 h each. Fifty-two samples were collected each year. Half of the samples were used for OCPs analysis and half for CUPs analysis (Supplement Tables S1 and S2).

Secondly, to assess the seasonal variation of the particle size distribution of pesticides, particle-phase air samples were collected in the area of Brno, the second largest city in the Czech Republic. From October 2009 to October 2010, a high volume air sampler (HV 100-P, Baghirra, CZ) equipped with a multistage cascade impactor (PM_{10} sampling head and six stage impactor, Tisch Environmental, USA) was used to collect six particle size fractions. The fractions represented particles with aerodynamic diameters of < 0.49, 0.49–0.95, 0.95–1.5, 1.5–3.0, 3.0–7.2 and 7.2–10 µm and were collected on QFFs (TE-230-QZ, 141 mm × 148 mm, Tisch, Environmental, USA and QM-A, 203 mm × 254 mm, Whatman, UK, for the backup filters (< 0.49 µm)). Sampling was conducted simultaneously at a rural site (Telnice) and at an urban site (Kotlařská). The rural site (49°6′21″ N, 16°42′58″ E) was located 14 km southeast of the Brno city centre. The main source of pollution at this site is likely agricultural activity, especially from cereals and grapes, which are the main local crops. The urban site (49°12′20″ N, 16°35′50″ E) was located in a university botanical garden, close to a major traffic junction in the centre of Brno. Only a small amount of pesticides are used within the botanical garden, and do not include any of the target pesticides in the present study. The main sources of pesticides at this site are likely pesticides used in nearby buildings/building materials, and atmospheric transport from the agricultural areas surrounding Brno. Eleven weekly samples were used for CUPs analysis and twelve for OCPs analysis at each site. The remaining samples were analyzed for other SVOCs, presented elsewhere (Degrendele et al., 2014; Okonski et al., 2014). To reach the limit of detection of these compounds, samples were grouped by season (two or three filters) (Tables S3 and S4). The sample volume was on average 9734 m^3 (~ 65 $m^3 h^{-1}$, 7 day sampling duration).

All filters and PUFs were wrapped in aluminum foil, sealed in plastic bags and stored at −18 °C until analysis.

2.2 Sample preparation and analysis

Filters and PUFs were extracted with toluene for OCP analysis and with methanol for CUP analysis, using an automated warm Soxhlet extractor (Büchi Extraction System B-811) for three cycles, each consisting of 60 min of warm Soxhlet and 30 min of solvent rinsing. The extracts were concentrated using a gentle stream of nitrogen. After extraction, OCP extracts were transferred to a glass column (30 mm i.d.) consisting of 0.5 g of activated silica, 30 g of H_2SO_4-modified activated silica and 1 g of non-activated silica and were eluted with 240 mL of DCM : Hexane (1 : 1 v/v). CUP extracts were passed through syringe filters (nylon membrane, 25 mm diameter, pore size 0.45 µm).

OCPs were analyzed by gas chromatography coupled to a tandem mass spectrometer (GC-MS/MS). CUPs were analyzed using an Agilent 1100 high performance liquid chromatograph (HPLC) with a Phenomenex Luna C-18 endcapped analytical column (100 mm × 2.1 mm × 3 µm). Analyte detection was performed by tandem mass spectrometry using an AB Sciex Qtrap 5500 operating in positive electron spray ionization (ESI+). Further information on all analytical parameters is given in the Supplement. Identification was based on a comparison of ion ratios and retention times (Table S5) with corresponding isotopically-labeled standards for CUPs and quantification was using internal standards: PCB-121 (Absolute Standards Inc., USA) for OCPs and alachlor-d13, acetochlor-d11, chlorpyrifos d-10, isoproturon d-3, fenitrothion d-6, desisopropylatrazine d-5, dimethoate d-6, diuron d-6, terbuthylazine d-5 and simazine d-10 (Toronto Research Chemicals, Canada; Dr. Ehrenstorfer LGC Standards, UK; Chiron AS, Norway; and Neochema, Germany) for CUPs.

2.3 QA/QC

Breakthrough of gas phase compounds was evaluated by separate quantification of each of the two PUFs placed in series for all the weekly air samples collected at the background site in 2012 and is presented in Tables S6 and S7. Based on the results of the breakthrough evaluation, the sampling set-up was deemed appropriate for the quantification of this set of pesticides. Thirteen field blanks and 28 laboratory blanks were analyzed as per samples. Blank levels of individual analytes were below detection (all OCPs and 21 CUPs) or otherwise low (on average $< 3.5\,\%$ of sample mass for detected compounds). The concentrations of OCPs and CUPs presented here have been blank corrected by subtracting the average of the field blanks. The OCP analytical method was evaluated using a certified reference material (ASLAB soil standard, Czech Republic) (Lohmann et al., 2012) and recoveries were assessed using spike-recovery tests of air sampling media. Mean OCP recoveries (± standard deviation) ranged from 87.2 ± 6.26 to $113 \pm 6.10\,\%$ with an average value of $95.8 \pm 8.11\,\%$ (Table S8). CUP recoveries were determined from spike-recovery tests of air sampling media and ranged from 52.4 ± 21.4 to $115 \pm 17.4\,\%$ (Table S9). The measured concentrations have not been adjusted for recoveries.

3 Results and discussion

3.1 Detection frequency at the background site

In general, the timing and frequencies of detection of CUPs related to their legal status, usage amounts and their persistence in the environment, while OCPs were consistently detected ($> 57\,\%$ of samples) throughout the whole sampling period (Table 1). In particular, α-HCH, γ-HCH, p,p'-DDE and p,p'-DDT were detected in every gas phase sample during the two years of sampling, emphasizing the environmental persistence of these OCPs.

The CUPs included in this study represent 24 % of all pesticides used in agriculture in the Czech Republic (Tables S10 and S11), with acetochlor, chlorpyrifos, chlorotoluron, isoproturon, metamitron, metazachlor, prochloraz and terbuthylazine used in the largest quantities (> 90 tonnes of active substance per year) and these CUPs were detected in > 25 % of air samples. Isoproturon (detected in 86.5 % of samples), metazachlor (86.5 %), chlorpyrifos (84.6 %), terbuthylazine (78.8 %), *S*-metolachlor (73.1 %) and fenpropimorph (65.4 %) were the most frequently detected. Acetochlor, atrazine, carbendazim, chlorotoluron, dimethachlor, diuron metamitron, metribuzin, prochloraz and pyrazon had detection frequencies of 15–55 % (Table 1), occurring mostly during periods of agricultural activities. Finally, azinphos methyl and fenitrothion were not detected in any samples and eight CUPs (alachlor, diazinon, dimethoate, disulfoton, fonofos, malathion, simazine, temephos and terbufos) were infrequently detected (< 6 %). Amongst these infrequently detected pesticides, only dimethoate is authorized for agricultural use in the Czech Republic and is used in very low amounts (Tables S10 and S11). Thus, the infrequent detections of these compounds are likely due to no or limited application in the sampling area.

We note that not all the CUPs are in current use in Czech Republic (Table 1); some pesticides, which we have categorized as CUPs to distinguish them from the OCPs, are banned in Czech Republic but remain in use elsewhere. For example, atrazine, a triazine pesticide banned in the European Union since 2003 (European Commission, 2004) remains one of the highest use pesticides in USA (US Environmental Protection Agency, 2013). Atrazine was detected in only one sample from May 2012 but had more frequent detections between July and November 2013 (Tables S12 and S13).

3.2 Total concentrations at the background site

Individual OCP and CUP concentrations are presented in Tables 1 and S12–S15.

