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Seasonal variation of endocrine disrupting potentials of pollutant mixtures associated with various size-fractions of inhalable air particulate matter☆

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A B S T R A C T

Ambient air pollution, namely exposure to air particulate matter (PM), has been shown to be connected with a number of adverse health effects. At least part of the effects can be caused by organic pollutant mixtures associated with PM, which can elicit a wide range of specific toxic potentials. These potentials could be affected by seasonal variation of pollutant mixtures and PM size fraction. To examine this, six size subfractions of PM_{10} were collected at rural and urban site in the Czech Republic in a year-long sampling campaign. The samples were assessed for aryl hydrocarbon (AhR)-mediated activity, estrogenicity and anti-androgenicity using mammalian cell models. The concentrations of detected toxic potentials differed among seasons. The greatest levels were observed in samples collected during winter when AhR-mediated effects and estrogenicity were at least 10-times greater than in summer. While the observed potentials were mostly less pronounced in samples from rural area, during winter, their AhR-mediated activity was twice as great as at the urban site. This was probably caused by the low-quality of fuel used for heating at the rural site. Assessed toxic potentials were associated mainly with PM size fractions with lesser aerodynamic diameters (<1 μm). Toxic potentials were compared with data from chemical analyses covering 102 chemicals from different pollutant groups to model their contribution to the observed effects. For AhR-mediated activity, chemical analyses explained on average 44% of the effect and the main identified effect-drivers were polycyclic aromatic hydrocarbons. For estrogenicity and anti-androgenicity, detected chemicals were able to explain on average less than 1.6% and 11% of the potentials, with their highest explicability reaching 13% and 57%, respectively. This was affected by the lack of data on specific toxic potency of some detected air pollutants, but also indicates a possible role of further not analyzed chemicals in these effects.

1. Introduction

According to the World Health Organization (WHO), air pollution represents the largest environmental risk to human health globally and exposure to air pollution was linked to more than 6 million premature deaths in 2012 (WHO, 2014). The adverse health effects have been associated mainly with the air particulate matter (PM) (Kappos et al., 2004), exposure to which has been linked to a wide range of diseases affecting mainly respiratory and cardiovascular systems (Cassee et al., 2013).

The size of PM plays an important role in its toxicological characteristics. While particles with an aerodynamic diameter less than 10 μm (PM_{10}) can enter the respiratory tract, only the fine fraction with diameters less than 2.5 μm ($PM_{2.5}$) is able to get deeper into the tract where the particles can more easily penetrate the air-blood barrier (Polichetti et al., 2009). The greatest risk is associated with very fine PM fraction (PM_1), not only because it can get into the gas-exchange region of the lungs, but also because this fraction contains a relatively large proportion of organic carbon that can serve as a universal carrier of organic compounds that might cause toxic effects (Cassee et al., 2013). Fine PM fractions

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were shown to contain greater concentrations of pollutants, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) and other chemicals that are known to be associated with adverse health effects (Čupr et al., 2013; Degrendele et al., 2014; Landlová et al., 2014). Thus, the size-specific distribution of toxic chemicals is of concern. Importantly, mixtures of pollutants in air can be very complex, containing possibly thousands of compounds, and it is quite challenging even for the current chemical analytical methods to describe their composition to estimate biological effects. This problem can be addressed by bioanalysis since the biological models integrate the effects of all chemicals present in the analyzed mixtures and thus they include also effects of chemicals that have not been identified yet and cover also possible interactions among chemicals (Hecker and Giesy, 2011).

Numerous air pollutants associated with PM have been shown to elicit diverse endocrine disrupting potentials (Rudel and Perovich, 2009). Significant part of the endocrine disrupting effect is mediated by the interference of pollutants with signaling of nuclear receptors such as estrogen receptor (ER) and androgen receptor (AR), or of aryl hydrocarbon receptor (AhR), which possesses similar characteristics (Balaguer et al., 2019). These receptors act as transcription factors and their dysregulation by environmental pollutants is being connected with many adverse health effects such as carcinogenesis, immunosuppression, or adverse effects on reproduction system. The receptors can interact with a wide range of pollutants from diverse chemical groups. Potential for interference with signaling of ER has been described for atmospheric pollutants such as some PAHs, PCDD/Fs, and organochlorinated as well as current use pesticides (OCPs and CUPs; Machala et al., 2001; Neale et al., 2017). Signaling of AR has been shown to be affected by some PAHs, OCPs, and CUPs (Neale et al., 2017). AhR-associated signaling can be affected by many PAHs, PCDD/Fs, CUPs and polychlorinated biphenyls (PCBs; Lee et al., 2013; Neale et al., 2017; Vondráček et al., 2017). These pollutants co-occur in the air in complex mixtures that humans are exposed to. Thus, information on bioactivity of the mixtures is of relevance and importance, since it can also integrate effects of not analyzed compounds as well as the interactions among the mixture components. The PM-associated chemical mixtures were previously shown to elicit AhR-mediated (dioxin-like), estrogenic, anti-estrogenic (mediated by ER) and anti-androgenic (mediated by AR) effects (Clemons et al., 1998; Novák et al., 2009; Wenger et al., 2009a, 2009b). These studies have focused mostly on a single size PM fraction such as either PM_{10} or PM_1 omitting the more detailed distribution of the toxic compounds among different size fractions of PM that is affecting the bioaccessibility of the chemicals within PM.

In a previous study, we have described the toxic potential of organic chemicals associated with six size sub-fractions of a set of PM_{10} samples coming from diverse pollution sources (Novák et al., 2014). That study has indicated that seasonal differences might play a role in the toxicological characteristics of PM_{10} size sub-fractions. The current study investigates the seasonal variability of the PM-associated endocrine disrupting potentials, namely ER, AR and AhR-mediated, and the distribution of these potentials among six size subfractions of inhalable PM, at an urban and a rural site throughout the whole year. Important goal was also to characterize the contribution of a wide spectra of detected chemicals to the specific toxic potentials assessed with bioassays and identify the main effect-drivers. Moreover, for AhR-mediated potential, we aimed to distinguish the contribution of persistent and non-persistent pollutant fraction to the overall toxic potential.

2. Material and methods

2.1. Air sampling and sample processing

Samples of ambient air were collected in the city of Brno, Czech Republic and its vicinity. Brno is the second largest city in the Czech Republic (~ 400,000 inhabitants). Samples were collected at two sites that differed in the type of dominant sources of pollution. The first locality, referred to as an urban site, was in Brno city center near an important traffic junction in an urban canyon (49°12′19″N, 16°35′50″E). The main source of pollution was probably vehicle traffic and domestic heating. The second locality referred to as a rural site was on the edge of a small village (~1500 inhabitants) 14 km southeast from Brno metropolitan area (49°6′20″N, 16°42′58″E). The village is situated in a rural area, where the main sources of pollution were probably agriculture and local heating in the winter months.

Samples of air PM were collected in parallel at both sites for one year (October 2009 to October 2010; Table 1) by use of a high-volume air sampler HV 100-P (Baghirra, Czech Republic) equipped with a multi-stage cascade impactor (TE6001 PM_{10} Sizes Selective Inlet, Tisch Environmental, USA), which collected six size sub-fractions of PM_{10}. The particles were sampled on slotted glass fiber collection substrata and glass fiber Hi-Vol filters (QM-A, Tisch, USA and Whatman, UK). The collected fractions represent particles with aerodynamic diameters of 7.2–10 μm (fraction A); 3–7.2 μm (B); 1.5–3 μm (C); 0.95–1.5 μm (D); 0.49–0.95 μm (E) and <0.49 μm (F).

The filters were weighed before and after sampling to assess masses of sampled PM in size sub-fractions. For the purpose of the present study, each month was represented by one-week sampling and samples from three months were pooled to represent one season (Table 1). For bioanalysis, the filters were extracted with dichloromethane, by use of an automatic extractor B-811 (Büchi System, Switzerland). Collected samples were assessed for 17 US EPA prioritized PAHs, 17 PCDD/Fs, 12 PCBs, 10 PBDEs, 10 HBCDS, 10 OCPs, and 26 CUPs. For further information on sampling, sample preparation and chemical analyses see papers with the results of chemical analyses (Degrendele et al., 2016, 2014; Okonski et al., 2014). For bioanalysis, a filter portion was extracted without any recovery standards. To obtain a persistent fraction of the samples, a half of the sample extract for bioanalysis was transferred to a glass column consisting of 0.5 g of activated silica, 30 g of sulfuric acid-modified activated silica, and 1 g of non-activated silica and were eluted with 240 mL of dichloromethane-hexane mixture (1 : 1 v/v). For bioanalysis, the samples were concentrated using a gentle stream of nitrogen and then transferred to dimethyl sulfoxide.

2.2. Bioassays

The AhR-mediated potential associated with air particles was assessed using the rat hepatocarcinoma cell line H4IIE-*luc* that is stably transfected with the luciferase gene under control of the AhR (Sanderson et al., 1996). Cells were grown and exposed in Dulbecco's Modified Eagle Media (PAA, Austria) supplemented with 10% fetal bovine serum (FBS; PAA, Austria). Estrogenic effects were assessed using human cervical carcinoma cell line HeLa9903 transfected with a luciferase gene under control of estrogen receptor activation (Ono, 2012). Cells were cultivated in DMEM without phenol red (PAA, Austria) supplemented with 10% FBS (PAA, Austria). In the exposure medium, 10% dialyzed FBS (PAA, Austria) treated with dextran-charcoal suspension (Sigma-Aldrich, Czech Republic) was used to decrease the levels of background steroids. Anti-androgenicity was assessed using human mammary carcinoma cell line MDA-kb2 stably transfected with luciferase

Table 1
Sampling duration and air volume of samples collected for analysis of specific toxic potentials. Individual weekly samples were pooled to obtain a single PM fractions sample set per season.

