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

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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. Major differences were found in the atmospheric distribution of OCPs and CUPs. The atmospheric concentrations of CUPs were driven by agricultural activities while secondary sources such as volatilization from surfaces governed the atmospheric concentrations of OCPs. Moreover, clear differences were observed in gas-particle partitioning; CUP partitioning was influenced by adsorption onto mineral surfaces while OCPs were mainly partitioning to aerosols through absorption. A predictive method for estimating the gas-particle partitioning has been derived and is proposed for polar and non-polar pesticides. Finally, while OCPs and the majority of CUPs were largely found on fine particles, four CUPs (carbendazim, isoproturon, prochloraz and terbuthylazine) had higher

concentrations on coarse particles (>3.0 μm), which may be related to the pesticide application technique. This finding is particularly important and should be further investigated given that large particles result in lower risks from inhalation (regardless the toxicity of the pesticide) and lower potential for long range atmospheric transport.

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pesticides (OCPs) are banned for agricultural purposes in most countries, including the Czech Republic, and have been replaced by what are often termed "current-use pesticides" (CUPs).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; Růzicková 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 (Glotfelty et al., 1989). Finally, pesticides are affected by air-surface exchange such as the volatilization from plants and soils, surface waters, and from old industrial sites (Cabrerizo et al., 2011). 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 particulate phases according to their physicochemical properties (vapor pressure, octanol-air partition coefficient K_{oa}), the concentration of total suspended particulate matter (TSP) and meteorological parameters (ambient temperature, relative humidity) (Cousins and Mackay, 2001; Lohmann and Lammel, 2004; 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 (Cindoruk, 2011; Scheyer et al., 2008; Sofuoglu et al., 2004) and some CUPs (Borrás et al., 2011; Götz et al., 2007; Sadiki and Poissant, 2008; Sanusi et al., 1999; Sauret et al., 2008; Yao et al., 2008) has been reported. However, the seasonal variation of this partitioning has only been investigated for two CUPs: chlorpyrifos (Li et al., 2014) and alachlor (Sauret et al., 2008). Similarly, knowledge of how CUPs are distributed among different particle sizes is very limited (Coscollà et al., 2014, 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 Supplementary Information (SI). 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, 7 day sampling duration). Particles were collected on quartz fiber filters (QFFs) (QM-A, 150 mm, Whatman, UK, pore size of 2.2 µm) and gas phase on polyurethane foam (PUF) (two in series, T3037, 110 x 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 hours each. Fifty-two samples were collected each year. Half of the samples were used for OCPs analysis and half for CUPs analysis (Tables S1 and S2).

Secondly, to assess the seasonal variation of the particle size distribution of pesticides, particulate-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 µm, 0.49-0.95 µm, 0.95-1.5 µm, 1.5-3.0 µm, 3.0-7.2 µm and 7.2-10 µm and were collected on QFFs (TE-230-QZ, 141 x 148 mm, Tisch, Environmental, USA and QM-A, 203 x 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, 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 x 2.1 mm x 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 SI. 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 during air sampling 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 (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 were below detection in field blanks) 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±6.10% with an average value of 95.8±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±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 detection frequency 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 - Health & Consumer Protection Directorate-General, 2003) remains one of the highest use pesticides in USA (U.S. 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+particulate phase) concentrations exceeding 100 pg.m^{-3}, and, except S-metolachlor, these pesticides are all used in quantities >100 tonnes/year in the Czech Republic (Tables S10 and S11). Similarly, carbendazim, chlorotoluron, dimethachlor, fenpropimorph, metamitron and terbuthylazine, which are all authorized for agricultural use and used in quantities >30 tonnes/year (SRS, 2014, 2013), have maximum concentrations higher than 10 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 pg.m^{-3} (vs. 159 pg.m^{-3} for chlorpyrifos). The lack of correlation may be caused by the use of a national pesticide usage database obscuring regional differences, which are of importance given the relatively low atmospheric residence time of CUPs (Coscollà et al., 2013b). Moreover, the pesticide physicochemical properties, their environmental persistence and the pesticide application technique used (e.g., seed treatment vs. spray application) may also influence the atmospheric concentrations of CUPs. Indeed, 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.

