The following are the reviewer comments followed by the author response to each comment. Author responses are given in italics. The revised manuscript with all altered sections highlighted in yellow follows the response to the reviewer comments.

Reviewer #2:

General comments
Data on size distribution of CUPs are scarce. Results of size distribution of CUPs in this paper improve our understanding of the impact of CUPs on human health and also on the environmental fate of CUPs. Data of this work is in good quality. However, some data description or discussion parts are not attractive enough and purpose of few parts of the discussion is not clear, so I suggest to rephrase them (see details in the specific comments).

Specific comments
P2: The words 'certain compounds', 'other compounds', 'nine pesticides', 'four pesticides' make the abstract sounds like this paper only report data or phenomenon while there is a lack of an explanation of the data. I suggest to rephrase the sentence in a more attractive way.
P2 L16: I suggest to clearly state how is the "anomalous partitioning...suggesting the influence of current pesticide application on gas-particle distributions".
P2 L19: Generally, 'find particles' means PM2.5 (<2.5 μm). Fine particles can reach lung via breathing. Here, if health effect of the size distribution of pesticides is emphasized, it is better to choose 2.5μm as the cut point.

Author response: Thank you for the suggestions. Given the considerable improvement on the gas-particle partitioning section, we have considerably modified the abstract and improve the clarity.

Part of the abstract modified:
"Major differences were found in the atmospheric distribution of OCPs and CUPs. The atmospheric concentrations of CUPs were driven by agricultural practices while secondary sources such as volatilization from surfaces governed the atmospheric concentrations of OCPs. Moreover, clear differences were observed in gas-particle partitioning with an influence of adsorption onto mineral surfaces for CUPs while OCPs were mainly partitioning to aerosol through absorption. A predictive method for estimating the gas-particle partitioning has been derived 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 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. "

Regarding the suggestion of 2.5 μm as the cut point, unfortunately in this case we are limited by the instrument chosen. For the size specific determination, we used a Tisch Environmental cascade impactor, and cut points were 0.49

µm, 0.95 µm, 1.5 µm, 3.0 µm, 7.2 µm and 10 µm. This provides us with a lot of information on the particle size distribution of the pesticides, but does not allow us to distinguish exactly at the 2.5 µm cut point.

P3 L14: "Finally, pesticides can volatilize from soils, plants and from old industrial sites." Volatilization from water bodies (e.g. ocean, lake) should be included. Actually, that means volatilization of pesticides happen during all kinds of air-surface exchange of pesticides.
Author response: We have corrected this. The text now reads: "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)."

P5 L1: For study of gas/particle partitioning, why collect PM10 but not total suspended particles (TSP)?

Author response: To study gas-particle partitioning, we were limited by the high-volume air sampler from the on-going air monitoring programme, which had a cut off of 10 µm. However, at typical Central European rural sites, the majority of TSP by mass is captured within the PM10 category (e.g., 90-91%, from Gomišček et al., 2004, Atmospheric Environment), and so we believe this does not significantly bias the results.

P7 L20: what does "timing" mean? The seasonality of detection frequency?

Author response: We have clarified this. The sentence now reads "In general, the detection frequency of CUPs […] (Table 1)."

P7 L21: "their persistence in the environment". But this section "3.1 Detection frequency at the background site" don't discussed the relation between detection frequency and the persistence of pesticides.

Author response: This section does not discuss the persistence of individual compounds but the detection frequency brings information relevant to environmental persistence. For example, CUPs which were not in use (e.g. fenitrothion, simazine and terbufos) were not detected or infrequently detected (<6%), suggesting less environmental persistence, in contrast to all OCPs, which were detected in more than half of the samples although they have been banned for decades, demonstrating their high persistence.

P9 L8-23: I am not clear this part of discussion is for explanation of which part of the data.

Author response: We agree with the reviewer that the logical flow of the discussion was not clear, and have adjusted accordingly. These sentences have been replaced with the following text:

"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."

P10: "3.3 Seasonal variations at the background site". Do the seasonal variations of pesticide concentration relating with air masses from different regions in different seasons? How about evaluating the air mass back trajectories (e.g. with the open software HYSPLIT).

Author response: We appreciate the suggestion. We investigated whether HYSPLIT would provide us with greater insight into the seasonal variations, but unfortunately the wind directions/back-trajectories do not provide additional information. On a local scale, the land-use surrounding the background site is agricultural in all directions in ~50 km radius of the site. Therefore, a back-trajectory in any direction would pass over many km^2 of agricultural fields, and no direction would clearly dominate as a source of emissions over any other. Similarly, on a larger scale, no clear source region is apparent; Central Europe is dominated by agricultural land use (Czech Republic is 55% agricultural land, and other countries in the region are also highly agricultural (Germany – 48%, Poland – 48%, Slovakia – 40%, Austria – 38%, Hungary – 60%; data from World Bank database - http://data.worldbank.org/). So, for this particular area, back trajectories do not help significantly in interpretation of seasonal variations.

Reviewer #3:

Review of "Pesticides in the atmosphere: a comparison of gas-particle partitioning and particle size distribution of legacy and current-use pesticides"
This manuscript reports a novel data set on the occurrence, gas-particle partitioning and size distribution of a number of pesticides. This is already a nice contribution.
On the other hand, there is some discussion on the processes driving this occurrence and partitioning, but my impression is that this side of the manuscript lacks of novelty, and does not make a great contribution. In any case, as the data set seems to be of good quality (and it is novel) I suggest

that this manuscript can be published after some modifications in the discussion.