Season	Site	Week 1	Week 2	Week 3	Air volume (m^3)
Spring	rural	31.03.10–07.04.10	30.04.10–06.05.10	31.05.10–07.06.10	31113
	urban	31.03.10–07.04.10	30.04.10–04.05.10	04.06.10–07.06.10	22117
Summer	rural	28.06.10–02.07.10	27.07.10–02.08.10	30.08.10–09.09.10	32619
	urban	05.07.10–12.07.10	02.08.10–08.08.10	09.09.10–15.09.10	29662
Autumn	rural	23.10.09–28.10.09	13.11.09–20.11.09	01.10.10–07.10.10	28940
	urban	23.10.09–29.10.09	13.11.09–20.11.09	01.10.10–06.10.10	28242
Winter	rural	14.12.09–22.12.09	27.01.10–03.02.10	24.02.10–24.02.10	22721
	urban	14.12.09–21.12.09	27.01.10–03.02.10	24.02.10–03.03.10	33788

gene whose expression is triggered by the activity of AR (Wilson et al., 2002). Cells were cultivated in L-15 medium (PAA, Austria) supplemented with 10% FBS (PAA, Austria). Exposure was performed using L-15 medium supplemented with 10% dialyzed FBS treated with dextran-coated charcoal suspension. A competing concentration of dihydrotestosterone (0.1 nM) was used for the detection of anti-androgenicity, for further detail see Pavlíková et al. (2012).

2.3. Data analysis

Results from bioassays are expressed in bioanalytical equivalent concentrations (BEQ_{bio}) of reference compounds (RC) specific for respective bioassay (2,3,7,8-tetrachlorodibenzo-*p*-dioxin, 17β-estradiol, and flutamide in case of AhR-mediated potential, estrogenicity, and anti-androgenicity, respectively) using equation (1A). Only non-cytotoxic concentrations of samples were used for the evaluation of the receptor-mediated effects. The cytotoxicity was assessed by detailed microscopical inspection before the luminescence measurement. The BEQ represents the concentration of the reference compound that would cause the same effect as the sample. Dose-response relationships were evaluated and EC_{25} values or IC_{20} in case of anti-androgenicity were derived using a log-logistic model with GraphPad Prism (GraphPad Software, Inc. La Jolla, California, USA) (Equation (1)).

$$BEQ_{bio} = \frac{EC_{25}\ (rc)}{EC_{25}\ (extract)} \text{ or } \frac{IC_{20}\ (rc)}{IC_{20}\ (extract)} \quad (1)$$

Bioanalytical equivalents based on the results of chemical analyses (BEQ_{chem}) of the samples representing each season were calculated using concentration addition concept (Equation (2)) as a sum of the contributions of individual compounds that was derived by multiplying the concentrations of chemicals (C) with their known relative potency values (REP) taken from literature or calculated from molar concentrations reported in ToxCast (US EPA, 2020) (Equation (3)).

$$BEQ_{chem} = \sum_{i=1}^{n} REP_i \cdot C_i \quad (2)$$

$$REP_i = \frac{EC_{50}\ (rc)}{EC_{50}\ (i)} \text{ or } \frac{EC_{25}\ (rc)}{EC_{25}\ (i)} \text{ or } \frac{IC_{20}(rc)}{IC_{20}\ (i)} \quad (3)$$

Correlations among BEQ_{bio}, BEQ_{chem} and/or sum concentrations of pollutant groups were calculated by use of nonparametric Kendall tau procedure and differences among BEQ_{bio} in different seasons, sites and PM fractions were calculated by factorial ANOVA with LSD post-hoc test using Statistica (StatSoft, Tulsa, OK, USA).

3. Results and discussion

3.1. Sample collection/gravimetric analyses

The yearlong sample collection has shown that concentrations of PM fluctuated significantly at both sampling sites (Fig. 1). Concentrations of PM_{10} were less during spring and summer and highest during winter at both sites. The PM_{10} levels were about twice as great at the urban site than at the rural one in spring-autumn. This was probably caused by the intensive traffic at the site. In winter, concentrations of PM_{10} were comparable at both locations. The main contribution to concentrations of PM in the rural village site originated from local heating that offset differences in traffic intensities at the two sites. The relatively greater proportions of coarse particles at the urban site throughout the year were probably caused by dust swirling and abrasion associated with intensive traffic (Masri et al., 2015). Concentrations of PM_{10} were mostly (spring-autumn) less than the annual air quality standard of 50 μg/m^3 (European Commission, 2018), which nevertheless was reached at both sites in winter. Although it was not possible to quantify precisely concentrations of $PM_{2.5}$ due to characteristics of the cascade impactor used, the annual mean concentrations of PM_3 that can serve as a proxy for $PM_{2.5}$ did not exceed the EU annual mean limit for $PM_{2.5}$ of 25 μg/m^3, but the concentrations were twice as great during winter. However, the WHO air quality guidelines for PM_{10} and $PM_{2.5}$ of annual means of 20 and 10 μg/m^3, respectively, were exceeded at both urban (34 and 25 μg/m^3) and rural (22 and 19 μg/m^3) sites (WHO, 2006). $PM_{0.95}$ (fraction E + F) contributed 51–57% and 60–77% of the overall PM_{10}

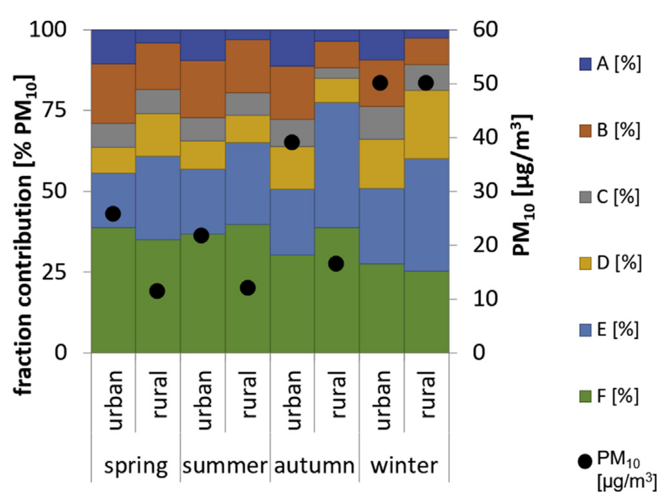

Fig. 1. Seasonal variation of gravimetric data of relative contribution of PM size subfractions to PM_{10} and volumetric levels of PM_{10}; A–F: size fractions of PM (A: 7.2–10; B: 3–7.2; C 1.5–3; D: 0.95–1.5; E: 0.49–0.95 and F: < 0.49 μm).

mass at urban and rural sites, respectively.

3.2. Biological analyses

Analyses focused on endocrine disrupting potentials of organic compounds associated with PM. Samples of air particulates from both sites contained compounds with significant AhR-mediated toxicity, estrogenic and anti-androgenic potentials (expressed as AhR BEQ_{bio}, ER $BEQ_{bio,}$ and antiAR $BEQ_{bio,}$ respectively; Fig. 2 and S1.1). The greatest effects across assessed endpoints were associated mainly with the finest fractions of PM. This was evident both when expressing concentrations per volume of air (volumetric measure) or when expressing the potentials per mass of PM weight (gravimetric measure; Fig. S1.2). This predominant association of bioactive chemicals with the two finest size fractions of PM was observed across all seasons in both urban and rural areas. Thus, most of the endocrine disrupting potential associated with PM_{10} and $PM_{2.5}$ was elicited by chemicals present in the fine and very fine PM fractions (Table S1.1). This can be explained both by the greater specific surface of the fine particles and by their composition, because, as has been described previously, these particles often contain relatively great concentrations of elemental and organic carbon with high sorption capacity (Čupr et al., 2013).

3.2.1. AhR-mediated toxic potential

Activation of AhR has been described to induce carcinogenicity, immunotoxicity and indirectly also endocrine disruption (Kortenkamp et al., 2012). AhR-mediated activities were observed in all PM size fractions (Fig. 2A and B; S1.1, S1.2 A, B) among all sampling seasons. This indicates that there were sources of AhR-active chemicals that were active around the year at both sites and the main source was probably traffic at both sites. Nevertheless, AhR-mediated potentials differed significantly among PM size fractions, sites and seasons. Their greatest levels were detected in samples collected during winter at both rural and urban sites. The sum of BEQ_{bio} concentrations for all size subfractions (PM_{10}) were 41 and 21 pg/m^3 at the rural and urban sites, respectively. In contrast, the least sum of concentrations of BEQ_{bio} in PM_{10} were observed during summer with concentrations of 0.9 and 1.8 pg/m^3 at rural and urban sites, respectively. Overall, the concentrations of AhR BEQ_{bio} were significantly different between the two sites as well as between winter and the other seasons. In winter, the sum of concentrations of PM_{10} BEQ_{bio} were more than 40 times and 10 times greater than during summer in rural and urban sites, respectively. The fine PM fractions contained the greatest concentrations of BEQ_{bio}, while the coarse fraction contained lesser concentrations. On average among sites and seasons, $PM_{0.95}$ (fractions E, F) were 35-times more potent than $PM_{3\text{-}10}$ (fractions A, B). Among seasons, the ratio was 60 and 10 at rural and urban sites, respectively. This shows that relative BEQ_{bio} distribution among PM size fractions was less shifted towards fine fractions at the urban site. This was probably due to greater proportions of coarse particles from intensive traffic at this site that could serve as a carrier of bioactive chemicals (Kelly and Fussell, 2012). The intensive traffic was probably also responsible for relatively greater concentrations of BEQ_{bio} at the urban site throughout the year except of winter