All of the banned CUPs included in this study had maximum concentrations lower than 2.5 pg.m^{-3} (excepting fonofos with a concentration of 8.03 pg.m^{-3} in one sample from August 2013), reflecting low current emissions. In particular, atrazine had a maximum concentration of 1.24 pg.m^{-3} in 2012 and lower concentrations (<0.250 pg.m^{-3}) in 2013. The level of simazine in the single sample in which it was detected was very low (<0.1 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 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 ng.m^{-3} for atrazine (Sanusi et al., 2000) and 3 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 ∑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.

The total concentrations of individual CUPs and OCPs were compared with previous studies (Table S16 and references therein). OCPs levels were comparable to other European background sites (Cabrerizo et al., 2011; Halse et al., 2011). ΣDDT concentrations in this study (1.14-96.3 pg m^{-3}) were considerably lower than those reported in India or in Africa (8-5930 and 8-2178 pg m^{-3}, respectively (Bogdal et al., 2013; Yadav et al., 2015)). The CUPs concentrations reported here were similar to those in the German Bight and North Sea (Mai et al., 2013), but were generally much lower than in Canada (Hayward et al., 2010; Yao et al., 2008), USA (Majewski et al., 2014; Peck and Hornbuckle, 2005) and France (Coscollà et al., 2013c, 2011; Sauret et al., 2008; Scheyer et al., 2008; Schummer et al., 2010).

3.3 Seasonal variations at the background site

Concentrations of ∑OCPs and ∑CUPs were lowest in January-February and highest in August-September for ∑OCPs and in April-May for ∑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 (18-25/12/13). 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 versus the inverse of temperature (Hoff et al., 1998):

$$\mathrm{lnP} = \frac{\mathrm{m}}{\mathrm{T}} + \mathrm{b} \qquad \text{(Eq. 1)}$$

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 S17). 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. This is in agreement with a previous study showing that atmospheric levels of OCPs at different European background sites were controlled by air-soil exchange (Cabrerizo et al., 2011). 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 S18). For some CUPs, their atmospheric lifetime in relation with OH reaction is relatively small (e.g. about 2 hours for chlorpyrifos (Muñoz et al., 2014)), which may explain the lack of maximum concentrations observed during the warmest periods. These results emphasize 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

It is well known that several sampling artifacts such as blow-on, blow-off, breakthrough and degradation may occur and affect the results about gas-particle partitioning (Melymuk et al., 2014). The reported gas-particle partitioning of pesticides are therefore operationally defined, given the sampling configuration, where gas-phase is defined as the mass of the sample captured on the PUF and particulate-phase is the mass captured on the QFF. Given the large volumes used in this study, breakthrough tests were performed (Table S7) and HCHs were excluded from the discussion of gas-particle partitioning to avoid any bias due to gas-phase breakthrough sampling. Breakthrough is typically the most significant sampling artifact; bias due to filter blow-on/blow-off is not expected to be significant (Melymuk et al., in press).

In this study, the pesticides fall into three groups: (1) predominantly particulate phase, (2) predominantly gas phase, and (3) those with significant gas and particulate phase fractions (average measured particulate mass fraction, θ_{meas}, $0.2< \theta_{meas}<0.8$). Six CUPs (carbendazim, chlorotoluron, diuron, fenpropimorph, isoproturon and prochloraz) were predominantly in the particulate phase ($\theta_{meas} > 0.84$). In particular, prochloraz, diuron and carbendazim (except in one sample in June 2012) were detected only in the particulate phase. A similar dominance of the particulate 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 slightly from our results. Three CUPs (chlorpyrifos, acetochlor and dimethachlor) and all the OCPs were predominantly found in the gas phase (average $\theta_{meas} < 0.20$). In particular, the average particulate-phase mass fractions of chlorpyrifos, *o,p*'-DDE, *p,p*'-DDE and *o,p*'-DDT were <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 (Li et al., 2014; Sadiki and Poissant, 2008; Van Dijk and Guicherit, 1999) and OCPs (Cindoruk, 2011; Sadiki and Poissant, 2008; Sanusi et al., 1999) is well documented. Finally, four CUPs (atrazine, metazachlor, S-metolachlor and terbuthylazine) were distributed between gas and particulate phases, with average θ_{meas} of 0.63, 0.59, 0.24 and 0.45, respectively.