Chlorpyrifos, metazachlor, acetochlor, isoproturon and *S*-metolachlor were the only CUPs with maximum total (gas + particle phase) concentrations exceeding 100 pg m^{-3}, and, excepting *S*-metolachlor, these pesticides are all used in quantities > 100 tonnes/year in the Czech Republic (SRS, 2013, 2014). Similarly, carbendazim, chlorotoluron, dimethachlor, fenpropimorph, metamitron and terbuthylazine, which are all authorized for agricultural use and used in quantities $> 30\,\mathrm{t\,year^{-1}}$ (SRS, 2013, 2014), have maximum concentrations higher than $10\,\mathrm{pg\,m^{-3}}$. However, beyond this broad categorization, a poor correlation was found between mass used per year and maximum concentration ($r^2 = 0.362$ and 0.184 in 2012 and 2013, respectively). For example, prochloraz, which was used in similar quantities to chlorpyrifos in 2013 (SRS, 2014), had maximum concentrations of only $1.95\,\mathrm{pg\,m^{-3}}$ (vs. $159\,\mathrm{pg\,m^{-3}}$ for chlorpyrifos). Atmospheric concentrations of CUPs are expected to depend strongly on the amount of local use, pesticide physicochemical properties and environmental persistence. The type of pesticide application (e.g., seed treatment vs. spray application) is also a major influence on pesticide release to air. Moreover, parameters of particular application techniques lead to differing emissions; for example, spray application parameters such as the volatility and viscosity of the pesticide formulation, equipment, weather conditions at the time of application (wind speed and direction, temperature, relative humidity and stability of air at the application site) and operator care, attitude and skill have been identified as factors that influence the emission of pesticide droplets to the air (Gil and Sinfort, 2005), thereby affecting local air concentrations. Although spray droplets are not expected to have been directly sampled, the parameters of regional pesticide application could influence the atmospheric levels measured at the Košetice site. Moreover, the use of a national pesticide use database in this comparison may obscure regional differences, which are of importance given the relatively low atmospheric residence time of CUPs (Coscollà et al., 2013b).

All of the banned CUPs included in this study had maximum concentrations lower than $2.5\,\mathrm{pg\,m^{-3}}$ (excepting fonofos with a concentration of $8.03\,\mathrm{pg\,m^{-3}}$ in one sample from August 2013), reflecting low current emissions. In particular, atrazine had a maximum concentration of $1.24\,\mathrm{pg\,m^{-3}}$ in 2012 and lower concentrations ($< 0.250\,\mathrm{pg\,m^{-3}}$) in 2013. The level of simazine in the single sample in which it was detected was very low ($< 0.1\,\mathrm{pg\,m^{-3}}$). Similarly, in a recent study, these CUPs were detected in only one sample over the Central North Sea at low concentrations ($< 1\,\mathrm{pg\,m^{-3}}$) (Mai et al., 2013). In contrast, from 1984–1994 (before the European ban), atrazine and simazine were frequently detected in precipitation (Dubus et al., 2000). These triazines were also routinely detected in atmospheric samples in France during the same period with concentrations up to $51\,\mathrm{ng\,m^{-3}}$ for atrazine (Sanusi et al., 2000) and $3\,\mathrm{ng\,m^{-3}}$ for simazine (Chevreuil et al., 1996). Thus, the low atmospheric concentrations of atrazine and simazine observed in this study are likely a result of the European ban on use.

Of the OCPs, p,p'-DDE, γ-HCH and α-HCH had the highest contributions, accounting on average for 56.3, 15.5 and 11.7 % of $\sum$OCPs. The ratio of p,p'-DDT/(p,p'-DDE + p,p'-DDD) is often used as an indicator of aged technical DDT. A lower ratio is indicative of aged (degraded) DDT, while a value > 1 indicates fresh application (Li et al., 2007). In this study, this ratio ranged from 0.0271 to 0.370, suggesting aged DDT.

3.3 Seasonal variations at the background site

Concentrations of $\sum$OCPs and $\sum$CUPs were lowest in January–February and highest in August–September for $\sum$OCPs and in April–May for $\sum$CUPs. Individual CUPs and OCPs with consistent detection ($> 25\,\%$ of samples) were generally grouped according to their seasonal trends (Fig. 1). The first group (group A, Fig. 1a) comprises compounds with one growing season concentration peak (April–September). The second group (group B, Fig. 1b) comprises compounds with two peaks, one during the growing season and the second in the plowing season (October–November).

Acetochlor, fenpropimorph, *S*-metolachlor and terbuthylazine are in group A and had maximum concentrations in the April–July period. Dimethachlor and metazachlor are also included in this group but had later peaks, during August–September. These two compounds are used for oil plants and are usually applied later in the summer for weed control of winter grains; this may explain their later maximum concentrations, as has been previously reported for metazachlor (Mai et al., 2013). The peak in concentrations of CUPs in this group is likely associated with the fresh application of pesticides, but also with a contribution from volatilization from soils, plants and surface water at higher temperatures. However, in the case of acetochlor, fenpropimorph and *S*-metolachlor, which had maximum concentrations during April–May, their total concentrations seemed predominantly influenced by agricultural activity rather than volatilization, as the timing of the peak corresponded with the application season (April–May) rather than with the highest summer temperatures (July–August). A similar pattern of high concentrations during the growing season has been previously reported for acetochlor, alachlor, dimethoate and terbuthylazine (Hayward et al., 2010; Mai et al., 2013; Peck and Hornbuckle, 2005).

Group B comprises chlorpyrifos, isoproturon, prochloraz, chlorotoluron, diuron, and likely metribuzin, although this is less conclusive due to more limited detection. The first group B peak is attributed to the same factors as described for group A. The off-season (second peak) concentrations are attributed to direct application of pesticides for future cereal crops which usually take place during autumn (Garthwaite et al., 2014). Moreover, volatilization from pre-treated seeds, plants, soils and water and wind erosion facilitated by the plowing of fields, which usually take place during this period, may also contribute to the second peak. In the case of soil volatilization, these compounds, except for isoproturon and metribuzin, are moderately persistent in the soil (Table 1; half-life in soil $>$ 45 days) and thus, once they have entered the soil from application or deposition, higher soil concentrations may persist unless anthropogenic soil activity such as plowing occurs. However, terbuthylazine also has moderate persistence in soil and did not have an autumn peak. It is notable that the peak concentrations of chlorpyrifos, isoproturon and chlorotoluron were generally higher (up to 4.15 times) in autumn compared to the growing season, suggesting that, for these compounds, autumn emissions are a larger source than emissions during the growing season. October–November peaks of chlorpyrifos have been previously reported in China (Li et al., 2014) and Canada (Hayward et al., 2010).

Carbendazim, a fungicide used mostly for oil plants, had a single growing season peak in 2012 (in April–June) and two peaks in 2013 (one in May–June and one in

September–October). Additionally, this compound had a relative high concentration (12.1 pg m^{-3}) during the last sampled week (18–25 December 2013). It is unclear what caused these differences between the two study years.

Of the OCPs, β-HCH, γ-HCH and o,p'-DDD followed the group A seasonal trend, with one peak occurring between May–August. p,p'-DDE, o,p'-DDT and p,p'-DDT behaved as per group B, with two peaks each year. Other OCPs did not have clear seasonal variations. In general, the seasonal trends observed for OCPs were much less pronounced than for CUPs (Fig. S2). For example, the ratio of summer-to-winter concentrations of OCPs ranged from 0.758 (p,p'-DDD) to 6.54 (p,p'-DDT) with an average value of 2.90, while for CUPs, it ranged from 0.188 (diuron) to 167 (metazachlor) with an average value of 28.4.

The seasonal variability in pesticides is related to and indicative of the sources of the pesticide. The major cause of the seasonal variability in OCPs is expected to be seasonality in volatilization from soils and other surfaces, thus seasonal variability should be related to temperature variability. Conversely, when seasonality is driven by use/application, as for the CUPs, the relationship with temperature should be weaker and the summer/winter ratios should be greater.