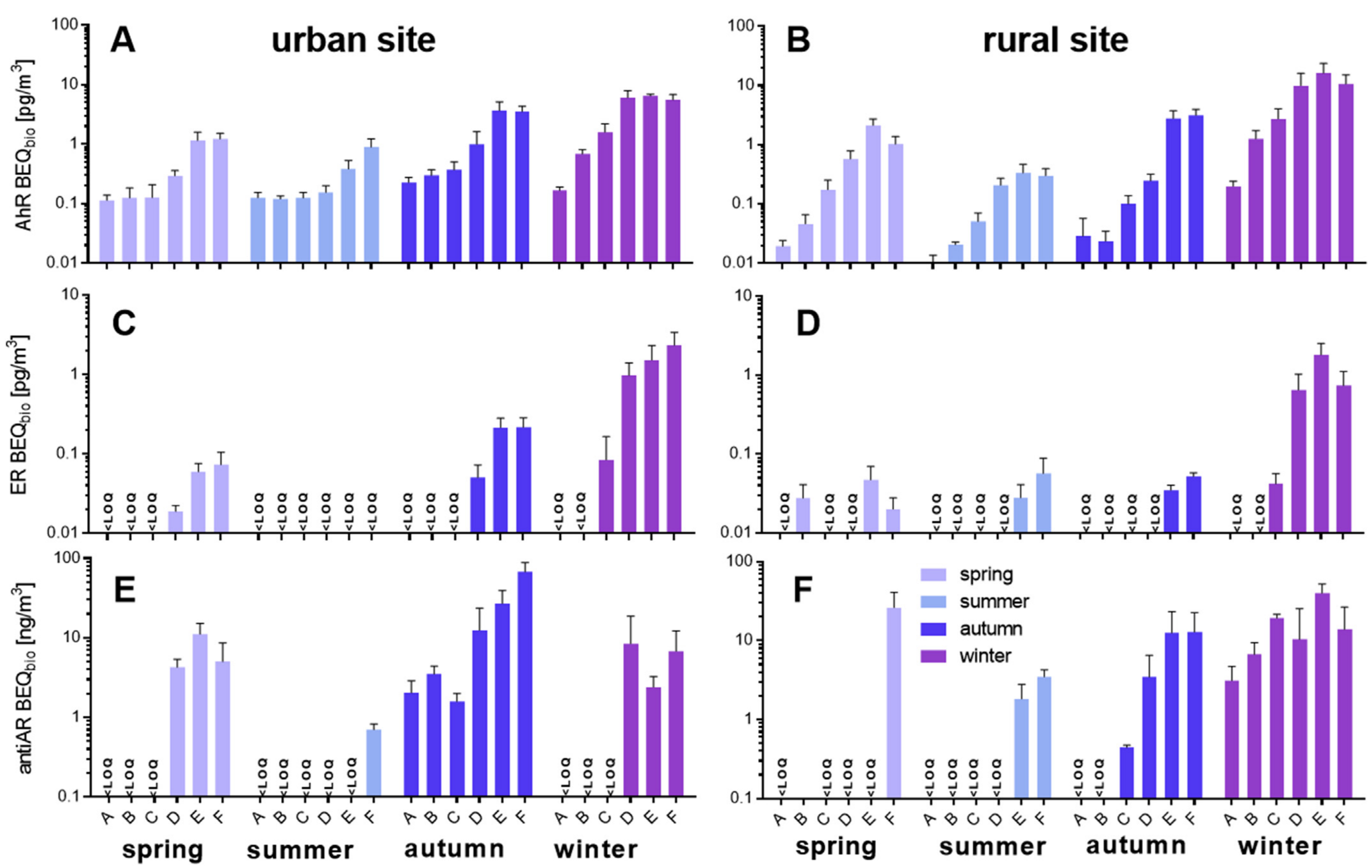

Fig. 2. BEQ_{bio} of PM size fractions expressed per volume of air; A, B – AhR BEQ_{bio}– bioanalytical equivalent of AhR-mediated activity expressed as concentration of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin; C, D – ER BEQ_{bio}– estrogenicity bioanalytical equivalent of 17β-estradiol, LOQ - limit of quantification <0.017 pg/m^3; E, F – antiAR BEQ_{bio}– anti-androgenic bioanalytical equivalent of flutamide, LOQ - limit of quantification <0.3 ng/m^3; The data expressed as a mean from three independent experiments + SEM; A–F: size fractions of PM (A:7.2–10; B: 3–7.2; C 1.5–3; D: 0.95–1.5; E: 0.49–0.95 and F: < 0.49 μm). The results on not logarithmic scale are shown in Supplementary Figure S1.1.

when the concentrations of BEQ were two-fold greater at the rural site. At the rural site, the greatest BEQ_{bio} concentrations in winter samples could be associated with burning of low-quality fuel or even domestic waste. At the urban site, natural gas was mostly used for heating. Thus, the difference among the seasons was less pronounced at that location since heating of residences was not contributing to pollution of air during colder seasons as much as at the rural site and the intensity of traffic, another source of bioactive chemicals, was relatively uniform over the year.

When comparing the autumn data from our year-long sampling at the urban site with data obtained from a 28-day sampling at the same spot in late November/December in 2007 (Novák et al., 2014), the overall concentrations of BEQ_{bio} associated with PM_{10} were greater during the earlier study (17.9 pg/m^3) compared to the present study (9.1 pg/m^3). Alternatively, when comparing data from November/December 2007 with the winter data from the present study, the sum concentration of AhR BEQ_{bio} associated with PM_{10} were similar, 17.9 and 20.5 pg/m^3, respectively. Nevertheless, the distribution of AhR BEQ_{bio} across PM size fractions differed between the two studies. While the concentrations in the fine fractions D, E and F were similar in the present study (6.0 ± 0.4 pg/m^3 in mean ± SD), concentrations of BEQ_{bio} observed during 2007 increased from the coarse to fine fractions, with the greatest concentration (10.9 pg/m^3) in the finest fraction. Thus, the concentrations of AhR BEQ_{bio} in PM_{10} in colder seasons were comparable between the two studies, but the distribution of BEQ_{bio} among PM_{10} sub-fractions at this site was dependent more on local conditions at the time of sampling. During winter of 2006, concentrations of AhR-mediated potential in PM_1 were assessed at urban and rural sites in Switzerland by use of a murine cell line reporter-gene assay (Wenger et al., 2009a, 2009b). Concentrations of AhR BEQ_{bio} were 19–87 and 10–85 pg/m^3 at the Swiss rural and urban sites, respectively. In the study, results of which are given here, concentrations of AhR-mediated potential associated with $PM_{0.95}$ which represented the combination of the two finest PM fractions, contained 12 and 27 pg/m^3 at the rural and urban site, respectively (Table S1.1). A contribution of $PM_{2.5}$ and PM_1 subfractions to PM_{10} was assessed in samples from urban or rural locations in Spain using a yeast reporter-gene assay (Mesquita et al., 2014). The $PM_{2.5}$ and PM_1 fractions explained 112% and 84% of PM_{10}-associated BEQ_{bio}, respectively. In our study, the trend was similar, the closest expressible size fractions PM_3 and $PM_{0.95}$ were overall responsible for 95% and 75% of PM_{10}-associated BEQ_{bio}, respectively. Concentrations of AhR BEQ_{bio} were correlated with concentrations of PAHs, OCPs and PCDD/Fs as well as BEQ_{chem}, which supports the assumption that these chemicals are important contributors to BEQ_{chem} (Fig. 3).

Limited sample masses were available for the assessment of relative contributions of persistent organic compounds (POPs) to the overall concentrations of BEQ_{bio} in samples. Since AhR-mediated effect is known to be elicited by both persistent and non-persistent organic compounds (Denison and Nagy, 2003), the persistent sample fraction was used preferentially for the assessment of this endpoint (AhR BEQ_{bio} POPs). The effect of persistent compounds was quantifiable only in ultra-fine PM fractions throughout the year and fine fractions during cold seasons (Table S1.2). In samples with quantifiable concentrations of AhR BEQ_{bio} POPs, the POPs explained on average 0.54% (0.13–2.79%) of the overall AhR BEQ_{bio}. Thus, non-persistent chemicals played a prominent role in AhR-mediated toxic potential in samples of air particulate matter.

3.2.2. Estrogenicity

Interaction of environmental pollutants with ER signaling is relatively thoroughly characterized and it has been associated with

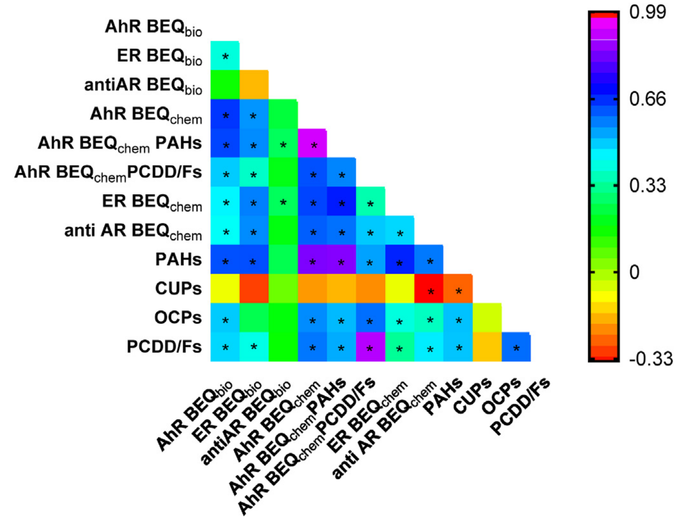

Fig. 3. Correlation of assessed and modeled bioanalytical equivalent (BEQ_{bio} and BEQ_{chem}, respectively) and sum concentrations of pollutant groups (Kendall tau; significant values are labeled with asterisk); AhR BEQ – bioanalytical equivalent of aryl hydrocarbon receptor-mediated activity, ER BEQ – bioanalytical equivalent of estrogenicity, antiAR BEQ - bioanalytical equivalent anti-androgenicity; BEQ_{chem} PAHs - equivalent modeled based on levels of polycyclic aromatic compounds, BEQ_{chem} PCDD/Fs - equivalent modeled based on levels of polychlorinated dioxins and furans.