Specific comments:
- Gas-particle partitioning is thought to be a fast process (fast response times to equilibration). I doubt that concurrent emissions lead to lack of equilibrium between gas and particle.

Author response: We agree with the reviewer that equilibrium between gaseous and particulate phases is generally a fast process (although for compounds with logKoa>10 such as PBDEs, previous research have pointed out that G/P equilibrium may not have been reached months after emissions, see Cetin and Odabasi, 2008, Chemosphere and Li et al., 2015, ACP). We have now considerably modified the section on gas-particle partitioning.

- Page 23653, line 13-15. These two statements need a citation or two.

Author response: We have now included two citations related with those statements (Glotfelty et al., 1989 and Cabrerizo et al., 2011).

- Page 23653-line 21. In addition to Pankow 1987, other papers have contributed to substantiate this statement.

Author response: We have now added the references to two reviews about gas-particle partitioning by Cousins and Mackay, 2001 and by Lohmann and Lammel, 2004.

- Page 23655, line2. The average sample volume was above 4000 m3, which it looks too much for a temperate region. I wonder about the breakthrough of some of the compounds. This potential artifact should be evaluated before the assessment of gasparticle partitioning. Looking at tables S6 and S7, it seems that potential breakthrough is observed for HCHs, metribuzin, isoproturon, and few others. The nice fact, is that the breakthrough has been evaluated for each sample, and therefore, when it is detected, my impression is that those particular samples should not be used for assessment of gas-particle partitioning.

Author response: The breakthrough experiments took place only in 2012 for 26 samples for both OCPs and CUPs. In 2013, the two PUFs were analyzed together. So unfortunately we cannot use this information to exclude particular samples from the overall dataset. Based on this breakthrough experiment, several CUPs were previously removed from the results. We appreciate the suggestion regarding HCHs and metribuzin, and agree that since breakthrough happened in some cases and that these compounds were infrequently detected (in the particulate phase or in general), we removed them from the section on gas-particle partitioning. In case of isoproturon, this compound was detected in 13 samples in the upper PUF and only once in the

lower PUF. Thus, the breakthrough of isoproturon seems to be minor and the sampling procedure with 2 PUFs and such high volume is considered appropriate for trapping this compound in the gaseous phase. The manuscript now includes:

"It has been 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)."

- Page 23661. I guess that recent application and surface-air exchange are important processes for explaining the atmospheric occurrence of OCP (Cabrerizo et al. ACP 2011) and CUPs. For CUPs, it is possible that a relevant fraction of them is degradaed after weeks/months of application, which would explain a lack of maximum values for the time periods with higher temperatures.

Author response: We have now added the reference to the study from Cabrerizo et al. We also added a statement about the rapid atmospheric degradation of some CUPs.
The manuscript now includes "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)." and "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."

- For many CUPs there is no previous literature on volatilization and gas-particle partitioning, but for some CUPs and especially HCHs and DDTs the literature is abundant and should be cited and discussed. Alternatively, there are studies on soil-air partitioning of pesticides (for example the recent Davie-Martin EST 2015) that could be temptatively used for assessing gas-particle partitioning.

Author response: Thank you for the interesting suggestion. As a consequence, we have now significantly modified the section on gas-particle partitioning. These changes are highlighted in the proposed revised manuscript which is currently included as a supplement. Indeed, we plotted logKp vs. logKoa and logKsa and found significant correlations for both OCPs

and CUPs. However, major differences were observed for CUPs, with a higher Kp for similar Koa, revealing the influence of adsorptive contributions to Kp. The predicted soil-air partitioning coefficient derived by Davie-Martin et al; (2015) was found to be a really good predictor of gas-particle partitioning of pesticides.

- Figure 2 and 3. The aerosol type may be different for different seasons, thus different OC type, leading to different partitioning. In addition there is an important uncertainty on the KOA temperature dependence. I doubt that these plots can be used to say anything about lack of equilibrium.

Author response: We have now moved these figures into the SI.

- I would appreciate to see a Kp versus Koa plot for the different compounds and sampling events.

Author response: We have now included different figures of Kp vs Koa and Ksa for all samples, and also for spring and autumn.

- The manuscript makes a contribution with a novel dataset. The size distribution work is also a nice contribution. However, I think that the gas-particle partitioning assessment should be significantly improved in order to make a clear contribution to the field.

Author response: We appreciate the suggestion and believe the addition of the comparison with Ksa, and more thorough discussion of the important factors in CUP partitioning has helped to significantly improve the discussion of gas-particle partitioning (section 3.4).