Significant correlations ($0.20<r^2<0.94$ and $p<0.05$) between air temperatures and the gas-particle partitioning coefficient (K_p, in $m^3 \mu g^{-1}$, see SI for details) were observed for all OCPs, with higher particulate fractions associated with lower temperatures. Amongst the CUPs, the measured 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 other CUPs suggests that the gas-particle partitioning of the majority of the CUPs is determined by processes which are not or minimally sensitive to temperature.

To better understand the mechanisms influencing gas-particle partitioning of pesticides, K_p was compared with K_{oa} and with the soil-air partitioning coefficient (K_{sa}, dimensionless) for four CUPs (chlorpyrifos, isoproturon, metazachlor and terbuthylazine) and three OCPs (*p,p'*-DDD, *p,p'*-DDE and *p,p'*-DDT) (Fig. 2). The temperature-dependency of K_{oa} (Table S19 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. K_{sa} data used in this study were adopted from the relationship of Davie-Martin et al. (2015), based on laboratory experiments on 22 OCPs and CUPs, as:

$$\log K_{sa} = -26.2 + 0.714 \log K_{oa,298.15K} + \frac{8291}{T_{amb}} - 0.0128RH + 0.121\log(100 f_{oc})$$

(Eq. 2)

where, T_{amb} is the ambient temperature (K), RH is the relative humidity (%) and f_{OC} is the organic carbon content of soil. Average monthly RH values and an experimental f_{oc} of 0.03 (Holoubek et al., 2009) were used.

Both K_{oa} and K_{sa} were significantly ($p<0.05$) correlated with K_p for both OCPs and CUPs (r^2 = 0.51-0.73; Fig. 2). However, clear differences were noted between these two classes of compounds. For same K_{oa} (or K_{sa}), the K_p values of CUPs were notably higher than those of the OCPs. This suggests that absorption into organic matter alone, described by K_{oa}, is not sufficient to explain the observed gas-particle partitioning of CUPs and that other types of interactions occur. In other words, while absorption into the organic matter fraction is the dominant process for weakly or non-polar compounds such as OCPs, additionally adsorption to mineral surfaces or soot is significant for more polar compounds such as the CUPs. Indeed, Götz et al., (2007) estimated that the contribution of OM to K_p was 74% for DDT but only 1 and 5% for isoproturon and terbuthylazine, respectively, for which adsorption to mineral surfaces dominated K_p (contributions of 95 and 86%, respectively) and concluded that a predictive model based only on absorptive contribution to organic matter is not recommended for polar compounds such as CUPs. Therefore, assuming absorption to govern sorption, such as in the K_{oa} model (Harner and Bidleman; 1998), will generally lead to high agreement of predicted K_p values with observations for OCPs but low agreement (underestimates) for CUPs (Fig. S5-S6). Thus, a predictive model based only on absorptive contribution to organic matter is not recommended for polar compounds such as CUPs (Götz et al., 2007). However, we note that in Fig. 2a the two slopes intersect around $\log K_{oa}$ of 13. This suggests that for the few polar pesticides with $12<\log K_{oa}<13$, the K_{oa}-based approach is still appropriate.

Interestingly, the predicted method derived for soil-air partitioning which takes into account both absorption (K_{oa}) and adsorption (T, RH) (Davie-Martin et al., 2015) was a better predictor for gas-particle partitioning, given that similar slopes (0.857 ± 0.0332) were observed for OCPs and CUPs (Fig. 2b). The difference between the intercepts is 1.25. Based on this relationship, we propose an improved method for prediction of gas-particle partitioning of pesticides:

$$\log K_p = 0.857 \cdot \left(-26.2 + 0.714 \log K_{oa,298.15\,K} + \frac{8291}{T_{amb}} - 0.0128RH + 0.121 \log(100 f_{oc})\right) - 10.5 + p$$

(Eq. 3)

with p being a factor accounting for polarity, p = 1.25 for CUPs and p = 0 for OCPs. By using eq. 3, good agreements between predicted and measured logK_p of CUPs and OCPs are found (rmse = 0.61, Fig. 3), with few exceptions for some CUPs.