adverse effects on reproduction, development and plays a role in carcinogenicity (Janošek et al., 2006; McLachlan, 2016). Estrogenic potential was detected mainly in finer PM fractions collected during colder seasons. At both sites, the greatest concentrations were observed during winter, while the potential was less during the other seasons or even not quantifiable during summer at the urban site (Fig. 2C and D; Fig. S1.1, S1.2 C, D). At both locations, concentrations of BEQ_{bio} associated with $PM_{0.95}$ were more than 29-fold greater during winter than during spring. Concentrations of BEQ_{bio} were namely in winter relatively high compared to data reported in literature. During winter in Belgium, concentrations of ER BEQ_{bio} in PM_{10} was 0.04–0.12 pg/m^3 (Croes et al., 2016), while concentrations in total suspended PM samples collected in France during autumn and winter were 0.02 and 0.11 pg/m^3 of ER BEQ_{bio}, respectively (Oziol et al., 2017). Both studies used human-based reporter-gene cell models (BG1Luc4E2 and MELN, respectively). In the study, results of which are reported here, during autumn, concentrations in PM_{10} from urban and rural sites were 0.48 and 0.08 pg/m^3, while in winter they were 4.91 and 3.24 pg/m^3 at those two sites, respectively. During winter, concentrations of ER BEQ_{bio} in PM_1 from urban and rural sites in Switzerland were 0.08–1.25 and 0.07–0.77 pg/m^3, respectively (Wenger et al., 2009a). In our study, $PM_{0.95}$ contained 3.8 and 2.5 pg/m^3 at the urban and rural sites, respectively. Thus, the winter PM from the Czech Republic seemed to contain greater concentrations of estrogenic compounds than did PM in Switzerland or Belgium, although a possible difference in the responses of the employed bioassays could affect the results. Concentrations of ER BEQ_{bio} were correlated with concentrations of PAHs and PCDD/Fs (Fig. 3). Some previous studies observed an anti-estrogenic potential associated with PM from diverse sampling sites in central Europe (Novák et al., 2014, 2013, 2009). The main difference between the previous studies and the current work is the use of HeLa9903 cell line rather than the MVLN model for detection of total ER agonist potential. Because it is not likely that the shift from anti-estrogenic to estrogenic effects would be explained by a change of composition of the mixture of environmental pollutants, these results indicate that the previously used MVLN cell line is more sensitive to anti-estrogenic compounds and/or less sensitive to estrogenic compounds associated with ambient air. Thus, during those previous studies, estrogenicity could have been masked by the presence of anti-estrogens. This is supported by the fact that most of other similar studies using various *in vitro* models have reported mainly estrogenic potentials in PM samples correspondingly to the current study (Croes et al., 2016; Matsumoto et al., 2005; Oziol et al., 2017; Wang et al., 2004; Wenger et al., 2009b).

3.2.3. Anti-androgenicity

Similarly to situation for estrogenicity, the interaction of xenobiotics with the AR is associated with effects on reproduction, development and plays role in hormone-dependent cancer (Janošek et al., 2006; McLachlan, 2016). While androgenic effects of the PM extract were not observed, some PM samples were significantly anti-androgenic and, as in case of estrogenicity, this effect was quantifiable mainly in the fine fractions of PM from both sites among seasons (Fig. 2E and F; Fig. S1.1, S1.2 E, F). The greatest effect was observed in samples from the urban site during autumn and the rural site during winter, where the anti-androgenic potential was quantifiable in all size sub-fractions of PM_{10}. The potential was associated mainly with the fine PM fractions. The combination of two finest fractions corresponding to $PM_{0.95}$ contained 45% of summed antiAR BEQ_{bio} of PM_{10} from winter rural site and 88% in case of autumn urban site. The combination of fractions corresponding to PM_3 contained even 89% of summed BEQ_{bio} of PM_{10} from winter rural site and 95% in case of autumn urban site (Table S1.1). Although anti-androgenic activity of ambient air samples has been previously detected (Érseková et al., 2014; Novák et al., 2014, 2009), the anti-androgenic potentials were not expressed as an equivalent concentration of a standard anti-androgen, so it is not possible to directly compare previous results with results of the current study. However, since the potential is expressed in flutamide equivalents in both studies, the current data can be compared with results of the study by Oziol et al. (2017). In France, during winter, total suspended PM contained 5−10 ng/m^3 of flutamide antiAR BEQ_{bio}, while in the current study summed 18 and 71 ng/m^3 flutamide antiAR BEQ_{bio} were observed in winter PM_{10} from the urban and rural sites, respectively. Concentrations of antiAR BEQ_{bio} were not significantly correlated with any group of analyzed chemicals (Fig. 3).

3.2.4. Bioanalytical equivalent concentration modeled from chemical analysis (BEQ_{chem})

Overall bioactive potentials of mixtures of chemicals acting through the same mode of action can be modeled by the concentration addition concept (Villeneuve et al., 2000). Accuracy of the predicted values is affected by availability and quality of relative potencies (REPs) of individual chemicals included in the modeling. In this study, REPs obtained from literature were preferentially derived from studies using the same cell models to those used for BEQ_{bio} characterization in the current study. In case REPs from the same model were not available, data from similar reporter gene model based on cells from the same organism were employed. For a few chemicals, there were no available REP values obtained with model from the same organism. In such a case, we have employed other available REPs. Although the interspecies differences could affect the overall modeled BEQ_{chem} levels, their impact was probably very low or negligible since this was the case only for several chemicals that occurred at very low concentrations. All used REP data are listed in detail in Table S1.3.

Toxicity characteristics for the studied modes of action were available for 54% of the detected chemicals in the US EPA ToxCast database (US EPA, 2020), nevertheless for many of them these specific toxicity data were not available in neither primary literature nor ToxCast (Fig. 5). The percentage of detected chemicals without available relative potencies was 15, 40 and 45% for AhR-mediated toxicity, estrogenicity and anti-androgenicity, respectively.

Concentrations of chemicals detected in samples representing each season used for predictive modeling were taken from previously published papers (Degrendele et al., 2016, 2014; Okonski et al., 2014). PAHs represented the chemical group that was responsible for the greatest proportion of the detected AhR-mediated potential, with the greatest contributions from benzo(*k*) fluoranthene and indeno(*1,2,3-c,d*)pyrene (Fig. S1.3, Table S2.1). Since they were not distinguished by the chemical analysis, contributions of two pairs of PAHs (benzo(*b*)fluoranthene with benzo(*j*)fluoranthene and dibenz(*ac*)anthracene with dibenz(*ah*) anthracene, respectively) were modeled using a mean value of their REP (Table S1.3; Degrendele et al., 2014). Since the differences of their REP values are relatively small, this approach has not significantly affected the modeled BEQ_{chem} levels. PCDD/Fs congeners, which were often considered prototypal AhR ligands in the past, elicited two orders of magnitude lesser concentrations of BEQ_{chem} than PAHs, which corresponds to the comparison of effects of the persistent and nonpersistent fractions (Fig. S1.4; Table S1.2; Table S2.1). Among PCDD/Fs, the main contributors to total concentrations of BEQ_{chem} were 23478-PeCDF, 2378-TCDF, and 234678-HxCDF. The greatest concentrations of BEQ_{chem} contributed by PCDD/Fs were associated with the finest fractions of PM and those concentrations were significantly correlated with the concentrations of BEQ_{bio} (Fig. 3). The other groups of chemicals included in the modeling to predict AhR-mediated BEQ_{chem} were non-ortho-substituted co-planar PCBs (Fig. S1.5) and nine current-use pesticides (Fig. S1.6), but their contribution to predicted concentrations of BEQ_{chem} were even less than for PCDD/Fs. The prominent role of PAHs in AhR-mediated toxic potential was supported by strong correlations between concentrations of PAHs and concentrations of BEQ_{bio} (Fig. 3). The concentrations of BEQ_{bio} were significantly correlated with concentrations of PCDD/Fs and OCPs although these chemical groups were not the main drivers of AhR-mediated potency.

For estrogenic potential, the PAHs benzo(*a*)pyrene, fluoranthene and benzo(*a*)anthracene along with the flame retardant BDE-47 made the greatest contribution to concentrations of BEQ_{chem} (Fig. S1.7; Table S2.2), while contributions of pesticides were significantly less. Relative contributions of currently used pesticides to estrogenicity was greatest during the vegetation period while PAHs dominated during colder seasons.

Anti-androgenic potential seems to be relatively common among the analyzed chemicals (Fig. 5). Almost a third of the detected chemicals have available anti-androgenic potencies. Thus, thirty chemicals could be used for predicting antiAR BEQ_{chem} of the pollutant mixture, which was dominated by benzo(*a*)pyrene but also brominated diphenyl ethers played a significant role (Figure S1.8; Table S2.3). At the rural site in spring, the primary driver of antiAR BEQ_{chem} was acetochlor, which most likely came from application in agriculture.

3.2.5. Contribution of analyzed compounds to the detected biological potentials

The results of chemical analyses of samples collected during individual seasons were used to characterize the possible contributions of detected pollutants to the observed specific toxic potentials of samples. Comparison between concentrations of BEQ_{bio} and BEQ_{chem} for AhR-mediated toxic potential is shown in Table 2 and Fig. 4. On average, for AhR-mediated responses, 44% of BEQ_{bio} could be accounted for by BEQ_{chem} among locations, seasons and size fractions, but in case of several samples (urban-summer-F,

Table 2

Specific toxic potentials of samples assessed with bioassays expressed as bioanalytical equivalents of respective model compounds ($BEQ_{bio} \pm SD$) and bioanalytical equivalents predicted from levels of chemicals (BEQ_{chem}) with a percentage of BEQ_{bio} explained by the chemical analyses. AhR - aryl hydrocarbon receptor-mediated response (tetrachlorodibenzo-*p*-dioxin equivalent); ER – estrogenicity (17β-estradiol equivalent); anti-AR – anti-androgenicity (flutamide equivalent); A-F: size fractions of PM (A: 7.2–10; B: 3–7.2; C 1.5–3; D: 0.95–1.5; E: 0.49–0.95 and F: < 0.49 μm).