Reviewer #4:
This manuscript reported measurements for selected OCP and CUPs in air at two atmospheric monitoring stations in Czech Republic. The novelty of this work is several current used pesticides have been detected in certain atmospheric samples. As for the part of gas-particle partitioning of OCPs and CUPs, I am doubt if the air sampling method used in this work is applicable to fulfill this proposal. As it is described in the manuscript, a high-volume air sampler was used to collect weekly air sample, with an average of 4310 m3. It is well known that there are several weaknesses to use highvolume air sampler for the determination of gas/particle partitioning for semi-volatile organic compounds. First, fine particles less than the pore size of the QFF may penetrate the filter and part of them can be caught by the PUF. Second, with 7 days sampling time, particle-bound OCPs or CUPs may happen with desorption and enter into gaseous phase. These aspects may lead overestimated gaseous concentrations for both OCPs and CUPs. Especially for the polar CUPs, their occurrence in the gaseous phase might be just

caused by the fine particles caught by PUF slice. Therefore, such samples can only provide a sum concentration of OCPs and CUPs in the atmosphere, and are not efficient for evaluation of gas/particle partitioning process at all. Moreover, as the authors intended to compare the gas-particle partitioning of and size distributions of both OCPs and CUPs, the factors, e.g. the fraction of total organic carbon in the particles and humidity of air which could affect the partitioning process of OCPs and CUPs should be included in the study as well. However, there are no such data available to support the dada analysis. Furthermore, there are many studies have been published for OCPs in rural atmosphere, and some CUPs have been included as well. As the CUPs have relatively high polarity, their gas/particle partitioning behaviors may differ to the legacy OCPs, and should be highlighted in the discussion of the manuscript However, this issue is not presented in the manuscript.
Overall, it seems that the entire work such as sampling method and sample analysis have not been systematical organized that the measurements of this work could not support a reliable evaluation for seasonal gas/particle partitioning and size distribution of CUPs. I guess this manuscript is hard to be accepted for publication in ACP.

Author response: We appreciate the reviewers concerns regarding the sampling method, but we disagree that high volume air sampling is inappropriate to characterize gas-particle partitioning.
Any air sampling method is susceptible to sampling artifacts based on the design of the sampler and choice of sampling media, and it is true that to some extent, the discussion of gas-particle partitioning is operationally defined based on where the cut-off between gaseous and particulate phase is chosen. However, these inherent challenges in air sampling should not preclude us from attempting to infer information from air sampling, assuming appropriate actions are taken to reduce sampling artifacts as much as possible.
High volume air samplers are an extremely commonly used method to determine gas- and particle-phase concentrations (for example, Sauret et al. 2008, Atmos. Env.; Yang et al. 2013, ES&T; Lohmann et al. 2000, ES&T; sites in the EMEP monitoring network; sites in the North American Integrated Atmospheric Deposition Network (IADN) - e.g., Venier and Hites, 2008)
While several sampling artefacts (blow on, blow off, breakthrough, degradation) may occur during sampling, the influence of blow on and blow offs is small relative to the influence of environmental factors such as temperature (Melymuk et al; in press, Environmental Pollution). Breakthrough is considered as the major sampling artifact that could severely affects the results about gas-particle partitioning. The extent of breakthrough has been assessed in this study (Tables S6-7) and several CUPs were removed from the list of compounds. Based on the suggestions of Reviewer #3, we now also decided to exclude also all HCHs from the discussion on gas-particle partitioning due to concerns about breakthrough. Therefore, given these considerations and the fact that high volume sampling techniques are widely used, we consider the gas and particulate concentrations reported in this study as valid.
Regarding the section on gas-particle partitioning, based on the reviewer suggestions (reviewers 3&4) major modifications have been made to section 3.4. These changes are highlighted in the revised manuscript which is

currently included as a supplement. We now more concisely investigated the relationship between logKp and logKoa and logKsa (the soil-air partitioning coefficient) and major differences were found for OCPs and CUPs, suggesting the influence of adsorptive contributions to Kp for CUPs.

Specific comments
Title “Pesticides in the atmosphere: a comparison of gas-particle partitioning and particle size distribution of legacy and current-use pesticides”
There are only limited OCPs and CUPs studied in this work, it is not appropriate to use such title.

Author response: The title is informative as required by ACP. Indeed, there are only limited OCPs and CUPs investigated in this study but the key goal of a title is to be wide enough such that it will attract many readers from different disciplines while remaining informative about the nature of the work. We believe that this title fulfill both purposes.

Abstract: It is hard to understand the important findings of this work when I read the abstract. For example “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”, this statement is suitable for most organic chemicals including organic pesticides, should be not a major finding of this study.

Author response: We agree with the reviewer that this part of the abstract could apply to many organics, including polar pesticides. Given the new findings, we have now considerably changed the abstract:

“Major differences were found in the atmospheric distribution of OCPs and CUPs. The atmospheric concentrations of CUPs were driven by agricultural practices while secondary sources such as volatilization from surfaces governed the atmospheric concentrations of OCPs. Moreover, clear differences were observed in gas-particle partitioning with an influence of adsorption onto mineral surfaces for CUPs while OCPs were mainly partitioning to aerosol through absorption. A predictive method for estimating the gas-particle partitioning has been derived 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 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. “

P23653, L5, “and the relative lack of information regarding their toxic effects” Are you sure there are lack information for toxic effects of CUPs? Which CUP do you mean?

Author response: For many CUPs, there are available information about the acute effects related with pesticides but this is limited concerning the chronic effects linked with a lifetime exposure (e.g agricultural workers). Moreover, in case of chlorpyrifos which has been widely studied, the European Food Safety Authority listed several points which were not available in order to assess the human health risk of this compound (e.g. dermal absorption data for different formulations, standard hydrolysis study; http://www.efsa.europa.eu/sites/default/files/scientific_output/files/main_documents/3640.pdf). Additional discussion about these gaps can be found in Bányiová et al; 2015 (Environmental Science and Pollution Research) and 2016 (Chemosphere).

P23654, L5, “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” if gas-particle partitioning and particle size distribution are the major objectives of this study, the characters of the particle itself should be examined as well, e.g. TOC and organic matter fraction on PM10 and grain size of particles, and origin of the particles.