The relationship between K_p and K_{sa} suggest similar partitioning from the gas phase to aerosols and to soils including absorption to organic matter and adsorption to mineral surfaces. In fact, the role of adsorption to mineral surfaces in air-soil exchange studies has been rather neglected over the last decades (Mackay, 2001; Odabasi and Cetin, 2012a; Wang et al., 2012; Wei et al., 2014) and should be further considered (Davie-Martin et al., 2015; Goss et al., 2004).

The seasonal variation of the relationship of K_p with K_{oa} and K_{sa} was also examined (Fig. S7). Given that many CUPs were mainly detected in spring and autumn, we choose these two seasons (spring and autumn were defined from March to June and from September to November, respectively). Interestingly, better correlations were obtained between K_p and K_{oa} for CUPs in autumn compared to spring (r^2 = 0.71 and 0.49, respectively, $p<0.05$) while there was no variation for OCPs (r^2 = 0.63). This suggests that a process other than absorption in organic matter gains significance for CUPs in spring but less in autumn. This could be related to a higher concentration (specific surface area) of mineral dust during the spring sampling period (adsorption, see above). Pesticide application technique could potentially affect gas-particle partitioning through mass transport kinetics limitations (non-equilibrium). Indeed, 10× higher particulate fractions were found for chlorpyrifos for two samples in spring 2012 (θ_{meas}=0.19 and 0.33), suggesting a potential influence of application or agricultural activities. However, there is limited knowledge in this area. The differences in RH in spring and autumn (73.1 vs. 83.5 %, respectively) may also have contributed to the observed differences, as water layers and deliquescence may affect OM accessibility (higher in spring). Götz et al., (2007) estimated that the influence of absorption on K_p for polar pesticides was negligible for RH between 40 and 80% while it was dominant for RH>80% (contributing to 30-90%). Similarly, Davie-Martin et al., (2015) found that RH had a negligible effect on K_{sa} for RH>80% for semi-arid soils. The influence of RH on K_p has generally not been considered in predictive methods except with polyparameter linear free energy relationships (pp-LFER, (Goss, 1997)), which considers all types of molecular interactions. Unfortunately, many input parameters needed for this method are not available for CUPs or are associated with large uncertainties (Davie-Martin et al., 2015; Götz et al., 2007). The new predictive K_p model proposed in this study and based on easily accessible parameters allows consideration of both meteorological variables (RH, T), compound-specific properties (K_{oa}, factor accounting for the polarity, p) and soil composition (f_{oc}).

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 θ_{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 S20-S23), nine pesticides had highest concentrations on particles <0.95 µm, four pesticides had highest concentrations in the >1.5 µm 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.

Particulate phase concentrations of ∑CUPs at the rural site ranged from 110 to 408 pg.m^{-3} and were higher than at the urban site (∑CUPs = 30.3 – 112 pg.m^{-3}). In contrast, similar concentrations were observed for ∑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 µm. 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 µm), which accounted for 43-63% and 50-91% of the total particulate phase mass, respectively. It is interesting to note that the size distribution of diuron, fenpropimorph and *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 µm 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 µm) in all seasons at both sites. Indeed, when the maximum total concentration occurred (i.e. in spring or summer), 45-70% of the total particulate phase mass of these compounds was on particles >3.0 µm. 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 (PPDB, 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). The lack of f_{om} data is a limitation in understanding the particle size distributions, however, we note that 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 and found three major differences than what is observed for OCPs. Firstly, regarding their seasonal variations, atmospheric concentrations of CUPs were largely driven by agricultural practices while secondary sources such as volatilization from surfaces governed atmospheric concentrations of OCPs. Secondly, clear differences were observed in gas-particle partitioning, with an influence of adsorption onto mineral surfaces for CUPs while OCPs were mainly partitioning to aerosols through absorption. Based on the recent work of Davie-Martin et al., (2015), a basic predictive method for K_p is proposed for polar and non-polar pesticides, which relies on easily accessible parameters. This method should be tested for other sampling sites and aerosol composition to determine its broader utility for polar pesticides in cases when parameters needed for pp-LFER are not available. Finally, while OCPs and the majority of CUPs were largely found on fine particles, four CUPs (carbendazim, isoproturon, prochloraz and terbuthylazine) had higher concentrations on coarse particles (>3.0 µm) which may be caused by the pesticide 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.