Site	Season	PM size	AhR [pg/m^3]			ER [pg/m^3]			antiAR [ng/m^3]		
			BEQ_{bio}	BEQ_{chem}	(%)	BEQ_{bio}	BEQ_{chem}	(%)	BEQ_{bio}	BEQ_{chem}	(%)
Urban site			0.11 ± 0.026	0.0264	(23.3%)	<0.017	8.9×10^{-5}	(- %)	<1.2	1.5×10^{-5}	(- %)
		B	0.12 ± 0.058	0.0418	(33.6%)	<0.017	1.2×10^{-4}	(- %)	<1.2	1.7×10^{-5}	(- %)
		C	0.13 ± 0.081	0.0534	(42.1%)	<0.017	1.2×10^{-4}	(- %)	<1.2	2.0×10^{-5}	(- %)
		D	0.29 ± 0.065	0.1459	(49.5%)	0.02 ± 0.004	2.4×10^{-4}	(1.3%)	4.3 ± 1.1	2.9×10^{-5}	(0.7%)
		E	0.93 ± 0.45	0.3766	(40.6%)	0.06 ± 0.017	7.1×10^{-4}	(1.2%)	11.2 ± 4	6.6×10^{-5}	(0.6%)
		F	1.23 ± 0.29	0.5508	(44.9%)	0.07 ± 0.032	1.2×10^{-3}	(1.7%)	5 ± 3.6	1.7×10^{-4}	(3.6%)
	Summer	A	0.13 ± 0.027	0.0005	(0.4%)	<0.017	2.0×10^{-5}	(- %)	<1.4	1.1×10^{-5}	(- %)
		B	0.12 ± 0.015	0.0183	(15.3%)	<0.017	5.3×10^{-5}	(- %)	<1.4	4.9×10^{-5}	(- %)
		C	0.12 ± 0.029	0.0069	(5.5%)	<0.017	7.3×10^{-5}	(- %)	<1.4	1.6×10^{-5}	(- %)
		D	0.15 ± 0.046	0.0415	(26.8%)	<0.017	1.3×10^{-4}	(- %)	<1.4	2.4×10^{-5}	(- %)
		E	0.38 ± 0.15	0.1050	(27.5%)	<0.017	2.8×10^{-4}	(- %)	<1.4	2.1×10^{-5}	(- %)
		F	0.89 ± 0.34	1.6067	(179.7%)	<0.017	4.1×10^{-3}	(- %)	0.7 ± 0.13	4.0×10^{-4}	(57.3%)
	Autumn	A	0.23 ± 0.048	0.0677	(30%)	<0.017	1.0×10^{-4}	(- %)	2.05 ± 0.85	1.1×10^{-5}	(0.54%)
		B	0.3 ± 0.072	0.0591	(19.7%)	<0.017	1.7×10^{-4}	(- %)	3.5 ± 0.9	2.3×10^{-5}	(0.68%)
		C	0.37 ± 0.13	0.4139	(111.9%)	<0.017	1.8×10^{-3}	(- %)	1.57 ± 0.34	3.0×10^{-5}	(1.96%)
		D	1 ± 0.62	0.4262	(42.7%)	0.05 ± 0.022	1.4×10^{-3}	(2.8%)	3.72 ± 2.59	7.9×10^{-5}	(2.15%)
		E	3.67 ± 1.47	1.1535	(31.4%)	0.21 ± 0.067	3.5×10^{-3}	(1.6%)	26.97 ± 12.57	3.1×10^{-4}	(1.18%)
		F	3.55 ± 0.82	0.8820	(24.9%)	0.22 ± 0.067	2.4×10^{-3}	(1.1%)	67.81 ± 20.54	3.7×10^{-4}	(0.55%)
	Winter	A	0.17 ± 0.021	0.0406	(24.4%)	<0.017	1.0×10^{-4}	(- %)	<0.82	1.2×10^{-5}	(- %)
		B	0.69 ± 0.12	0.1179	(17.2%)	<0.017	2.6×10^{-4}	(- %)	<0.82	3.5×10^{-5}	(- %)
		C	1.6 ± 0.59	0.5406	(33.9%)	0.03 ± 0.003	1.1×10^{-3}	(3.9%)	<0.82	9.4×10^{-5}	(- %)
		D	6.03 ± 1.87	2.5996	(43.1%)	1.03 ± 0.221	6.4×10^{-3}	(0.6%)	8.45 ± 10.22	5.8×10^{-4}	(6.9%)
		E	6.5 ± 0.45	4.5276	(69.7%)	1.51 ± 0.812	1.2×10^{-2}	(0.8%)	2.4 ± 0.86	1.1×10^{-3}	(47.3%)
		F	5.57 ± 1.3	4.0613	(73%)	2.33 ± 1.06	1.0×10^{-2}	(0.5%)	6.78 ± 5.5	1.1×10^{-3}	(17.2%)
Rural Site	Spring	A	0.02 ± 0.005	0.0083	(42.7%)	<0.017	6.8×10^{-5}	(- %)	<3.4	4.4×10^{-5}	(- %)
		B	0.05 ± 0.02	0.0222	(48.2%)	0.03 ± 0.013	9.6×10^{-5}	(0.3%)	<3.4	5.8×10^{-5}	(- %)
		C	0.17 ± 0.078	0.0502	(28.8%)	<0.017	1.3×10^{-4}	(- %)	<3.4	5.7×10^{-5}	(- %)
		D	0.58 ± 0.204	0.1700	(29.3%)	<0.017	2.9×10^{-4}	(- %)	<3.4	4.7×10^{-5}	(- %)
		E	2.13 ± 0.59	0.3884	(18.2%)	0.05 ± 0.023	7.1×10^{-4}	(1.5%)	<3.4	8.1×10^{-5}	(- %)
		F	1.03 ± 0.35	0.5117	(49.8%)	0.02 ± 0.008	9.5×10^{-4}	(4.7%)	26.28 ± 14.56	3.8×10^{-4}	(1.5%)
	Summer	A	0.01 ± 0.003	0.0001	(0.5%)	<0.017	2.3×10^{-5}	(- %)	<1.4	1.0×10^{-5}	(- %)
		B	0.02 ± 0.002	0.0220	(106.6%)	<0.017	7.4×10^{-5}	(- %)	<1.4	1.0×10^{-5}	(- %)
		C	0.05 ± 0.019	0.0585	(115%)	<0.017	1.3×10^{-4}	(- %)	<1.4	1.1×10^{-5}	(- %)
		D	0.21 ± 0.065	0.0245	(11.8%)	<0.017	9.8×10^{-5}	(- %)	<1.4	1.1×10^{-5}	(- %)
		E	0.34 ± 0.13	0.0402	(12%)	0.03 ± 0.013	1.4×10^{-4}	(0.51%)	3.44 ± 2.37	1.2×10^{-5}	(0.37%)
		F	0.3 ± 0.093	0.0768	(25.6%)	0.06 ± 0.033	1.9×10^{-4}	(0.34%)	3.62 ± 0.92	1.7×10^{-5}	(0.48%)
	Autumn	A	0.02 ± 0.007	0.0003	(1.8%)	<0.017	2.4×10^{-5}	(- %)	<1.4	2.1×10^{-6}	(- %)
		B	0.02 ± 0.011	0.0237	(100.9%)	0.02 ± 0	1.5×10^{-4}	(0.94%)	<1.4	5.9×10^{-6}	(- %)
		C	0.1 ± 0.038	0.0699	(69.4%)	<0.017	6.3×10^{-4}	(- %)	0.56 ± 0.19	1.3×10^{-5}	(2.35%)
		D	0.27 ± 0.07	0.3895	(145.7%)	<0.017	2.4×10^{-3}	(- %)	3.49 ± 3.02	4.7×10^{-5}	(1.37%)
		E	2.8 ± 0.97	1.0375	(37.1%)	0.04 ± 0.005	4.4×10^{-3}	(12.7%)	12.56 ± 10.7	1.5×10^{-4}	(1.2%)
		F	3.47 ± 0.6	1.1455	(33%)	0.05 ± 0.006	3.0×10^{-3}	(5.9%)	12.86 ± 5.24	1.3×10^{-4}	(1.06%)
	Winter	A	0.2 ± 0.044	0.0523	(26.4%)	<0.017	9.9×10^{-5}	(- %)	3.13 ± 1.62	8.5×10^{-6}	(0.27%)
		B	1.27 ± 0.46	0.3159	(25%)	<0.017	7.1×10^{-4}	(- %)	6.71 ± 2.71	7.0×10^{-5}	(1.05%)
		C	2.75 ± 1.32	1.2446	(45.3%)	0.04 ± 0.014	2.7×10^{-3}	(6.4%)	19.35 ± 2.19	2.0×10^{-4}	(1.08%)
		D	10 ± 6.16	5.0900	(50.8%)	0.65 ± 0.38	1.2×10^{-2}	(1.9%)	23.81 ± 15	1.0×10^{-3}	(4.4%)
		E	16.3 ± 7.51	7.4489	(45.7%)	1.81 ± 0.72	1.7×10^{-2}	(1%)	3.03 ± 0.27	1.3×10^{-3}	(44.5%)
		F	10.6 ± 4.54	2.4982	(23.5%)	0.74 ± 0.37	5.9×10^{-3}	(0.8%)	15.21 ± 17.45	4.6×10^{-4}	(3.03%)

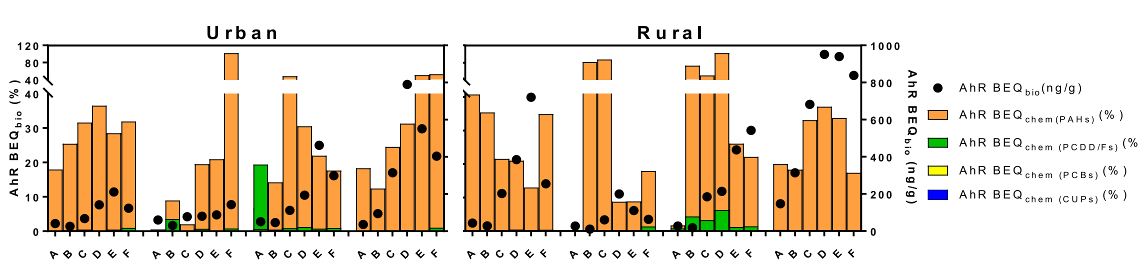

Fig. 4. Seasonal variation of gravimetrically expressed AhR BEQ_{bio} and a contribution of the detected chemical classes to the BEQ_{bio}; A–F: size fractions of PM (A:7.2–10; B: 3–7.2; C 1.5–3; D: 0.95–1.5; E: 0.49–0.95 and F: < 0.49 μm); AhR $BEQ_{chem\ (PCBs)}$ and $BEQ_{chem\ (CUPs)}$ levels are lower than 0.3%; concentrations of chemicals used for BEQ_{chem} modeling were taken from Degrendele et al. (2014).