Author response: We agree with the reviewer that it would have been ideal to know the characters of the particles. Unfortunately, at the time of sampling and analysis, it was not possible to measure those parameters. Regarding the importance of knowing f_{OM} for the analysis of pesticide size distribution, we would like to argue that we observed distinct differences for different pesticides for the same samples, so with the same f_{OM}. However, we acknowledge this as an uncertainty in the discussion, and mention this in the manuscript.

Air sampling
P23655, L3, what is the pore size of QM-A?

Author response: We apologize for omitting this information from the manuscript. The pore size of QM-A is 2.2 µm and it is now included in the manuscript.

I am wondering, if it is necessary to collect 7-days, 4310 m3 for each air sample. I do not think it is so hard to determine the OCPs and CUPs selected in this study with 500 or 1000 m3 air. When the authors intend to estimate gas/particle partitioning, you do need consider about breakthrough of both particle-bound and gases chemicals, and degradation as well.

Author response: It may not be necessary to collect 7 days or 4310m3 for every compound, but in some cases, these large volumes were enough to detect some CUPs but insufficient for quantification (<LOQ; Tables S12-S13), indicating in this study the large sample volumes were useful, particularly for the CUPs. It is true that larger volume or sampling time are associated with potential higher sampling artefacts. However, as mentioned earlier, blow on and blow off were considered to have minor effects and gas-phase breakthrough was considered (Tables S6 and S7) and several CUPs were removed from the analysis as they were experiencing breakthrough. We now include these sources of uncertainties at the beginning of the section on gas-particle partitioning. The manuscript now includes: "It has been 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)."

P23657, In the section "results and discussion", it is not necessary to emphases "Detection frequency at the background site".

Author response: We believe that this section is needed as it provides information about the persistence of OCPs in the environment (i.e. all OCPs were detected in >50% of the samples) while highlighting the different CUPs that were highly detected and will be further discussed in the next sections.

P23660, L8-13, there are many other studies for CUPs in rural air, you may compare with literature data if you like.

Author response: Thank you for the suggestion. We have now added a Table in the SI reporting comparisons with concentrations of individual OCPs and CUPs at different sites, and a reference to these studies in the manuscript text.

P23660, "Seasonal variations at the background site", you may use air mass back trajectories to figure out possible origin for high concentrations of OCPs and CUPs determined in this work. At least, the authors should not always simply address the high concentrations to certain application of pesticides around the sampling site. A statistics analysis may be helpful as well.

Author response: As we have described in the response to reviewer #1, examination of the wind directions/back-trajectories does not provide additional information, as the land-use surrounding the background site is agricultural in all directions in ~50 km radius of the site. Therefore, a back-trajectory in any direction would pass over many km^2 of agricultural fields, and no direction would clearly dominate as a source of emissions over any other. Similarly, on a larger scale, no clear source region is apparent; Central Europe is dominated by agricultural land use (Czech Republic is 55% agricultural land, and other countries in the region are also highly agricultural (Germany – 48%, Poland – 48%, Slovakia – 40%, Austria – 38%, Hungary – 60%; data from World Bank database - http://data.worldbank.org/)
The reason of attributing the higher CUP concentrations to direct application around the sampling site is that many of these CUPs have a short atmospheric lifetime and thus are unlikely to be associated with long-range transport. For example, the lifetime of chlorpyrifos in relation with OH reaction is about 2 h (Muñoz et al., 2014).

P23663, L17-26, this paragraph should be move to introduction.

Author response: Thank you for the recommendation. We have now moved this paragraph to the introduction.

For the section “Gas-particle partitioning at the background site”, there are many studies for Gas-particle partitioning of OCPs, which can be refered and compared with this work.

Author response: Thank you for the recommendation. We have now compared our results for OCPs with previous studies.

The following pages contain the revised manuscript with all changes marked in yellow.

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):

$$\ln P = \frac{m}{T} + b \quad \text{(Eq. 1)}$$

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 (θ_{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 θ_{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 logK_{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, Figure 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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References

Bidleman, T.F., Billings, W.N., Foreman, W.T., 1986. Vapor-particle partitioning of semivolatile organic compounds: estimates from field collections. Environ. Sci. Technol. 20, 1038–43.

1 Bogdal, C., Scheringer, M., Abad, E., Abalos, M., van Bavel, B., Hagberg, J., Fiedler, H.,
2 2013. Worldwide distribution of persistent organic pollutants in air, including results of
3 air monitoring by passive air sampling in five continents. TrAC Trends Anal. Chem. 46,
4 150–161. doi:10.1016/j.trac.2012.05.011

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

9 Cabrerizo, A., Dachs, J., Jones, K.C., Barceló, D., 2011. Soil-Air exchange controls on
10 background atmospheric concentrations of organochlorine pesticides. Atmos. Chem.
11 Phys. 11, 12799–12811. doi:10.5194/acp-11-12799-2011

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

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

18 Coscollà, C., Castillo, M., Pastor, A., Yusa, V., 2011. Determination of 40 currently used
19 pesticides in airborne particulate matter (PM 10) by microwave-assisted extraction and
20 gas chromatography coupled to triple quadrupole mass spectrometry. Anal. Chim. Acta
21 693, 72–81. doi:10.1016/j.aca.2011.03.017