Supporting Information

Description of samples collected, analytical methods for CUPs and OCPs, usage of pesticides in the Czech Republic, Clausius-Clapeyron plots, description of calculation for predicted particulate fractions and atmospheric concentrations of individual CUPs and OCPs are provided.

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TABLE

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})
Acetochlor	H	Y	14	2.20E-05[c]	9.07[e]	50.0	ND-181	ND-158	ND-23.2	0.14 ± 0.32
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
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
Azinphos Methyl	I	N	10	5.00E-07[c]	8.76[f]	0.00	ND	ND	ND	ND
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
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
Chlorpyrifos	I	Y	50	1.43E-03[c]	8.41[h]	84.6	ND-159	ND-158	ND-9.43	0.037 ± 0.064
Diazinon	I	N	9.1	1.20E-02[c]	9.14[e]	1.92	ND-0.18	ND-0.18	ND	0.0
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
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
Disulfoton	I	N	30	7.20E-03[c]	8.07[d]	1.92	ND-2.22	ND	ND-2.22	1
Diuron	H	N	76	1.15E-06[c]	10.4[f]	32.7	ND-1.23	ND	ND-1.23	1.0 ± 0.00
Fenitrothion	I	N	2.7	6.76E-04[c]	7.72[d]	0.00	ND	ND	ND	ND
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
Fonofos	I	N	99	2.70E-02[c]	7.48[d]	5.76	ND-8.03	ND	ND-8.03	1.0 ± 0.00
Isoproturon	H	Y	12	5.50E-06[c]	11.2[g]	86.5	ND-413	ND-122	ND-291	0.84 ± 0.29
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
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
Metazachlor	H	Y	8.6	9.30E-05[c]	9.76[e]	86.5	ND-344	ND-262	ND-275	0.59 ± 0.38
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

Prochloraz	F	Y	120	1.50E-04[c]	13.6[d]	55.8	ND-1.95	ND	ND-1.95	1.0 ± 0.00
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
Simazine	H	N	60	8.10E-07[c]	9.59[g]	1.92	ND-0.087	ND	ND-0.087	1
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
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
Terbufos	I	N	8	3.46E-02[c]	7.49[d]	1.92	ND-0.80	ND	ND-0.61	1
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
∑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
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
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
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
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
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
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
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
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
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
∑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] (University of Hertfordshire, 2013). [d] (US EPA, 2014). [e] (Coscollà et al., 2013b). [f] (Coscollà et al., 2013a). [g] (Götz et al., 2007). [h] (Odabasi and Cetin, 2012b). [i] (Shoeib and Harner, 2002). [j] (Zhang et al., 2009).