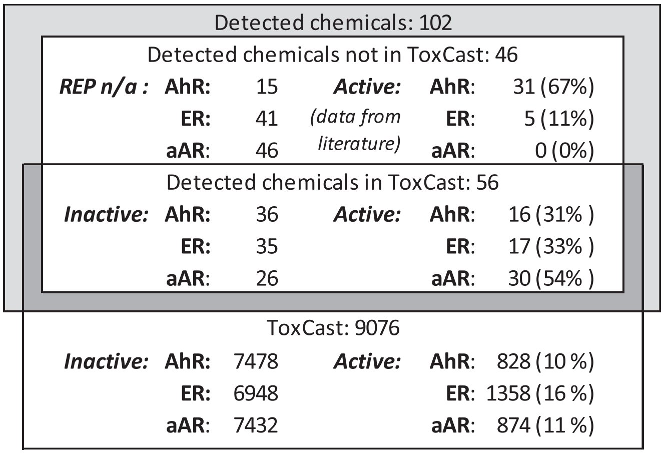

Fig. 5. Overview of the active and inactive chemicals detected in the study and availability of information on their bioactivity in ToxCast database and literature for AhR-mediated (AhR), estrogenic (ER) and anti-androgenic (aAR) effect; for AhR and ER data were available only for 52 of 56 chemicals present in ToxCast; REP n/a – data on activity are not available in literature. The used REP data (preferentially obtained with the same bioassay) are listed in detail in Table S1.3.

urban-autumn-C, rural-summer-B, C, rural-autumn-B, D) the model completely explained the potential observed in the bioassays. At both sites, the BEQ_{chem} was almost completely accounted for by concentrations of PAHs, while PCDD/Fs-contributed about 1% of concentrations of BEQ_{chem} and PCBs and CUPs contributed even less at both sites. Greatest contributions of CUPs were observed at the rural site during spring and summer. This was clearly connected with agricultural activities at the site during this period of the year and it was associated, when concentrations were expressed both volumetrically and gravimetrically, with the coarse PM fractions. This demonstrates that the coarser particles, despite their lesser concentrations and specific surface areas, served as a transport medium for CUPs. Thus, erosion by wind, probably the main source of coarse particles at the rural site, seems to play the main role in CUPs mobilization (Degrendele et al., 2016). Anyway, contributions of CUPs to the overall BEQ_{chem} were rather minor.

For estrogenicity and anti-androgenicity, detected chemicals accounted on average for 1.6 and 11% of BEQ_{bio} (Table 2), while the highest explained levels were 13% and 57%, respectively. This shows that the main drivers of these endocrine disrupting activities in most ambient air particulates samples have not yet been identified. Thus, it is probable that some chemicals significantly contributing to these potentials are missing in the analysis. This could be the case of phthalates that were not analyzed in the current study because of technical reasons but are known to interact with estrogen and androgen receptors (Kwon and Ji, 2016) and have been detected in ambient air PM in significant levels (Salgueiro-González et al., 2013). However, we are even not able to take into account the effects of all detected chemicals, since their specific toxic properties are not completely described yet. Namely in case of estrogenicity and anti-androgenicity, for almost half of the chemicals there were no available data on their bioactivity neither in the ToxCast database nor in primary literature (Fig. 5). Thus, these chemicals could be potentially contributing to the effects, but their contribution could not be accounted for in BEQ_{chem}.

4. Conclusions

It was shown that chemicals with the assessed biological potentials were associated mainly with fine and ultra-fine fractions of PM throughout the year at both rural and urban site. The importance of these fractions for risk assessment is further increased by the fact that these fractions are known to penetrate deeply into the respiratory tract where the chemicals can be more efficiently absorbed into the organism. Concentrations of BEQ_{bio} exhibited a clear seasonal pattern for all studied toxic potentials. The greatest concentrations were observed during colder seasons, when concentrations at the rural site were comparable with the urban site for all assessed endpoints. This was probably due mainly to combustion of low-quality fuel for local heating at the rural site. For AhR-mediated effects, a significant part of the detected BEQ_{bio} was associated mainly with PAHs, while contributions of other chemical groups, such as PCDD/Fs, CUPs and PCBs were less pronounced. In case of estrogenicity, the contributions of PAHs were more pronounced in colder seasons and pesticides contributed greater proportions during the growing season. With the current knowledge of chemical-specific REPs, besides AhR-mediated potential we were able to explain only a limited portion of observed toxic potentials and the main drivers of potencies were not identified for estrogenicity or anti-androgenicity. This shows an urgent need to describe a bioassay-specific REP values for a larger spectrum of ambient air pollutants to be able to assess their potential role in these endocrine disrupting activities. It is also possible that the list of analyzed chemicals does not sufficiently cover air pollutants with estrogenic and anti-androgenic potential. The results also emphasize the need to apply bioassays as a complementary tool in monitoring of air quality, because chemical analysis alone cannot indicate effects elicited by co-occurring mixtures of compounds.

Declaration of competing interest

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Jiří Novák: Conceptualization, Investigation, Methodology, Data curation, Formal analysis, Writing - original draft, Visualization. **Anita Vaculovič:** Data curation, Formal analysis, Investigation. **Jana Klánová:** Conceptualization, Funding acquisition, Writing - review & editing. **John P. Giesy:** Writing - review & editing. **Klára Hilscherová:** Conceptualization, Data curation, Supervision, Writing - review & editing, Project administration.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2020.114654.

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Supplementary information 1 - Seasonal variation of endocrine disrupting potentials of pollutant mixtures associated with various size-fractions of inhalable air particulate matter

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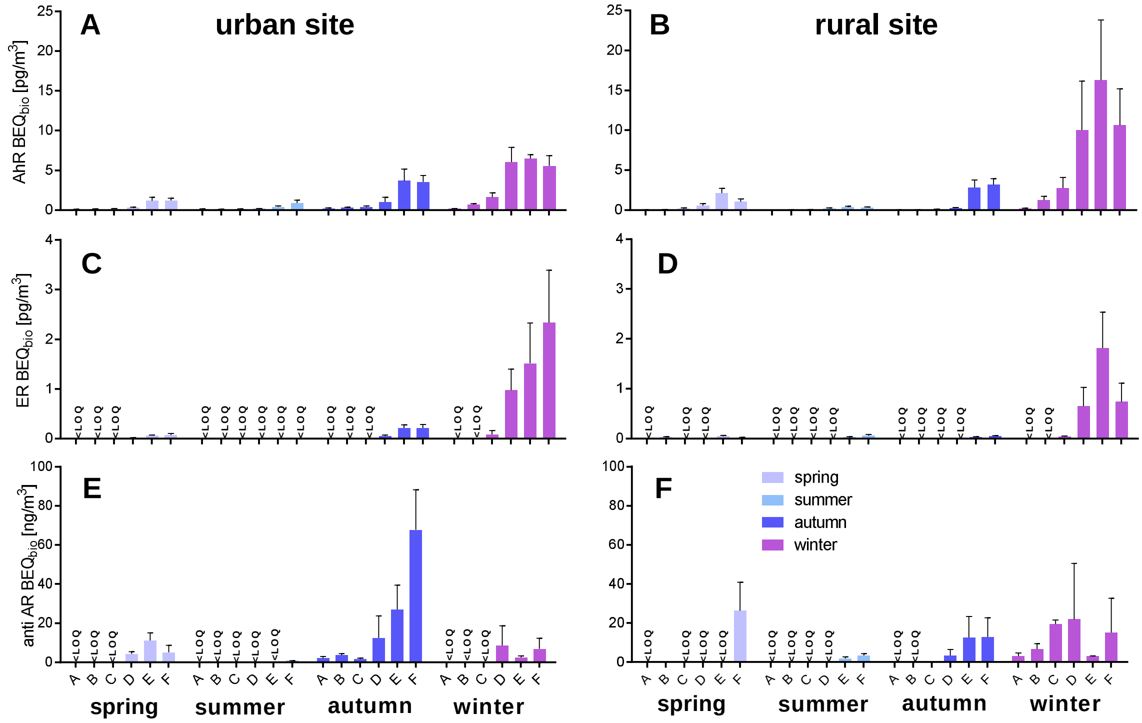

Figure S1.1 Assessed bioanalytical equivalents of PM size fractions expressed per volume of air

A, B – AhR BEQ_{bio}– bioanalytical equivalent of AhR-mediated activity expressed as concentration of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin; C, D – ER BEQ_{bio}– estrogenicity bioanalytical equivalent of 17β estradiol, LOQ - limit of quantification <0.017 pg/m^3; E, F – antiAR BEQ_{bio}– anti-androgenic bioanalytical equivalent of flutamide, LOQ - limit of quantification <0.0003 µg/m^3; The data expressed as a mean from three independent experiments+ SD; A-F: size fractions of PM (A:7.2-10; B: 3-7.2; C 1.5-3; D: 0.95-1.5; E: 0.49-0.95 and F: < 0.49µm).