An examination of the temperature dependence using the Clausius–Clapeyron equation (see SI) supported this hypothesis. The gaseous pesticide concentrations were expressed as linear regressions of the natural logarithm of partial pressure vs. the inverse of temperature (Hoff et al., 1998):

$$\ln P = \frac{m}{T} + b \tag{1}$$

where m and b are the slope and the intercept of the linear regression, respectively. Partial pressures of individual compounds were calculated for each sample using gas phase concentrations and the ideal gas law.

The temperature-dependence of gas-phase concentrations was statistically significant at the 99 % confidence level for all OCPs except α-HCH, with slopes ranging from −2792 (δ-HCH) to −9802 (p,p'-DDT), indicating that OCP concentrations increased with air temperature (Table S16). Generally, a steep slope and high r^2 indicate that temperature-controlled air–surface cycling and short-term transport influenced the ambient gas phase concentrations (Hoff et al., 1998; Wania and Haugen, 1998), while a shallow slope and low r^2 suggest that other factors (i.e., advection, primary sources, atmospheric deposition, degradation) and LRAT influenced concentrations (Lee et al., 2000). Thus, the Clausius–Clapeyron relationships suggest that gas phase concentrations of all OCPs except α-HCH were controlled by re-volatilization from surfaces close to the sampling site. Temperature accounted for 23–84 % of the variability in atmospheric concentrations for these compounds. The lower temperature dependence of α-HCH suggested that air concentrations were also influenced by LRAT or other confounding factors. For the CUPs which were sufficiently detected in the gas phase, only terbuthylazine and *S*-metolachlor had a significant temperature dependency (Table S17). This emphasizes the difference in the sources of OCPs and CUPs, with the former being influenced by volatilization while the latter are influenced by temperature-independent local sources (notably pesticide application) or LRAT.

3.4 Gas-particle partitioning at the background site

Over the last decades, a number of studies have been conducted on the gas-particle partitioning of organic compounds and several parameters were identified to influence this distribution, such as the physicochemical properties of the target compounds (assessed with the sub-cooled liquid vapour pressure (P_L^0) and/or octanol-air partition coefficient (K_{OA})), the TSP concentration and meteorological parameters (particularly ambient temperature and relative humidity) (Junge, 1977; Pankow, 1987). The influence of temperature on gas-particle partitioning has been demonstrated for chlorpyrifos (Li et al., 2014) and alachlor (Sauret et al., 2008), but the seasonality of gas-particle partitioning of most of the selected CUPs has not been measured in environmental samples.

In this study, the pesticides fall into three groups: (1) predominantly particle phase, (2) predominantly gas phase, and (3) those with significant gas and particle phase fractions. Six CUPs (carbendazim, chlorotoluron, diuron, fenpropimorph, isoproturon and prochloraz) were predominantly in the particle phase (average measured particulate fraction, $\theta_{\text{meas}} > 0.84$). In particular, prochloraz, diuron and carbendazim (except in one sample in June 2012) were detected only in the particle phase. A similar dominance of the particle phase has been reported for carbendazim (Mai et al., 2013) and fenpropimorph (Van Dijk and Guicherit, 1999), but diuron was reported to have an average θ of 0.75 (Scheyer et al., 2008), which differs from our results. Three CUPs (chlorpyrifos, acetochlor and dimethachlor) and all the OCPs were predominantly found in the gas phase (average $\theta_{\text{meas}} < 0.20$). In particular, the average particle-phase fraction of chlorpyrifos, α-HCH, β-HCH, γ-HCH, o,p'-DDE, p,p'-DDE and o,p'-DDT was < 0.04 (Table 1). Of the OCPs, only p,p'-DDD and p,p'-DDT had particulate phase fractions > 0.10. The dominance of the gas phase for chlorpyrifos (Van Dijk and Guicherit, 1999; Li et al., 2014; Sadiki and Poissant, 2008) and OCPs (Cindoruk, 2011; Sadiki and Poissant, 2008; Sanusi et al., 1999) has been well documented. Finally, four CUPs (atrazine, metazachlor, S-metolachlor and terbuthylazine) were distributed between gas and particle phases, with average θ_{meas} of 0.63, 0.59, 0.24 and 0.45, respectively.

We compared the gas-particle partition coefficient (K_{p}, in $\text{m}^3\,\mu\text{g}^{-1}$), both from direct measurements and predictions based on the absorption theory using K_{OA} (Harner and Bidleman, 1998). The temperature-dependency of K_{OA} (Table S18 and Fig. S3) was determined from published relationships (for all OCPs and chlorpyrifos) or from extrapolation (remaining CUPs) based on regression analysis for other compounds and validated for chlorpyrifos (Fig. S4). Details of the calculations can be found in the SI. The comparison between the measured and predicted gas-particle partitioning coefficient (K_{p}) of individual OCPs and CUPs is presented in Figs. 2 and 3.

The predicted log K_{p} of all OCPs and CUPs was directly related to temperature ($r^2 > 0.99$ and $p < 0.05$) due to the consideration of the temperature dependence of K_{OA} in the calculations. However, the relationship with temperature was not apparent in all measured log K_p values. Significant correlations ($0.20 < r^2 < 0.94$ and $p < 0.05$) between air temperatures and measured log K_p were observed for all OCPs except α-, β- and δ-HCH, with higher particulate fractions associated with lower temperatures. Amongst the CUPs, the measured log K_p of *S*-metolachlor and terbuthylazine also correlated with air temperatures ($r^2 = 0.29$ and 0.28, respectively and $p < 0.05$). The lack of observed relationships in the case of CUPs suggests that the gas-particle partitioning of the majority of the CUPs is driven by non-temperature dependent parameters.

As it can be seen in the Figs. 2 and 3, good agreements between the measured and predicted log K_p were observed for γ-HCH, o,p'-DDD, p,p'-DDD, o,p'-DDT and p,p'-DDT, and for dimethachlor, although the number of data points was limited for this CUP ($N = 5$). The K_{OA}-based model accurately represented the influence of temperature on log K_p of o,p'-DDE, p,p'-DDE, chlorpyrifos and terbuthylazine (similar slopes in Figs. 2 and 3) but systematically over-estimated (for DDEs) or under-estimated (for the two CUPs) the log K_p. For the remaining OCPs and CUPs, no good agreements between the model and the measurements were found. Those differences in the log K_p may be due to the influence of pesticide application in the case of CUPs, leading to a non-equilibrium distribution between gas and particle phases at certain times of the year. For example, chlorpyrifos was mainly present in gas-phase regardless of temperature (average for 2012–2013: $\theta_{meas} = 0.037 \pm 0.064$) but 10× higher particulate fractions were found for two samples in spring 2012 ($\theta_{meas} = 0.19$ and 0.33), suggesting the influence of application or agricultural activities rather than temperature. Differences between predicted and measured values might also be due to the choice of the fraction of organic matter ($f_{om} = 0.2$) (Sofuoglu et al., 2004), or to uncertainties in temperature-dependent K_{OA} values of CUPs. It may also suggest that other sorption processes, such as adsorption to elemental carbon or to mineral surfaces may be significant for CUPs (Götz et al., 2007) or that equilibrium between atmospheric gas and particle fractions, which is implicitly assumed by the K_{OA} model, was not reached, as has been noted previously for some PBDEs (Cetin and Odabasi, 2008).

3.5 Particle size distribution at the urban and rural sites

The particle size distribution of CUPs and OCPs was determined at the rural (Telnice) and urban (Kotlářská) site. Only the pesticides with significant particle fractions (average $\theta_{\text{meas}} > 10\,\%$) and detection will be discussed in this section. However, because chlorpyrifos is one of the most widely used insecticides in the world (Solomon et al., 2014), we also include it in the further discussion. Amongst the pesticides with sufficient detection (Tables S19–S22), nine pesticides had highest concentrations on particles $< 0.95\,\mu\text{m}$, four pesticides had highest concentrations in the $> 1.5\,\mu\text{m}$ fraction and one pesticide showed no size distribution pattern. The seasonal size distributions of fenpropimorph and isoproturon are shown in Fig. 4 as representative of the pesticides dominated by the fine and coarse fractions, respectively.