FIGURES

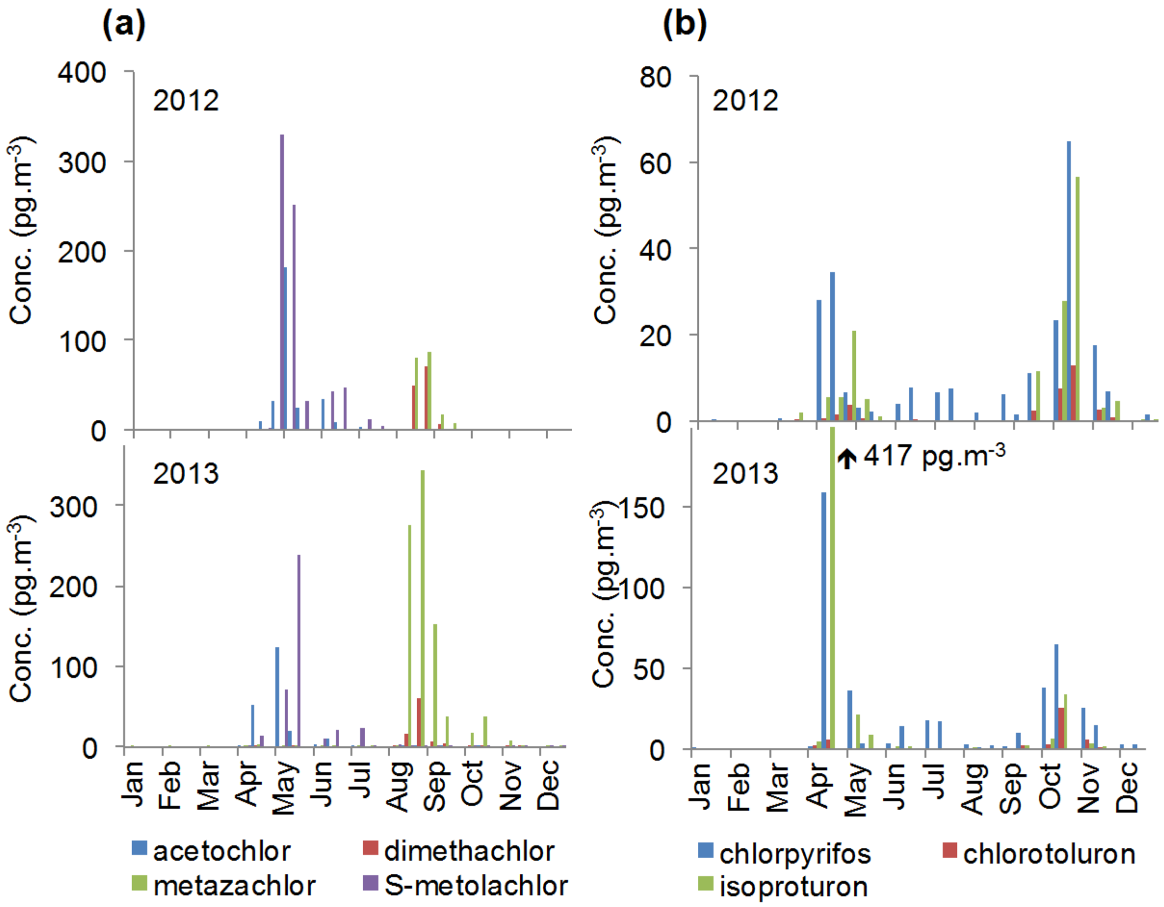

Figure 1: Seasonal variation of selected CUPs with (a) one peak per year during the growing season and (b) two peaks per year, in April-July and October-November

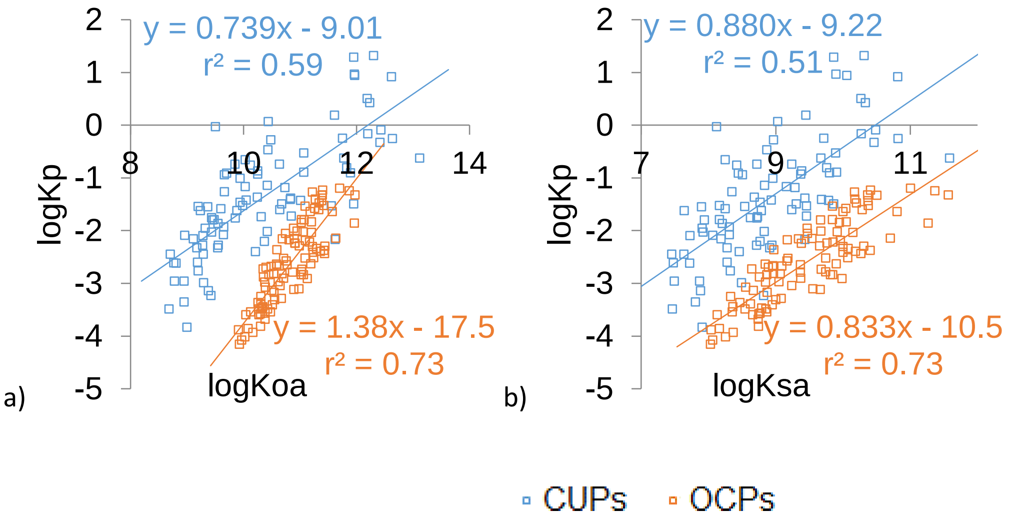

Figure 2: Comparison of logKp with logKoa (a) and with logKsa (b) for OCPs and CUPs