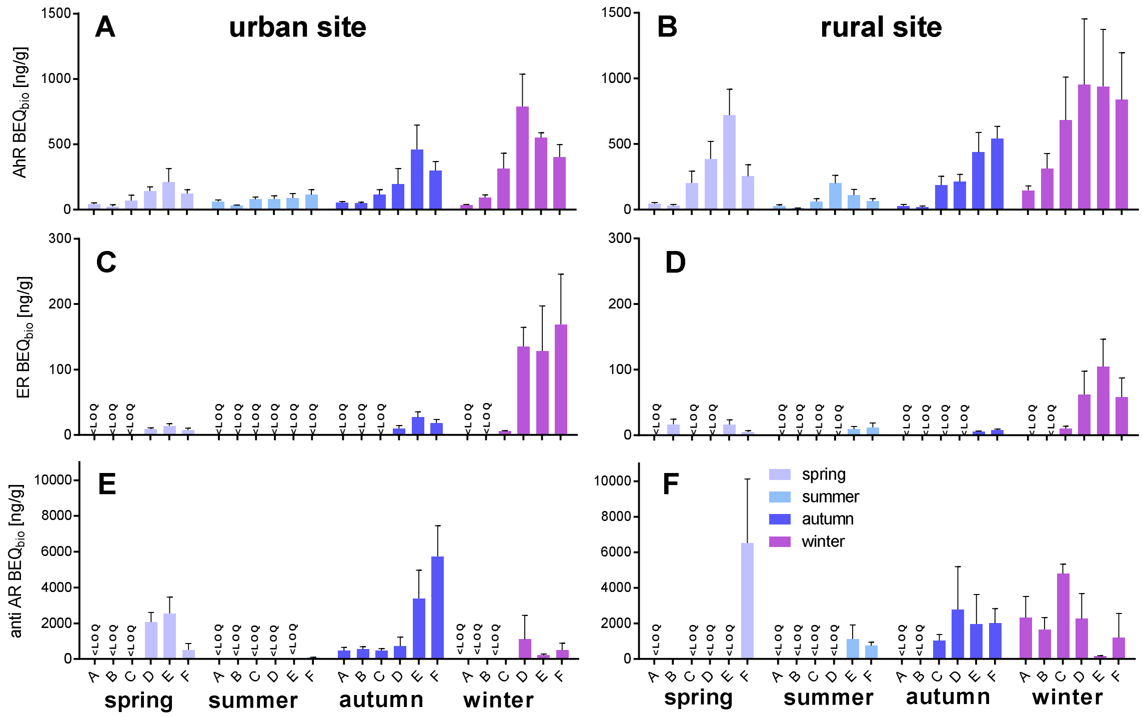

Figure S1.2 Assessed bioanalytical equivalents of PM size fractions expressed per weight of particulate matter

A, B – AhR BEQ$_{bio}$– bioanalytical equivalent of AhR-mediated activity expressed as concentration of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin; C, D – ER BEQ$_{bio}$– estrogenicity bioanalytical equivalent of 17β estradiol, LOQ - limit of quantification <12.8 ng/g; E, F – antiAR BEQ$_{bio}$– anti-androgenic bioanalytical equivalent of flutamide, LOQ - limit of quantification <12.4 mg/g; The data expressed as a mean from three independent experiments+ SD; A-F: size fractions of PM (A:7.2-10; B: 3-7.2; C 1.5-3; D: 0.95-1.5; E: 0.49-0.95 and F: < 0.49µm).

Table S1.1 Bioanalytical equivalent (BEQ_{bio}) estimation of cumulative $PM_{0.95}$, PM_3 and PM_{10} size fractions with their percentage contribution to PM_{10} BEQ_{bio}. Values in italics – the estimation is probably underestimated since some of PM subfractions used for calculation were without quantifiable effect

Site	Season	PM size	AhR BEQ_{bio} [pg/m^3] (BEQ_{bio} PM_{10} [%])	ER BEQ_{bio} [pg/m^3] (BEQ_{bio} PM_{10} [%])	anti-AR BEQ_{bio} [µg/m^3] (BEQ_{bio} PM_{10} [%])
Urban site	Spring	$PM_{0.95}$	**2.15 (77 %)**	**0.13 (88 %)**	**0.01 (87 %)**
		PM_3	**2.58 (92 %)**	*0.15 (100 %)*	*0.01 (100 %)*
		PM_{10}	**2.81 (100 %)**	*0.15 (100 %)*	*0.01 (100 %)*
	Summer	$PM_{0.95}$	**1.28 (71 %)**	*<0.017*	*0.0001 (100 %)*
		PM_3	**1.56 (86 %)**	*<0.032*	*0.0001 (100 %)*
		PM_{10}	**1.8 (100 %)**	*<0.102*	*0.0001 (100 %)*
	Autumn	$PM_{0.95}$	**7.22 (79 %)**	**0.43 (90 %)**	**0.03 (88 %)**
		PM_3	**8.59 (94 %)**	*0.48 (100 %)*	**0.04 (95 %)**
		PM_{10}	**9.11 (100 %)**	*0.48 (100 %)*	**0.04 (100 %)**
	Winter	$PM_{0.95}$	**12.06 (59 %)**	**3.85 (78 %)**	**0.01 (38 %)**
		PM_3	**19.69 (96 %)**	**4.91 (100 %)**	**0.02 (100 %)**
		PM_{10}	**20.54 (100 %)**	*4.91 (100 %)*	*0.02 (100 %)*
Rural Site	Spring	$PM_{0.95}$	**3.16 (79 %)**	**0.07 (71 %)**	*0.01 (100 %)*
		PM_3	**3.91 (98 %)**	*0.07 (71 %)*	*0.01 (100 %)*
		PM_{10}	**3.98 (100 %)**	*0.1 (100 %)*	*0.01 (100 %)*
	Summer	$PM_{0.95}$	**0.64 (69 %)**	**0.09 (100 %)**	**0.003 (100 %)**
		PM_3	**0.9 (97 %)**	*0.09 (100 %)*	*0.003 (100 %)*
		PM_{10}	**0.93 (100 %)**	*0.09 (100 %)*	*0.003 (100 %)*
	Autumn	$PM_{0.95}$	**6.27 (94 %)**	**0.09 (100 %)**	**0.02 (83 %)**
		PM_3	**6.63 (99 %)**	*0.09 (100 %)*	**0.02 (100 %)**
		PM_{10}	**6.67 (100 %)**	*0.09 (100 %)*	*0.02 (100 %)*
	Winter	$PM_{0.95}$	**26.92 (65 %)**	**2.55 (79 %)**	**0.02 (45 %)**
		PM_3	**39.7 (96 %)**	**3.25 (100 %)**	**0.03 (89 %)**
		PM_{10}	**41.16 (100 %)**	*3.25 (100 %)*	**0.04 (100 %)**

Table S1.2 AhR-mediated bioanalytical equivalent of persistent fraction of the samples (POP BEQbio; mean±SD); percentage of contribution of persistent fraction to BEQbio to non-fractionated sample in parenthesis; LOD <0.001 pg/m³

Season	PM fraction	AhR POP BEQ_{bio} (pg/m³) (%) Urban site		Rural site	
Spring	A	<0.001	(-%)	<0.001	(-%)
	B	<0.001	(-%)	<0.001	(-%)
	C	<0.001	(-%)	<0.001	(-%)
	D	0.001 ± 0.001	(0.5%)	0.001 ± 0.0005	(0.23%)
	E	0.003 ± 0.001	(0.29%)	0.003 ± 0.0003	(0.13%)
	F	0.01 ± 0.002	(0.48%)	0.003 ± 0.001	(0.27%)
Summer	A	<0.001	(-%)	<0.001	(-%)
	B	<0.001	(-%)	<0.001	(-%)
	C	<0.001	(-%)	<0.001	(-%)
	D	<0.001	(-%)	<0.001	(-%)
	E	<0.001	(-%)	<0.001	(-%)
	F	0.003 ± 0.001	(0.26%)	0.003 ± 0.0004	(0.95%)
Autumn	A	<0.001	(-%)	<0.001	(-%)
	B	<0.001	(-%)	<0.001	(-%)
	C	<0.001	(-%)	<0.001	(-%)
	D	0.003 ± 0.0002	0.29%	<0.001	(-%)
	E	0.01 ± 0.001	0.17%	0.01 ± 0.002	(0.21%)
	F	0.03 ± 0.007	0.83%	0.012 ± 0.003	(0.34%)
Winter	A	<0.001	(-%)	<0.001	(-%)
	B	<0.001	(-%)	<0.001	(-%)
	C	0.003 ± 0.001	0.17%	0.004 ± 0.001	(0.15%)
	D	0.02 ± 0.008	0.31%	0.02 ± 0.001	(0.24%)
	E	0.13 ± 0.037	1.95%	0.07 ± 0.021	(0.43%)
	F	0.16 ± 0.067	2.79%	0.04 ± 0.003	(0.34%)

Table S1.3 Relative potency values (REPs) that were used for calculation of chemical data-based bioanalytical equivalents (BEQ_{chem}) were obtained either from experiments from the current study or from literature. Literature was preferentially searched for REP values specific for the bioassays employed in the current study. Where no such REPs were available, we used data from analogical bioassays as indicated. When there was more than one relevant literature source available, geometrical mean of REP values was calculated. No. chemicals – number of chemicals with available REP values