Particle phase concentrations of $\sum$CUPs at the rural site ranged from 110 to 408 pg m^{-3} and were higher than at the urban site ($\sum$CUPs = 30.3–112 pg m^{-3}). In contrast, similar concentrations were observed for $\sum$OCPs at the both rural (14.4–50.1 pg m^{-3}) and urban (18.2–42.2 pg m^{-3}) sites. As suggested by the seasonal trends at the background site, this indicates that current agricultural emissions are driving CUP concentrations, while OCPs are the result of diffuse pollution and thus do not have a strong urban-rural gradient. In general, seasonal variations of particulate OCPs and CUPs were similar to those observed at the background site. However, in these samples, the second autumn peak was observed only for diuron, isoproturon and chlorotoluron at lower concentrations than during the growing season.

One CUP (alachlor) had sporadic detection outside of the growing season and no clear trend in particle size distributions at either site (Tables S20 and S22). Nine CUPs (acetochlor, atrazine, chlorpyrifos, diuron, fenpropimorph, metazachlor, *S*-metolachlor, simazine and terbufos) had higher concentrations on fine particles and were on average 35–76 % associated with particles $< 0.95\,\mu\text{m}$. This distribution did not shift significantly when concentrations were normalized by particle mass in each size fraction (Table S22). To the best of our knowledge, only one study has reported the particle size distribution of CUPs (Coscollà et al., 2013b) and this included acetochlor and fenpropimorph in common with our study, also found largely on fine particles. Similarly, p,p'-DDD and p,p'-DDT also had highest concentrations on fine particles ($< 0.95\,\mu m$), which accounted for 43–63 % and 50–91 % of the total particle phase mass, respectively. It is interesting to note that the size distribution of diuron, fenpropimorph, p,p'-DDD and p,p'-DDT did not show any variation by season or site. The presence of these compounds in the fine fraction (per air volume and per particle mass) is attributed to the sorption of gas phase pesticides to fine particles due to their higher surface area and the coagulation of ultrafine to fine particles (Coscollà et al., 2013b). Moreover, as the mechanisms of wet and dry deposition are less efficient for removing particles in the 0.1–1 and 0.05–2 µm size range respectively (Zhang and Vet, 2006), these compounds are expected to have higher atmospheric residence times compared to compounds which are mostly present on coarse particles.

Four pesticides (carbendazim, isoproturon, prochloraz and terbuthylazine) were found predominantly on coarse particles ($> 3.0\,\mu m$) in all seasons at both sites. Indeed, when the maximum total concentration occurred (i.e. in spring or summer), 45–70 % of the total particle phase mass of these compounds was on particles $> 3.0\,\mu m$. Similar size distributions were observed when the concentrations were normalized by mass (Table S22). In general, coarse particles are the result of mechanical processes such as wind erosion of soil particles and most of these pesticides are moderately persistent in the soil ($DT_{50} = 40$–120 days) and thus might be subject to wind erosion. The presence of pesticides on coarse particles could also be related to the pesticide application technique, as it has been shown that the type and amount of emissions during application (either drift or airborne residues) are strongly related to the application technique, and independent of the physicochemical properties of the compound applied (FOCUS, 2008). A very wide range of application techniques are used; for example, prochloraz exists as an emulsifiable concentrate, while carbendazim, isoproturon and terbuthylazine mostly exist as soluble concentrates, and chlorpyrifos can be applied as either a soluble concentrate or as solid particles directly to soil (University of Hertfordshire, 2013). The f_{om}, not measured in this study, may influence observed particle distributions, particularly given that fine particles may contain a higher carbonaceous fraction (Putaud et al., 2004). However, individual samples (therefore with the same f_{om} values) had some CUPs predominantly found on coarse particles and others predominantly found on fine particles, suggesting that factors other than f_{om} are controlling their particle size distribution. We hypothesize that differences in type of application (emulsifiable vs. soluble concentrates, type of spray application, application to plants vs. soil vs. seeds) may lead to differences in the particle size distribution of pesticides, yet very little specific information is available on how particle size distribution relates to application techniques.

Coarse particles have a shorter residence time in the atmosphere because they settle rapidly and are efficiently removed by wet and dry deposition. Moreover, these particles are less likely to penetrate deeply into the human respiratory system (Englert, 2004). Thus, should these distributions apply on a wider scale, carbendazim, isoproturon, prochloraz and terbuthylazine could be considered as pollutants with low risks of human inhalation exposure (discarding the potential toxicity of individual substances) and LRAT potential. Additional research on the link between pesticide application techniques and local/regional atmospheric concentrations and distributions are needed in order to reduce inhalation exposure of agricultural workers.

4 Conclusions

Although OCPs have been banned for agricultural use decades ago, this study highlights the fact that they are still frequently detected in atmospheric samples at a background site in Central Europe due to their persistence in environmental matrices. Presently, more than 270 plant protection products are registered for agricultural use in the Czech Republic (SRS, 2014) with limited knowledge on potential environmental and human risks. This study improves knowledge of the characterization of atmospheric behavior of 27 CUPs, representing about 24 % of the national market. In general, atmospheric concentrations of CUPs were driven by agricultural practices while secondary sources such as volatilization from surfaces governed atmospheric concentrations of OCPs. Due to their high volatility, OCPs were mainly present as gases while individual CUPs showed more varied gas-particle partitioning due to their wide range of physicochemical properties. Amongst the CUPs studied, chlorpyrifos had similar detection frequencies and gas-particle partitioning behavior to OCPs. Given that this compound has been detected in the Arctic environment (Vorkamp and Riget, 2014), a clear assessment of its potential bioaccumulative and toxic behavior is needed prior its inclusion or exclusion to the category of persistent organic pollutants. The majority of the investigated pesticides had higher concentrations on fine particles ($< 0.95\,\mu m$) but four CUPs (carbendazim, isoproturon, prochloraz and terbuthylazine) had higher concentrations on coarse particles ($> 3.0\,\mu m$) which may be caused by the application technique. This finding is particularly important and should be further investigated given that large particles results in lower risks from inhalation (regardless the toxicity of the pesticide) and lower potential for long range atmospheric transport.

The Supplement related to this article is available online at doi:10.5194/acpd-15-23651-2015-supplement.

Acknowledgements. We thank Roman Prokeš, Lenka Vaňková, and Pavlína Karásková for their contributions with sampling and laboratory work, Gerhard Lammel for suggestions on data interpretation and Tereza Kalábová for help with statistics. This research has been financially supported by the Czech Ministry of Education (LO1214 and LM2011028), EU FP7 projects CSI:ENVIRONMENT (PITN-GA-2010-264329) and ArcRisk (226534), and the project “Employment of Best Young Scientists for International Cooperation Empowerment” (CZ.1.07/2.3.00/30.0037) co-financed from European Social Fund and the state budget of the Czech Republic.

The article processing charges for this open-access publication were covered by the Max Planck Society.

References

Bidleman, T. F., Billings, W. N., and Foreman, W. T.: Vapor-particle partitioning of semivolatile organic compounds: estimates from field collections, Environ. Sci. Technol., 20, 1038–1043, doi:10.1021/es00152a013, 1986.

Borras, E., Sanchez, P., Munoz, A., and Tortajada-Genaro, L. A.: Development of a gas chromatography-mass spectrometry method for the determination of pesticides in gaseous and particulate phases in the atmosphere, Anal. Chim. Acta, 699, 57–65, doi:10.1016/j.aca.2011.05.009, 2011.