22 Coscollà, C., Hart, E., Pastor, A., Yusà, V., 2013a. LC-MS characterization of contemporary
23 pesticides in PM10 of Valencia Region, Spain. Atmos. Environ. 77, 394–403.
24 doi:http://dx.doi.org/10.1016/j.atmosenv.2013.05.022

25 Coscollà, C., Munoz, A., Borras, E., Vera, T., Rodenas, M., Yusa, V., 2014. Particle size
26 distributions of currently used pesticides in ambient air of an agricultural Mediterranean
27 area. Atmos. Environ. 95, 29–35. doi:10.1016/j.atmosenv.2014.06.022

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

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

36 Cousins, I.T., Mackay, D., 2001. Gas--particle partitioning of organic compounds and its
37 interpretation using relative solubilities. Environ. Sci. Technol. 35, 643–647.
38 doi:10.1021/es001123m

1 Davie-Martin, C.L., Hageman, K.J., Chin, Y.-P., Rougé, V., Fujita, Y., 2015. Influence of
2 temperature, relative humidity, and soil properties on the soil–air partitioning of
3 semivolatile pesticides: Laboratory measurements and predictive models. Environ. Sci.
4 Technol. 49, 10431–10439. doi:10.1021/acs.est.5b02525

5 Degrendele, C., Okonski, K., Melymuk, L., Landlová, L., Kukučka, P., Čupr, P., Klánová, J.,
6 2014. Size specific distribution of the atmospheric particulate PCDD/Fs, dl-PCBs and
7 PAHs on a seasonal scale: Implications for cancer risks from inhalation. Atmos. Environ.
8 98, 410–416. doi:http://dx.doi.org/10.1016/j.atmosenv.2014.09.001

9 Dubus, I.G., Hollis, J.M., Brown, C.D., 2000. Pesticides in rainfall in Europe. Environ. Pollut.
10 110, 331–344. doi:10.1016/S0269-7491(99)00295-X

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

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

15 European Commission - Health & Consumer Protection Directorate-General, 2003. Review
16 report for the active substance atrazine [WWW Document].

17 FOCUS, 2008. Pesticides in Air: Considerations for Exposure Assessment. Rep. Focus Work.
18 Gr. Pestic. Air (FOCUS Air Group).

19 Garthwaite, D.G., Hudson, S., Barker, I., Parrish, G., Smith, L., Pietravalle, S., 2014.
20 Pesticide usage survey report 250. Arable crops in the United Kingdom 2012 (including
21 aerial applications 2012). Department for Environment, Food & Rural Affairs.

22 Gil, Y., Sinfort, C., 2005. Emission of pesticides to the air during sprayer application: A
23 bibliographic review. Atmos. Environ. 39, 5183–5193.
24 doi:http://dx.doi.org/10.1016/j.atmosenv.2005.05.019

25 Glotfelty, D.E., Leech, M.M., Jersey, J., Taylor, A.W., 1989. Volatilization and Wind Erosion
26 of Soil Surface Applied Atrazine ,. J. Agric. Food Chem. 546–551.

27 Goss, K.-U., 1997. Conceptual Model for the Adsorption of Organic Compounds from the
28 Gas Phase to Liquid and Solid Surfaces. Envir Sci Technol 31, 3600–3605.
29 doi:10.1021/es970361n

30 Goss, K.U., Buschmann, J., Schwarzenbach, R., 2004. Adsorption of organic vapors to air-dry
31 soils: model predictions and experimental validation. Environ. Sci. Technol. 38, 3667–
32 3673.

33 Götz, C.W., Scheringer, M., MacLeod, M., Roth, C.M., Hungerbühler, K., 2007. Alternative
34 Approaches for Modeling Gas−Particle Partitioning of Semivolatile Organic Chemicals:
35 Model Development and Comparison. Environ. Sci. Technol. 41, 1272–1278.
36 doi:10.1021/es060583y

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

Halse, a. K., Schlabach, M., Eckhardt, S., Sweetman, a., Jones, K.C., Breivik, K., 2011. Spatial variability of POPs in European background air. Atmos. Chem. Phys. 11, 1549–1564. doi:10.5194/acp-11-1549-2011

Hayward, S.J., Gouin, T., Wania, F., 2010. Levels and Seasonal Variability of Pesticides in the Rural Atmosphere of Southern Ontario. J. Agric. Food Chem. 58, 1077–1084. doi:10.1021/jf902898f

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

Holoubek, I., Dušek, L., Sáňka, M., Hofman, J., Čupr, P., Jarkovský, J., Zbíral, J., Klánová, J., 2009. Soil burdens of persistent organic pollutants - Their levels, fate and risk. Part I. Variation of concentration ranges according to different soil uses and locations. Environ. Pollut. 157, 3207–3217. doi:10.1016/j.envpol.2009.05.031

Holoubek, I., Klánová, J., Jarkovský, J., Kohoutek, J., 2007. 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.