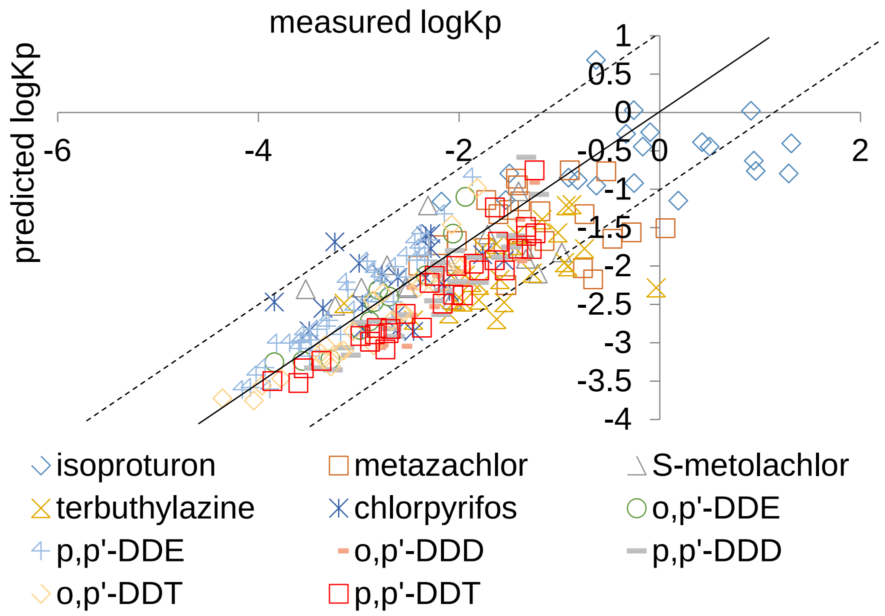

Figure 3: Comparison of predicted (see text, eq.3) and measured log K_p of individual OCPs and CUPs.

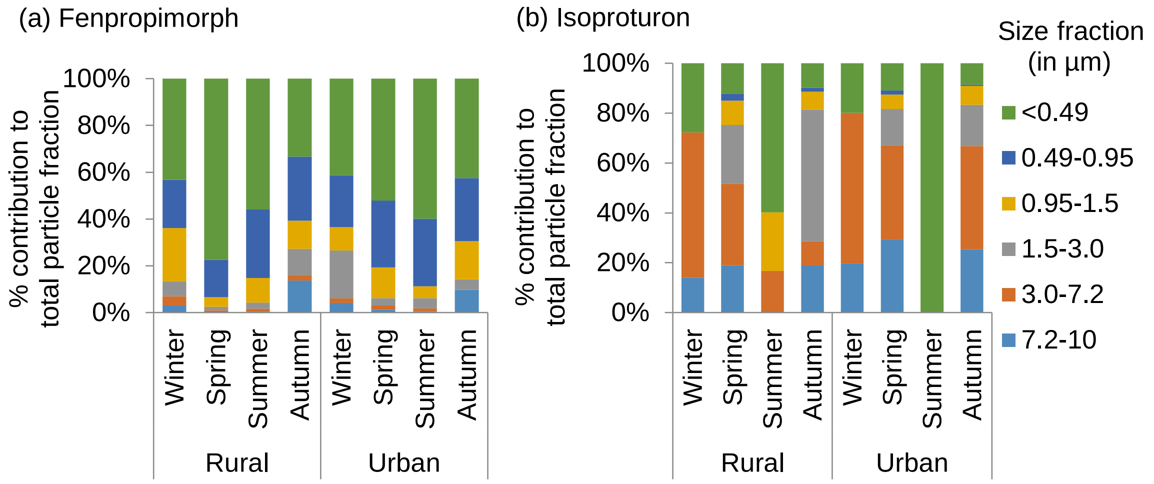

Figure 4: Seasonal particle size distribution of (a) fenpropimorph and (b) isoproturon at the rural and urban sites. Fenpropimorph represents the group of pesticides predominantly found on fine particles and isoproturon for the coarse particles

CAPTIONS

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