Cetin, B. and Odabasi, M.: Atmospheric concentrations and phase partitioning of polybrominated diphenyl ethers (PBDEs) in Izmir, Turkey, Chemosphere, 71, 1067–78, 2008.

Chevreuil, M., Garmouma, M., Teil, M.-J., and Chesterikoff, A.: Occurrence of organochlorines (PCBs, pesticides) and herbicides (triazines, phenylureas) in the atmosphere and in the fallout from urban and rural stations of the Paris area, Sci. Total Environ., 182, 25–37, doi:10.1016/0048-9697(95)05032-9, 1996.

Cindoruk, S. S.: Atmospheric organochlorine pesticide (OCP) levels in a metropolitan city in Turkey, Chemosphere, 82, 78–87, doi:10.1016/j.chemosphere.2010.10.003, 2011.

Coscollà, C., Hart, E., Pastor, A., and Yusà, V.: LC-MS characterization of contemporary pesticides in PM_{10} of Valencia Region, Spain, Atmos. Environ., 77, 394–403, doi:10.1016/j.atmosenv.2013.05.022, 2013a.

Coscollà, C., Yahyaoui, A., Colin, P., Robin, C., Martinon, L., Val, S., Baeza-Squiban, A., Mellouki, A., and Yusà, V.: Particle size distributions of currently used pesticides in a rural atmosphere of France, Atmos. Environ., 81, 32–38, doi:10.1016/j.atmosenv.2013.08.057, 2013b.

Degrendele, C., Okonski, K., Melymuk, L., Landlová, L., Kukučka, P., Čupr, P., and Klánová, J.: Size specific distribution of the atmospheric particulate PCDD/Fs, dl-PCBs and PAHs on a seasonal scale: implications for cancer risks from inhalation, Atmos. Environ., 98, 410–416, doi:10.1016/j.atmosenv.2014.09.001, 2014.

Dubus, I. G., Hollis, J. M., and Brown, C. D.: Pesticides in rainfall in Europe, Environ. Pollut., 110, 331–344, doi:10.1016/S0269-7491(99)00295-X, 2000.

Eisenreich, S. J., Looney, B. B., and Thornton, J. D.: Airborne organic contaminants in the Great Lakes ecosystem, Environ. Sci. Technol., 15, 30–38, doi:10.1021/es00083a002, 1981.

Englert, N.: Fine particles and human health – a review of epidemiological studies, Toxicol. Lett., 149, 235–42, doi:10.1016/j.toxlet.2003.12.035, 2004.

European Commission – Commission Decision 2004/248/EC of 10 March 2004 concerning concerning the non-inclusion of atrazine in Annex I to Council Directive 91/414/EEC and the withdrawal of authorisations for plant protection products containing this active substance, Official Journal L078, 16 March 2004, 0053–0055, 2004.

FOCUS: Pesticides in Air: Considerations for Exposure Assessment, Rep. Focus Work. Gr. Pestic. Air (FOCUS Air Group), SANCO/10553/2006 Rev 2 June 2008, Brussels, 327 pp., 2008.

Garthwaite, D. G., Hudson, S., Barker, I., Parrish, G., Smith, L., and Pietravalle, S.: Pesticide Usage Survey Report 250. Arable Crops in the UK 2012 (Including Aerial Applications 2012), Department for Environment, Food and Rural Affairs, York, UK, 2014.

Gil, Y. and Sinfort, C.: Emission of pesticides to the air during sprayer application: a bibliographic review, Atmos. Environ., 39, 5183–5193, doi:10.1016/j.atmosenv.2005.05.019, 2005.

Götz, C. W., Scheringer, M., MacLeod, M., Roth, C. M., and Hungerbühler, K.: Alternative approaches for modeling gas-particle partitioning of semivolatile organic chemicals: model development and comparison, Environ. Sci. Technol., 41, 1272–1278, doi:10.1021/es060583y, 2007.

Götz, C. W., Scheringer, M., MacLeod, M., Wegmann, F., and Hungerbühler, K.: Regional differences in gas-particle partitioning and deposition of semivolatile organic compounds on a global scale, Atmos. Environ., 42, 554–567, doi:10.1016/j.atmosenv.2007.08.033, 2008.

Harner, T. and Bidleman, T. F.: Octanol-air partition coefficient for describing particle/gas partitioning of aromatic compounds in urban air, Environ. Sci. Technol., 32, 1494–1502, doi:10.1021/es970890r, 1998.

Hayward, S. J., Gouin, T., and Wania, F.: Levels and seasonal variability of pesticides in the rural atmosphere of Southern Ontario, J. Agr. Food Chem., 58, 1077–1084, doi:10.1021/jf902898f, 2010.

Hoff, R. M., Brice, K. A., and Halsall, C. J.: Nonlinearity in the slopes of Clausius–Clapeyron plots for SVOCs, Environ. Sci. Technol., 32, 1793–1798, 1998.

Holoubek, I., Klánová, J., Jarkovský, J., and Kohoutek, J.: Trends in background levels of persistent organic pollutants at Kosetice observatory, Czech Republic. Part I. Ambient air and wet deposition 1996–2005, J. Environ. Monit., 9, 557–63, 2007.

Junge, C. F.: Fate of pollutants in the air and water environment, in: Basic Considerations about Trace Constitutents in the Atmosphere as Related to the Fate of Global Pollutants, edited by: Suffet, I. H., Wiley, New York, NY, 7–25, 1977.

Kannan, K., Ridal, J., and Struger, J.: Pesticides in the Great Lakes, in: Persistent Organic Pollutants in the Great Lakes, vol. 5N, edited by: Hites, R., Springer, Berlin, Heidelberg, 151–199, 2006.

Koblizková, M., Lee, S. C., and Harner, T.: Sorbent impregnated polyurethane foam disk passive air samplers for investigating current-use pesticides at the global scale, Atmos. Pollut. Res., 3, 456–462, 2012.

Lammel, G., Klánová, J., Kohoutek, J., Prokeš, R., Ries, L., and Stohl, A.: Observation and origin of organochlorine compounds and polycyclic aromatic hydrocarbons in the free troposphere over central Europe, Environ. Pollut., 157, 3264–3271, doi:10.1016/j.envpol.2009.05.028, 2009.

Lee, R. G. M., Burnett, V., Harner, T., and Jones, K. C.: Short-term temperature-dependent air–surface exchange and atmospheric concentrations of polychlorinated naphthalenes and organochlorine pesticides, Environ. Sci. Technol., 34, 393–398, doi:10.1021/es9907414, 2000.

Li, H., Ma, H., Lydy, M. J., and You, J.: Occurrence, seasonal variation and inhalation exposure of atmospheric organophosphate and pyrethroid pesticides in an urban community in South China, Chemosphere, 95, 363–369, doi:10.1016/j.chemosphere.2013.09.046, 2014.

Li, J., Zhang, G., Guo, L., Xu, W., Li, X., Lee, C. S. L., Ding, A., and Wang, T.: Organochlorine pesticides in the atmosphere of Guangzhou and Hong Kong: regional sources and long-range atmospheric transport, Atmos. Environ., 41, 3889–3903, doi:10.1016/j.atmosenv.2006.12.052, 2007.

Li, Y. F. and Macdonald, R. W.: Sources and pathways of selected organochlorine pesticides to the Arctic and the effect of pathway divergence on HCH trends in biota: a review, Sci. Total Environ., 342, 87–106, doi:10.1016/j.scitotenv.2004.12.027, 2005.

Lohmann, R., Klanova, J., Kukucka, P., Yonis, S., and Bollinger, K.: PCBs and OCPs on a east-to-west transect: the importance of major currents and net volatilization for PCBs in the Atlantic Ocean, Environ. Sci. Technol., 46, 10471–10479, doi:10.1021/es203459e, 2012.