Kannan, K., Ridal, J., Struger, J., 2006. Pesticides in the Great Lakes, in: Hites, R. (Ed.), Persistent Organic Pollutants in the Great Lakes, The Handbook of Environmental Chemistry. Springer Berlin Heidelberg, pp. 151–199. doi:10.1007/698_5_041

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

Lammel, G., Klánová, J., Kohoutek, J., Prokeš, R., Ries, L., Stohl, A., 2009. 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

Lee, R.G.M., Burnett, V., Harner, T., Jones, K.C., 2000. 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

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

Li, J., Zhang, G., Guo, L., Xu, W., Li, X., Lee, C.S.L., Ding, A., Wang, T., 2007. 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

Li, Y.F., Macdonald, R.W., 2005. 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:http://dx.doi.org/10.1016/j.scitotenv.2004.12.027

Lohmann, R., Klanova, J., Kukucka, P., Yonis, S., Bollinger, K., 2012. 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

Lohmann, R., Lammel, G., 2004. Adsorptive and absorptive contributions to the gas-particle partitioning of polycyclic aromatic hydrocarbons: State of knowledge and recommended parametrization for modeling. Environ. Sci. Technol. 38, 3793–3803. doi:10.1021/es035337q

Mackay, D., 2001. Multimedia Environmental Models The Fugacity Approach Second Edition, Second Edi. ed. Lewis.

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

Majewski, M.S., Coupe, R.H., Foreman, W.T., Capel, P.D., 2014. Pesticides in Mississippi air and rain: A comparison between 1995 and 2007. Environ. Toxicol. Chem. 33, 1283–1293. doi:10.1002/etc.2550

Melymuk, L., Bohlin, P., Sáňka, O., Pozo, K., Klánová, J., 2014. Current challenges in air sampling of semi-volatile organic contaminants: sampling artifacts and their influence on data comparability. Environ. Sci. Technol. doi:10.1021/es502164r

Melymuk, L., Bohlin-Nizzetto, P., Prokeš, R., Kukučka, P., Klánová, J., n.d. Sampling artifacts in active air sampling of semivolatile organic contaminants: Comparing theoretical and measured artifacts and evaluating implications for monitoring networks. Environ. Pollut. doi:doi:10.1016/j.envpol.2015.12.015

Muñoz, A., Ródenas, M., Borrás, E., Vázquez, M., Vera, T., 2014. The gas-phase degradation of chlorpyrifos and chlorpyrifos-oxon towards OH radical under atmospheric conditions. Chemosphere 111, 522–528. doi:10.1016/j.chemosphere.2014.04.087

Odabasi, M., Cetin, B., 2012a. Determination of octanol-air partition coefficients of organochlorine pesticides (OCPs) as a function of temperature: Application to air-soil exchange. J. Environ. Manage. 113, 432–439. doi:10.1016/j.jenvman.2012.10.010

Odabasi, M., Cetin, B., 2012b. 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.

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

Pankow, J.F., 1987. 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:http://dx.doi.org/10.1016/0004-6981(87)90363-5

Peck, A.M., Hornbuckle, K.C., 2005. Gas-Phase Concentrations of Current-Use Pesticides in Iowa. Environ. Sci. Technol. 39, 2952–2959. doi:10.1021/es0486418

PPDB, 2013. The Pesticide Properties DataBase (PPDB) [WWW Document]. Dev. by Agric. Environ. Res. Unit (AERU), Univ. Hertfordshire, 2006-2013.

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., Brink, H. ten, Tørseth, K., Wiedensohler, A., 2004. 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:http://dx.doi.org/10.1016/j.atmosenv.2004.01.041

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

Sadiki, M., Poissant, L., 2008. 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:http://dx.doi.org/10.1016/j.atmosenv.2008.07.041

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

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

Sauret, N., Wortham, H., Putaud, J.-P., Mirabel, P., 2008. 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:http://dx.doi.org/10.1016/j.atmosenv.2007.09.012

Scheyer, A., Morville, S., Mirabel, P., Millet, M., 2008. 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:http://dx.doi.org/10.1016/j.atmosenv.2008.05.029

Schummer, C., Mothiron, E., Appenzeller, B.M.R., Rizet, A.-L., Wennig, R., Millet, M., 2010. Temporal variations of concentrations of currently used pesticides in the atmosphere of Strasbourg, France. Environ. Pollut. 158, 576–584. doi:http://dx.doi.org/10.1016/j.envpol.2009.08.019

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

Shoeib, M., Harner, T., 2002. 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

Sofuoglu, A., Cetin, E., Bozacioglu, S.S., Sener, G.D., Odabasi, M., 2004. 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

Solomon, K.R., Williams, W.M., Mackay, D., Purdy, J., Giddings, J., Giesy, J., 2014. Properties and Uses of Chlorpyrifos in the United States, in: Giesy, J.P., Solomon, K.R. (Eds.), Ecological Risk Assessment for Chlorpyrifos in Terrestrial and Aquatic Systems in the United States, Reviews of Environmental Contamination and Toxicology. Springer International Publishing, pp. 13–34. doi:10.1007/978-3-319-03865-0_2

SRS, 2014. State Phytosanitary Administration. Usage of active substances in 2013, Czech Republic. http://eagri.cz/public/web/file/439536/celek_2013_EN.pdf.

SRS, 2013. State Phytosanitary Administration. Usage of active substances in 2012, Czech Republic. http://eagri.cz/public/web/file/439598/celek_2012_EN.pdf.

U.S. Environmental Protection Agency, 2013. Atrazine Updates [WWW Document]. Pestic. Reregistration.

University of Hertfordshire, 2013. The Pesticide Properties DataBase (PPDB) [WWW Document]. Dev. by Agric. Environ. Res. Unit (AERU), Univ. Hertfordshire, 2006-2013.