Mai, C., Theobald, N., Lammel, G., and Hühnerfuss, H.: Spatial, seasonal and vertical distributions of currently-used pesticides in the marine boundary layer of the North Sea, Atmos. Environ., 75, 92–102, doi:10.1016/j.atmosenv.2013.04.027, 2013.

Odabasi, M. and Cetin, B.: Determination of octanol-air partition coefficients of organochlorine pesticides (OCPs) as a function of temperature: application to air-soil exchange, J. Environ. Manage., 113, 432–9, 2012.

Okonski, K., Degrendele, C., Melymuk, L., Landlová, L., Kukučka, P., Vojta, Š., Jiri, K., Čupr, P., and Klánová, J.: Particle size distribution of halogenated flame retardants and implications for atmospheric deposition and transport, Environ. Sci. Technol., 48, 14426–14434, 2014.

Pankow, J. F.: Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere, Atmos. Environ., 21, 2275–2283, doi:10.1016/0004-6981(87)90363-5, 1987.

Peck, A. M. and Hornbuckle, K. C.: Gas-phase concentrations of current-use pesticides in Iowa, Environ. Sci. Technol., 39, 2952–2959, doi:10.1021/es0486418, 2005.

Putaud, J.-P., Raes, F., Van Dingenen, R., Brüggemann, E., Facchini, M. C., Decesari, S., Fuzzi, S., Gehrig, R., Hüglin, C., Laj, P., Lorbeer, G., Maenhaut, W., Mihalopoulos, N., Müller, K., Querol, X., Rodriguez, S., Schneider, J., Spindler, G., ten Brink, H., Tørseth, K., and Wiedensohler, A.: A European aerosol phenomenology – 2: chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe, Atmos. Environ., 38, 2579–2595, doi:10.1016/j.atmosenv.2004.01.041, 2004.

Růžičková, P., Klánová, J., Čupr, P., Lammel, G., and Holoubek, I.: An assessment of air-soil exchange of polychlorinated biphenyls and organochlorine pesticides across central and southern Europe, Environ. Sci. Technol., 42, 179–85, 2008.

Sadiki, M. and Poissant, L.: Atmospheric concentrations and gas-particle partitions of pesticides: comparisons between measured and gas-particle partitioning models from source and receptor sites, Atmos. Environ., 42, 8288–8299, doi:10.1016/j.atmosenv.2008.07.041, 2008.

Sanusi, A., Millet, M., Mirabel, P., and Wortham, H.: Gas-particle partitioning of pesticides in atmospheric samples, Atmos. Environ., 33, 4941–4951, doi:10.1016/S1352-2310(99)00275-7, 1999.

Sanusi, A., Millet, M., Mirabel, P., and Wortham, H.: Comparison of atmospheric pesticide concentrations measured at three sampling sites: local, regional and long-range transport, Sci. Total Environ., 263, 263–277, doi:10.1016/S0048-9697(00)00714-2, 2000.

Sauret, N., Wortham, H., Putaud, J.-P., and Mirabel, P.: Study of the effects of environmental parameters on the gas/particle partitioning of current-use pesticides in urban air, Atmos. Environ., 42, 544–553, doi:10.1016/j.atmosenv.2007.09.012, 2008.

Scheyer, A., Morville, S., Mirabel, P., and Millet, M.: Gas/particle partitioning of lindane and current-used pesticides and their relationship with temperature in urban and rural air in Alsace region (east of France), Atmos. Environ., 42, 7695–7705, doi:10.1016/j.atmosenv.2008.05.029, 2008.

Shen, L., Wania, F., Lei, Y. D., Teixeira, C., Muir, D. C. G., and Bidleman, T. F.: Atmospheric distribution and long-range transport behavior of organochlorine pesticides in North America, Environ. Sci. Technol., 39, 409–420, doi:10.1021/es049489c, 2004.

Shoeib, M. and Harner, T.: Using measured octanol-air partition coefficients to explain environmental partitioning of organochlorine pesticides., Environ. Toxicol. Chem., 21, 984–990, doi:10.1897/1551-5028(2002)021<0984:umoapc>2.0.co;2, 2002.

Sofuoglu, A., Cetin, E., Bozacioglu, S. S., Sener, G. D., and Odabasi, M.: Short-term variation in ambient concentrations and gas/particle partitioning of organochlorine pesticides in Izmir, Turkey, Atmos. Environ., 38, 4483–4493, doi:10.1016/j.atmosenv.2004.05.036, 2004.

Solomon, K. R., Williams, W. M., Mackay, D., Purdy, J., Giddings, J., and Giesy, J.: Properties and uses of chlorpyrifos in the United States, Reviews of Environmental Contamination and Toxicology: Ecological Risk Assessment for Chlorpyrifos in Terrestrial and Aquatic Systems in the United States, Heidelberg, 231, 13–34, 2014.

SRS: State Phytosanitary Administration. Usage of Active Substances in 2012, Czech Republic, available at: http://eagri.cz/public/web/file/242789/spotreba_UL_2012_anglicka_verze_.pdf (last access: November 2014), 2013.

SRS: State Phytosanitary Administration. Usage of Active Substances in 2013, Czech Republic, available at: http://eagri.cz/public/web/file/317729/Spotreba_UL_2013_kategorie_anglicka_verze_oprava.pdf, last access: November 2014.

US Environmental Protection Agency: Atrazine Updates, Pestic. Reregistration, http://www.epa.gov/pesticides/reregistration/atrazine/atrazine_update.htm (last access: November 2014), Washington D.C., 2013.

University of Hertfordshire: The Pesticide Properties DataBase (PPDB), Dev. by Agric. Environ. Res. Unit (AERU), Univ. Hertfordshire, 2006–2013, Hertfordshire, UK, 2013.

US EPA: Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.11, United States Environmental Protection Agency, Washington, DC, USA, 2014.

Van den Berg, F., Kubiak, R., Benjey, W. G., Majewski, M. S., Yates, S. R., Reeves, G. L., Smelt, J. H., and van der Linden, A. M. A.: Emission of pesticides into the air, Water Air Soil Pollut., 115, 195–218, doi:10.1023/A:1005234329622, 1999.

Van Dijk, H. F. G. and Guicherit, R.: Atmospheric dispersion of current-use pesticides: a review of the evidence from monitoring studies, Water Air Soil Pollut., 115, 21–70, doi:10.1023/A:1005293020536, 1999.

Vecchi, R., Marcazzan, G., and Valli, G.: A study on nighttime-daytime PM_{10} concentration and elemental composition in relation to atmospheric dispersion in the urban area of Milan (Italy), Atmos. Environ., 41, 2136–2144, doi:10.1016/j.atmosenv.2006.10.069, 2007.

Vorkamp, K. and Riget, F. F.: A review of new and current-use contaminants in the Arctic environment: evidence of long-range transport and indications of bioaccumulation, Chemosphere, 111, 379–395, doi:10.1016/j.chemosphere.2014.04.019, 2014.

Wania, F. and Haugen, J.: Temperature dependence of atmospheric concentrations of semivolatile organic compounds, Environ. Sci. Technol., 97, 1013–1021, doi:10.1021/es970856c, 1998.

Yao, Y., Harner, T., Blanchard, P., Tuduri, L., Waite, D., Poissant, L., Murphy, C., Belzer, W., Aulagnier, F., and Sverko, E.: Pesticides in the atmosphere across Canadian agricultural regions, Environ. Sci. Technol., 42, 5931–5937, doi:10.1021/es800878r, 2008.

Zhang, L. and Vet, R.: A review of current knowledge concerning size-dependent aerosol removal, China Part., 4, 272–282, doi:10.1016/S1672-2515(07)60276-0, 2006.

Zhang, N., Yang, Y., Liu, Y., and Tao, S.: Determination of octanol-air partition coefficients and supercooled liquid vapor pressures of organochlorine pesticides, J. Environ. Sci. Heal. B, 44, 649–656, doi:10.1080/03601230903163590, 2009.

Zhang, X. M., Meyer, T., Muir, D. C. G., Teixeira, C., Wang, X. W., and Wania, F.: Atmospheric deposition of current use pesticides in the Arctic: snow core records from the Devon Island Ice Cap, Nunavut, Canada, Environ. Sci. Impacts, 15, 2304–2311, doi:10.1039/c3em00433c, 2013.

Table 1. Physicochemical properties and atmospheric concentrations (in pg m^{-3}) of individual OCPs and CUPs at background site. ND indicates "not detected".

Compound	Type of pesticide[a]	In use[b]	Half-life in soil (days) (PPDB, 2013)	Vapor pressure (Pa)	$\log K_{OA}$	Detection frequency (%)	Range of total concentrations (pg m^{-3})	Range of gas phase concentrations (pg m^{-3})	Range of particle phase concentrations (pg m^{-3})	Average measured particulate fraction (θ_{meas})	Average predicted particulate fraction (θ_{pr})
Acetochlor	H	Y	14	2.20E-05[c]	9.07[e]	50.0	ND-181	ND-158	ND-23.2	0.14 ± 0.32	0.067
Alachlor	H	N	14	2.90E-03[c]	9.98[e]	5.77	ND-0.82	ND-0.23	ND-0.82	0.85 ± 0.26	0.31
Atrazine	H	N	75	3.90E-05[c]	9.62[g]	21.2	ND-1.24	ND-0.76	ND-0.49	0.63 ± 0.46	0.18
Azinphos Methyl	I	N	10	5.00E-07[c]	8.76[f]	0.00	ND	ND	ND	ND	0.036
Carbendazim	F	Y	40	9.00E-05[c]	10.6[f]	42.3	ND-12.5	ND-0.22	ND-12.5	0.98 ± 0.10	0.60
Chlorotoluron	H	Y	45	5.00E-06[c]	10.6[g]	48.1	ND-25.1	ND-0.48	ND-24.7	0.95 ± 0.20	0.61
Chlorpyrifos	I	Y	50	1.43E-03[c]	8.41[h]	84.6	ND-159	ND-158	ND-9.43	0.037 ± 0.064	0.015
Diazinon	I	N	9.1	1.20E-02[c]	9.14[e]	1.92	ND-0.18	ND-0.18	ND	0.0	0.077
Dimethachlor	H	Y	7.0	6.40E-04[c]	9.34[d]	40.4	ND-71.3	ND-70.8	ND-9.36	0.18 ± 0.37	0.011
Dimethoate	I	Y	2.6	2.47E-04[c]	9.15[f]	3.85	ND-0.08	ND	ND-0.08	1.0 ± 0.00	0.079
Disulfoton	I	N	30	7.20E-03[c]	8.07[d]	1.92	ND-2.22	ND	ND-2.22	1	< 0.01
Diuron	H	N	76	1.15E-06[c]	10.4[f]	32.7	ND-1.23	ND	ND-1.23	1.0 ± 0.00	0.50
Fenitrothion	I	N	2.7	6.76E-04[c]	7.72[d]	0.00	ND	ND	ND	ND	< 0.01
Fenpropimorph	F	Y	35	3.90E-03[c]	8.93[e]	65.4	ND-73.8	ND-1.27	ND-73.8	0.91 ± 0.28	0.051
Fonofos	I	N	99	2.70E-02[c]	7.48[d]	5.76	ND-8.03	ND	ND-8.03	1.0 ± 0.00	< 0.01
Isoproturon	H	Y	12	5.50E-06[c]	11.2[g]	86.5	ND-413	ND-122	ND-291	0.84 ± 0.29	0.84
Malathion	I	N	0.17	3.10E-03[c]	9.06[e]	3.85	ND-0.30	ND-0.30	ND-0.13	0.50 ± 0.70	0.066
Metamitron	H	Y	30	7.44E-07[c]	11.2[d]	25.0	ND-16.5	ND-16.5	ND-6.41	0.23 ± 0.44	0.85
Metazachlor	H	Y	8.6	9.30E-05[c]	9.76[e]	86.5	ND-344	ND-262	ND-275	0.59 ± 0.38	0.23

Table 1. Continued.

Compound	Type of pesticide[a]	In use[b]	Half-life in soil (days) (PPDB, 2013)	Vapor pressure (Pa)	$\log K_{OA}$	Detection frequency (%)	Range of total concentrations ($\mathrm{pg\,m^{-3}}$)	Range of gas phase concentrations ($\mathrm{pg\,m^{-3}}$)	Range of particle phase concentrations ($\mathrm{pg\,m^{-3}}$)	Average measured particulate fraction (θ_{meas})	Average predicted particulate fraction (θ_{pr})
Metribuzin	H	Y	11.5	1.21E-04[c]	10.0[d]	15.4	ND-5.46	ND-5.46	ND-1.83	0.22 ± 0.41	0.32
Prochloraz	F	Y	120	1.50E-04[c]	13.6[d]	55.8	ND-1.95	ND	ND-1.95	1.0 ± 0.00	1.0
Pyrazon	H	Y	31	1.00E-09[c]	9.01[d]	15.4	ND-2.25	ND-0.80	ND-2.25	0.91 ± 0.26	0.060
Simazine	H	N	60	8.10E-07[c]	9.59[g]	1.92	ND-0.087	ND	ND-0.087	1	0.17
S-metolachlor	H	Y	15	3.70E-03[c]	9.33[d]	73.1	ND-329	ND-309	ND-91.0	0.24 ± 0.34	0.11
Temephos	I	N	2	9.50E-06[c]	13.1[d]	5.77	ND-0.21	ND-0.21	ND-0.11	0.67 ± 0.58	1
Terbufos	I	N	8	3.46E-02[c]	7.49[d]	1.92	ND-0.80	ND	ND-0.61	1	< 0.01
Terbuthylazine	H	Y	75.1	1.20E-04[c]	9.03[f]	78.8	ND-53.8	ND-33.8	ND-31.6	0.45 ± 0.35	0.062
∑CUPs							ND-662	ND-365	ND-323		
α−HCH		N	175	3.44E-02[d]	7.61[i]	100	1.09–9.79	1.08–9.78	ND-0.031	< 0.01	0.016
β−HCH		N		3.44E-02[d]	8.88[i]	69.2	ND-0.59	ND-0.59	ND-0.074	0.033 ± 0.051	0.071
γ−HCH	I	N		3.44E-02[d]	7.85[i]	100	0.488–21.8	0.470–21.8	ND-0.043	< 0.01	< 0.01
δ−HCH		N		3.44E-02[d]	8.84[i]	57.7	ND-0.42	ND-0.42	ND-0.065	0.055 ± 0.097	0.065
o,p'-DDE		N		5.99E-03[d]	9.26[j]	96.2	ND-1.42	ND-1.42	ND-0.054	0.018 ± 0.071	0.17
p,p'-DDE		N		3.44E-03[d]	9.68[i]	100	1.14–71.4	0.612–71.4	ND-0.96	0.037 ± 0.074	0.30
o,p'-DDD		N		8.45E-04[d]	9.57[j]	73.1	ND-1.30	ND-1.28	ND-0.11	0.065 ± 0.16	0.13
p,p'-DDD		N		1.23E-03[d]	10.1[i]	75.0	ND-2.61	ND-2.56	ND-0.40	0.11 ± 0.18	0.30
o,p'-DDT	I	N	6200	1.68E-03[d]	9.45[i]	92.3	ND-9.18	ND-9.18	ND-0.11	0.033 ± 0.08	0.11
p,p'-DDT	I	N	6200	1.43E-04[d]	9.82[i]	100	0.414–9.99	0.13–9.99	ND-0.50	0.13 ± 0.19	0.18
∑OCPs		N					4.51–122	2.87–122	ND-1.96		

[a] H: Herbicide, I: Insecticide and F: Fungicide. [b] Y: Authorized for agricultural use in Czech Republic during the sampling period and N: Not authorized for agricultural purposes in Czech Republic during the sampling period. [c] PPDB (2013). [d] US EPA (2014). [e] Coscollà et al. (2013b). [f] Coscollà et al. (2013a). [g] Götz et al. (2007). [h] Odabasi and Cetin (2012). [i] Shoeib and Harner (2002). [j] Zhang et al. (2009).