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

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

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

Vecchi, R., Marcazzan, G., Valli, G., 2007. A study on nighttime-daytime PM10 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

Wang, X.P., Sheng, J.J., Gong, P., Xue, Y.G., Yao, T.D., Jones, K.C., 2012. Persistent organic pollutants in the Tibetan surface soil: Spatial distribution, air-soil exchange and implications for global cycling. Environ. Pollut. 170, 145–151. doi:10.1016/j.envpol.2012.06.012

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

Wei, Y.L., Bao, L.J., Wu, C.C., He, Z.C., Zeng, E.Y., 2014. Association of soil polycyclic aromatic hydrocarbon levels and anthropogenic impacts in a rapidly urbanizing region: Spatial distribution, soil-air exchange and ecological risk. Sci. Total Environ. 473-474, 676–684. doi:10.1016/j.scitotenv.2013.12.106

Yadav, I.C., Devi, N.L., Syed, J.H., Cheng, Z., Li, J., Zhang, G., Jones, K.C., 2015. Current status of persistent organic pesticides residues in air, water, and soil, and their possible effect on neighboring countries: A comprehensive review of India. Sci. Total Environ. 511, 123–137. doi:10.1016/j.scitotenv.2014.12.041

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

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

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

Zhang, X.M., Meyer, T., Muir, D.C.G., Teixeira, C., Wang, X.W., Wania, F., 2013. 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

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)	logK_{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

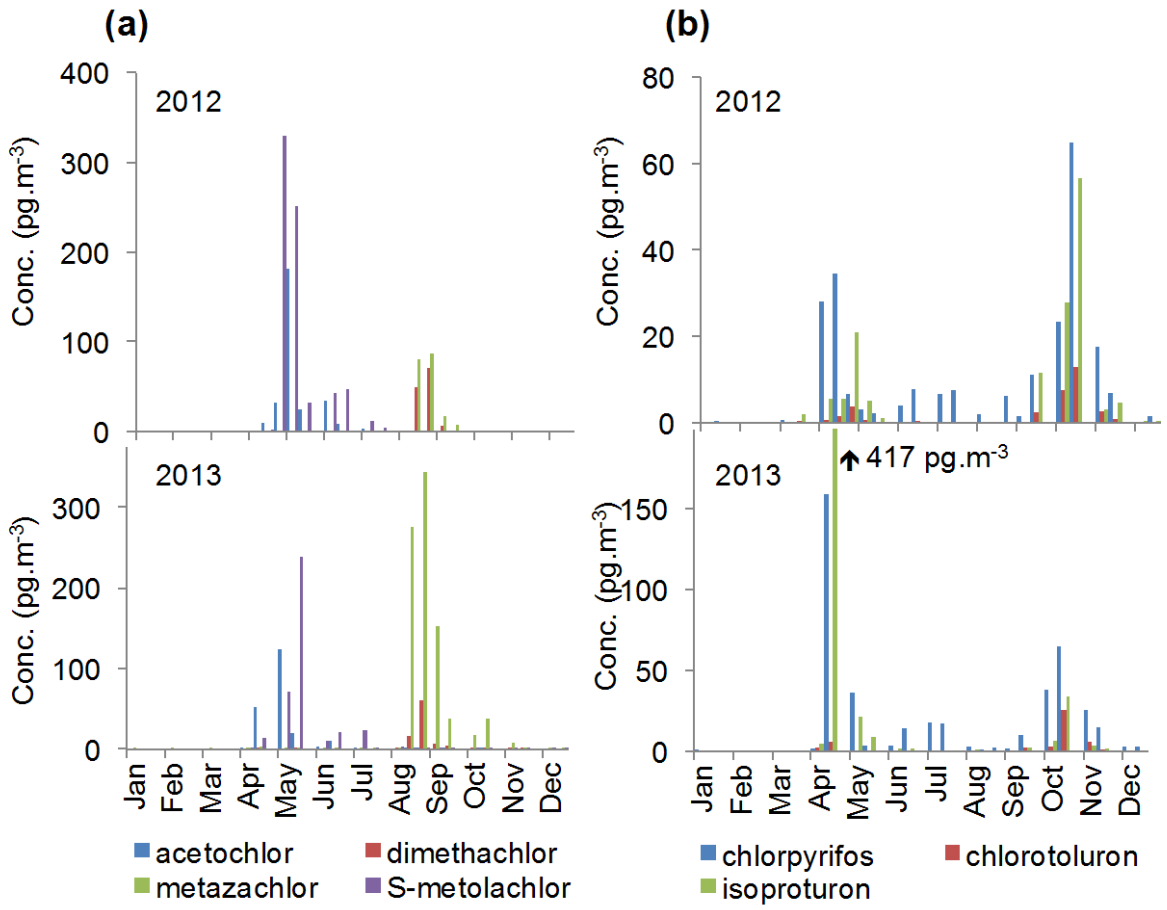

Figure 1: Seasonal variation of selected CUPs with (a) one peak per year during the growing season and (b) two peaks per year, in April-July and October-November