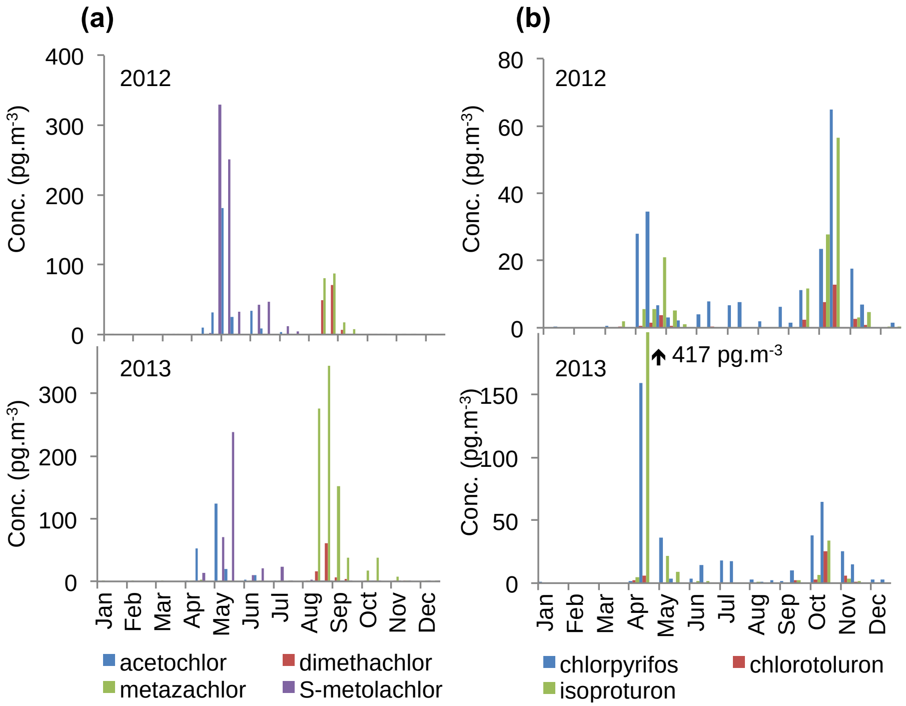

Figure 1. Seasonal variation of selected CUPs with **(a)** one peak per year during the growing season and **(b)** two peaks per year, in April–July and October–November.

Title Page
Abstract
Introduction
Conclusions
References
Tables
Figures
◀◀
▶▶
◀
▶
Back
Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

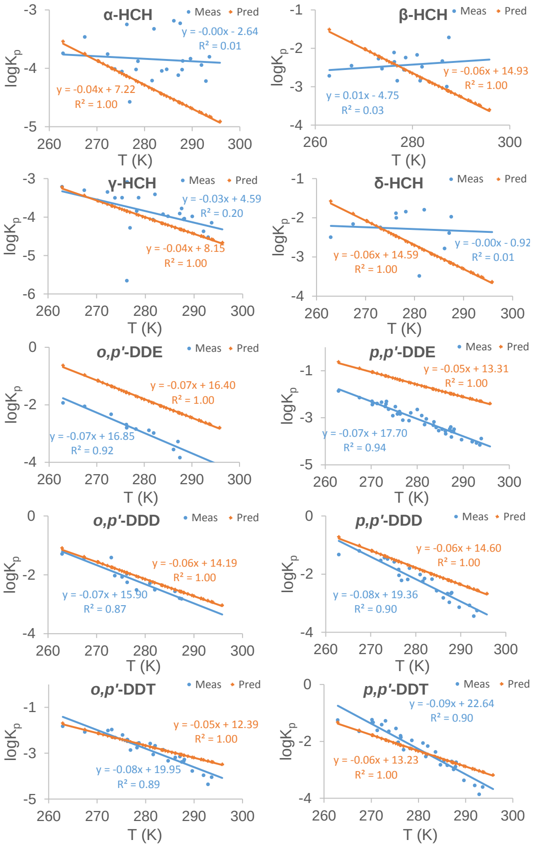

Figure 2. Comparison of the gas-particle partitioning coefficient log K_p ($m^3\,\mu g^{-1}$) based on measurements (blue dots) and predictions (based on the K_{OA} model, orange dots) of OCPs as a function of temperature (only the samples in which both phases were detected are considered).

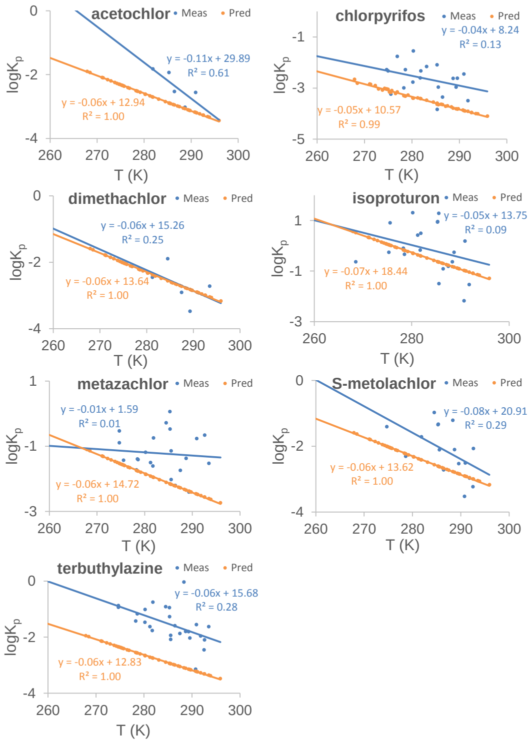

Figure 3. Comparison of the gas-particle partitioning coefficient log K_p ($\mathrm{m^3\,\mu g^{-1}}$) based on measurements (blue dots) and predictions (based on the K_OA model, orange dots) of CUPs as a function of temperature (only the samples in which both phases were detected are considered).

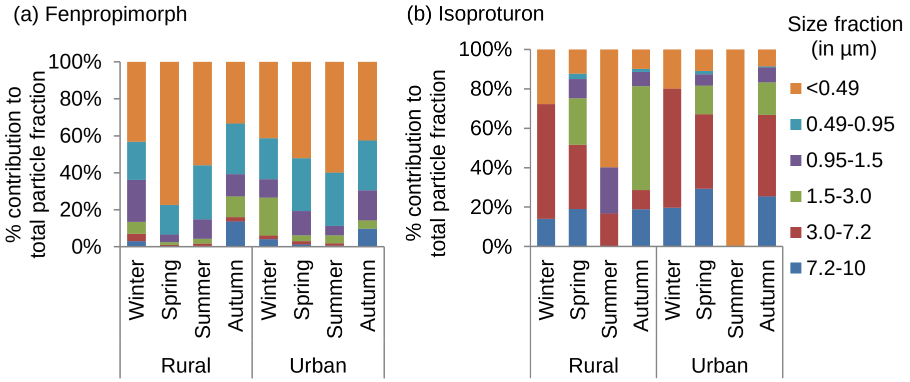

Figure 4. Seasonal particle size distribution of **(a)** fenpropimorph and **(b)** isoproturon at the rural and urban sites. Fenpropimorph represents the group of pesticides predominantly found on fine particles and isoproturon for the coarse particles.