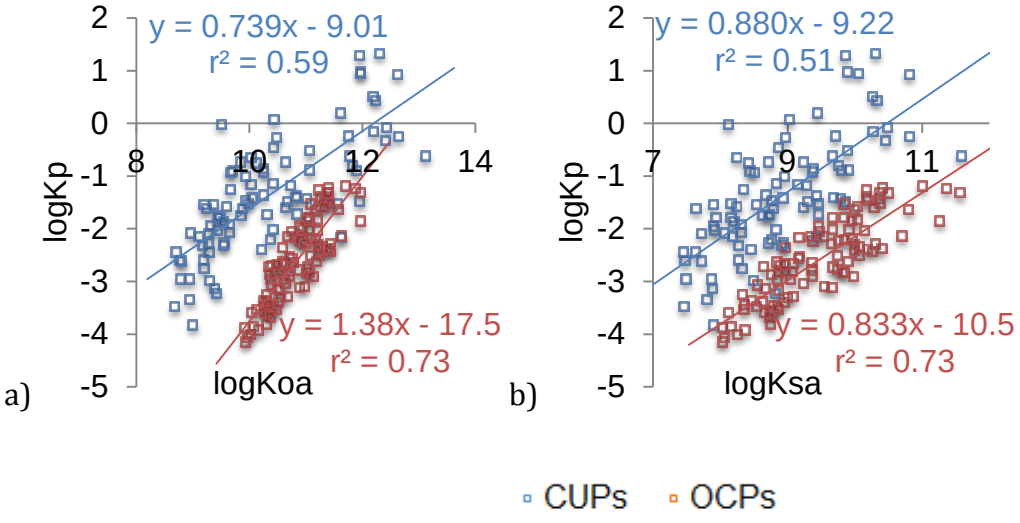

Figure 2: Comparison of logKp with logKoa (a) and with logKsa (b) for OCPs and CUPs

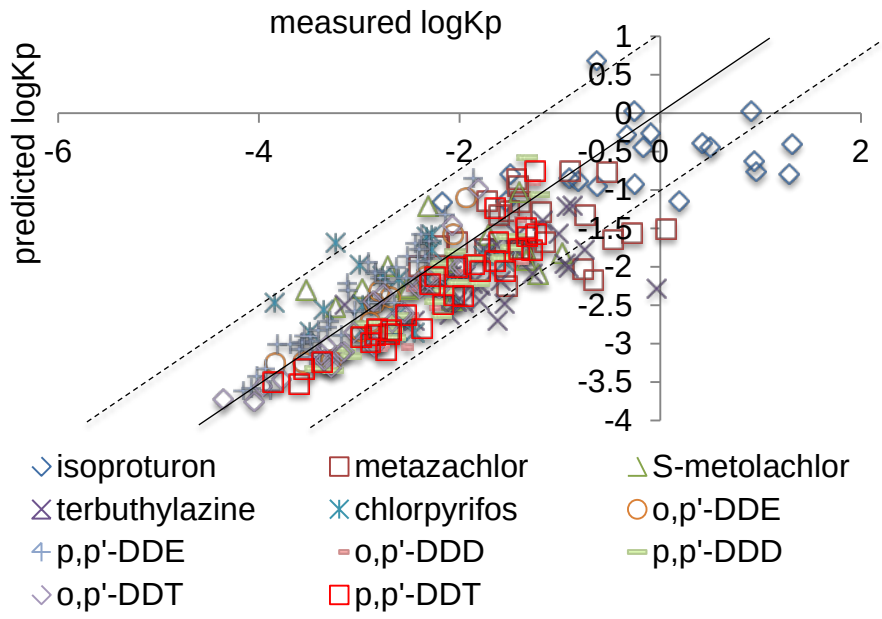

Figure 3: Comparison of predicted (see text, eq.3) and measured log K_p of individual OCPs and CUPs.

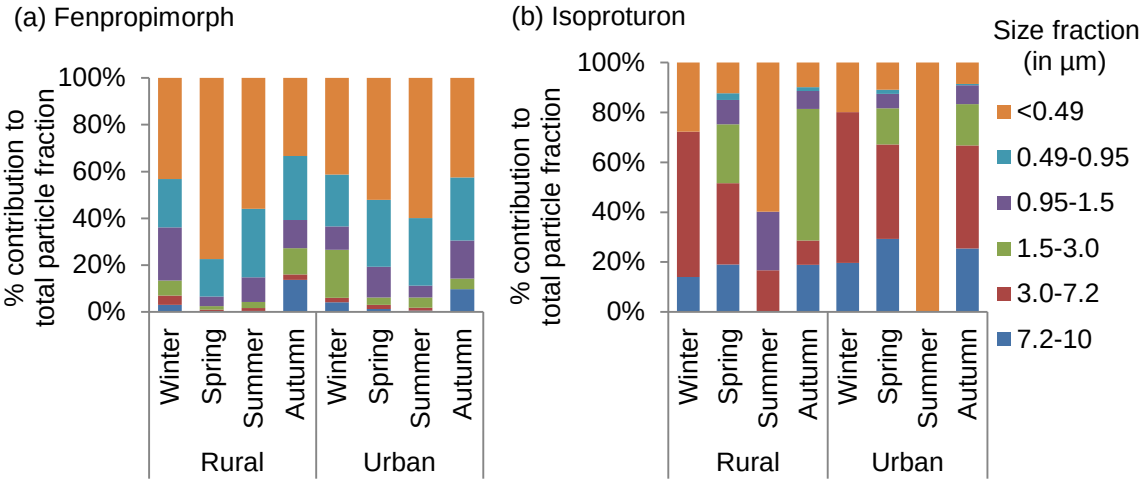

Figure 4: Seasonal particle size distribution of (a) fenpropimorph and (b) isoproturon at the rural and urban sites. Fenpropimorph represents the group of pesticides predominantly found on fine particles and isoproturon for the coarse particles

CAPTIONS

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