Assay	**Activation of AhR**			**Activation of ER**			**Inhibition of AR**	
No. chemicals	47			22			30	
Reference compound	2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD)			17β-Estradiol			Flutamide	
Chemical	REP	based on	Chemical	REP	based on	Chemical	REP	based on
2378-TCDD	$1.0×10^{+0}$	EC50[1,4, a]	BDE-100	$1.8×10^{-6}$	EC50[3,16, m,n]	Acetochlor	$6.1×10^{-1}$	IC20[3,15, j]
1234678-HpCDD	$5.6×10^{-2}$	EC50[1,4, a]	BDE-47	$2.6×10^{-6}$	EC50[3,12, j]	Alachlor	$8.2×10^{-1}$	IC20[3,15, j]
1234678-HpCDF	$1.1×10^{-2}$	EC50[1,4, a]	BDE-99	$3.3×10^{-7}$	EC5[3,16, m]	Anthracene	$1.0×10^{-2}$	IC20[3,15, j]
1234789-HpCDF	$4.4×10^{-2}$	EC50[2,5, b]	Benzo[a]anthracene	$7.9×10^{-7}$	EC25[3,14, l]	Azinphos-methyl	$4.0×10^{-2}$	IC20[3,15, j]
123478-HxCDD	$1.2×10^{-1}$	EC50[1,4, a]	Benzo[a]pyrene	$4.7×10^{-6}$	EC10[3,14, g]	BDE-100	$3.3×10^{+0}$	IC20[3,16, m]
123478-HxCDF	$1.3×10^{-1}$	EC50[2,5, b]	Benzo[b]fluoranthene	$3.4×10^{-6}$	EC10[3,14, g]	BDE-183	$3.3×10^{-2}$	IC20[3,16, m]
123678-HxCDD	$4.7×10^{-2}$	EC50[1,4, a]	Carbendazim	$5.3×10^{-7}$	EC50[3,12, j]	BDE-47	$1.2×10^{-2}$	IC20[3,16, m]
123678-HxCDF	$1.4×10^{-1}$	EC50[2,5, b]	Diazinon	$2.9×10^{-7}$	EC10[3,14, g]	BDE-99	$3.3×10^{-1}$	IC20[3,16, m]
123789-HxCDD	$5.4×10^{-2}$	EC50[1,4, a]	Dimethoate	$8.5×10^{10}$	EC50[3,12, j]	Benz[a]anthracene	$1.5×10^{-2}$	IC20[3,15, j]
123789-HxCDF	$1.1×10^{-1}$	EC50[2,5, b]	Fluoranthene	$2.5×10^{-7}$	EC50[3,12, j]	Benzo[a]pyrene	$1.6×10^{-1}$	IC20[3,12, g]
12378-PeCDD	$5.5×10^{-1}$	EC50[1,4, a]	Chlorpyrifos	$2.8×10^{-7}$	EC10[3,14, g]	Benzo[k]fluoranthene	$9.2×10^{-2}$	IC20[3,15, j]
12378-PeCDF	$2.4×10^{-2}$	EC50[1,4, a]	Isoproturon	$5.4×10^{-7}$	EC50[3,12, j]	Diuron	$1.8×10^{-2}$	IC20[3,15, j]
234678-HxCDF	$3.1×10^{-1}$	EC50[2,5, b]	Metamitron	$8.3×10^{-7}$	EC50[3,12, j]	Fenitrothion	$7.1×10^{-1}$	IC20[3,15, j]
23478-PeCDF	$5.8×10^{-1}$	EC50[2,5, b]	o,p'-DDD	$9.6×10^{-6}$	EC50[3,12, j]	Fluoranthene	$7.8×10^{-2}$	IC20[3,15, j]
2378-TCDF	$2.7×10^{-1}$	EC50[1,4, a]	o,p'-DDE	$6.3×10^{-6}$	EC50[3,13, k]	Fonofos	$3.1×10^{-2}$	IC20[3,15, j]
OCDD	$3.4×10^{-4}$	EC50[2,5, b]	o,p'-DDT	$8.4×10^{-5}$	EC50[3,12, j]	Indeno(1,2,3-cd)pyrene	$5.2×10^{-2}$	IC20[3,15, j]
OCDF	$1.6×10^{-3}$	EC50[2,5, b]	p,p'-DDD	$8.0×10^{-7}$	EC50[3,12, j]	Metolachlor	$2.1×10^{-2}$	IC20[3,12, f]
PCB 114	$4.9×10^{-6}$	EC50[1,4, a]	p,p'-DDE	$7.0×10^{-7}$	EC50[3,13, k]	o,p-DDD	$5.0×10^{-2}$	IC20[3,15, j]
PCB 123	$8.2×10^{-6}$	EC50[1,4, a]	p,p'-DDT	$3.4×10^{-6}$	EC50[3,12, j]	o,p'-DDE	$4.2×10^{-2}$	IC20[3,12, j]

PCB 126	1.4×10^{-1} EC50[1,4, a]	Terbufos	4.6×10^{-7} EC50[3,12, j]	p,p'-DDD	3.4×10^{2} IC20[3,12, j]
PCB 156	1.6×10^{-5} EC50[1,4, a]	Terbuthylazine	1.6×10^{-7} EC10[3,14, g]	o,p'-DDT	4.0×10^{-2} IC20[3,15, j]
PCB 157	4.1×10^{-5} EC50[1,4, a]	β-HCH	1.5×10^{-5} EC50[3,12, j]	p,p'-DDE	1.0×10^{-1} IC20[3,15, j]
PCB 169	3.3×10^{-4} EC50[1,4, a]			p,p'-DDT	4.3×10^{-2} IC20[3,15, j]
PCB 77	7.0×10^{-5} EC50[1,4, a]			Phenanthrene	1.3×10^{-2} IC20[3,15, j]
PCB 81	3.4×10^{-3} EC50[1,4, a]			Prochloraz	4.3×10^{-1} IC20[3,15, j]
Acenaphthylene	1.1×10^{-6} EC20[3,11, j]			Pyrene	2.0×10^{-2} IC20[3,15, j]
Benzo[a]anthracene	2.6×10^{-5} EC25[1,6, e]			TBECH	2.9×10^{-2} IC20[3,15, j]
Benzo[a]pyrene	1.7×10^{-4} EC25[1,6, e]			α-HBCD	4.3×10^{-3} IC20[3,15, j]
Benzo[b]fluoranthene	4.6×10^{-4} EC25[1,6, e]			α-HCH	6.9×10^{-3} IC20[3,15, j]
Benzo[g,h,i]perylene	2.6×10^{-6} EC25[1,4, c]			δ-HCH	5.7×10^{-3} IC20[3,15, j]
Benzo[j]fluoranthene	5.5×10^{-4} EC25[1,6, e]				
Benzo[k]fluoranthene	3.1×10^{-3} EC25[1,6, e]				
Dibenz[a,c]anthracene	5.7×10^{-4} EC25[1,4, c]				
Dibenz[a,h]anthracene	2.0×10^{-3} EC25[1,6, e]				
Fluoranthene	9.3×10^{-7} EC25[1,4, d]				
Chrysene	6.5×10^{-5} EC25[1,6, e]				
Indeno[1,2,3,c,d]pyrene	8.0×10^{-4} EC25[1,6, e]				
Pyrene	4.1×10^{-6} EC25[1,4, c, d]				
Carbendazim	1.2×10^{-8} EC10[1,7, f]				
Diazinon	1.0×10^{-8} EC20[1,9, g]				
Diuron	1.8×10^{-6} EC20[2,10, h]				
Fenitrothion	2.7×10^{-6} EC20[3,11, j]				
Chlorpyrifos	1.1×10^{-7} EC10[1,8, g]				
Isoproturon	3.3×10^{-6} EC20[3,11, j]				
Metamitron	1.8×10^{-6} EC20[3,11, j]				
Prochloraz	2.3×10^{-6} EC20[2,10, h]				
Terbuthylazine	1.3×10^{-5} EC50[2,10, i]				

[1] rat-based cell line	[4] H4EII-luc	[7] H4G1.1c2	[10] Hepa1c1c7	[13]MELN	[16]ER-CALUX	[a]Lee et al., 2013	[d]Machala et al., 2001	[g]Neale et al., 2017	[j]US EPA, ToxCast	[a]Lee et al., 2013
[2] mouse-based cell line	[5] H1L1	[8] DR-CALUX	[11] HepG2	[14]MVLN		[b]Brown et al., 2001	[e]Vondráček et al., 2017	[h]Takeuchi et al., 2008	[k]Pillon et al., 2005	[b]Brown et al., 2001
[3] human-based cell line	[6] AZ-AhR	[9] H1G1.1c2	[12] BG1 ER-luc	[15]MDAkb2		[c]Larsson et al., 2012	[f] Novák et al., 2018	[i]Ghisari et al., 2015	[l]Machala et al., 2001	[c]Larsson et al., 2012

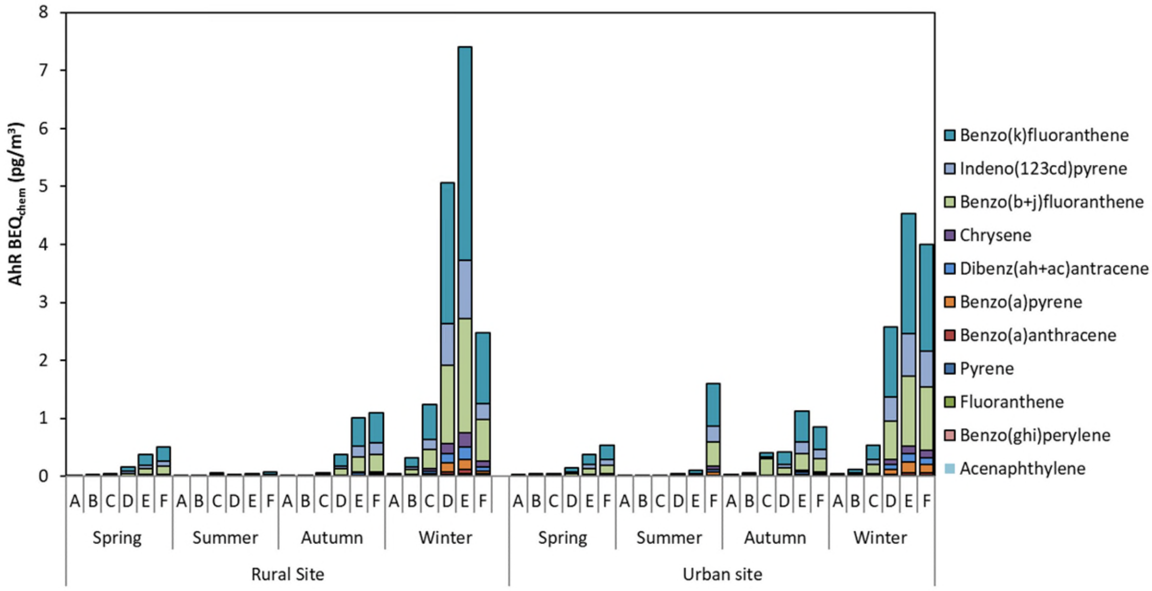

Figure S1.3 Contribution of individual PAHs to calculated AhR-mediated bioanalytical equivalent BEQ$_{chem}$; A-F: size fractions of PM (A: 7.2-10; B: 3-7.2; C: 1.5-3; D: 0.95-1.5; E: 0.49-0.95 and F: < 0.49µm). Concentrations of chemicals used for the BEQ$_{chem}$ modeling were taken from Degrendele et al. (2016, 2014).

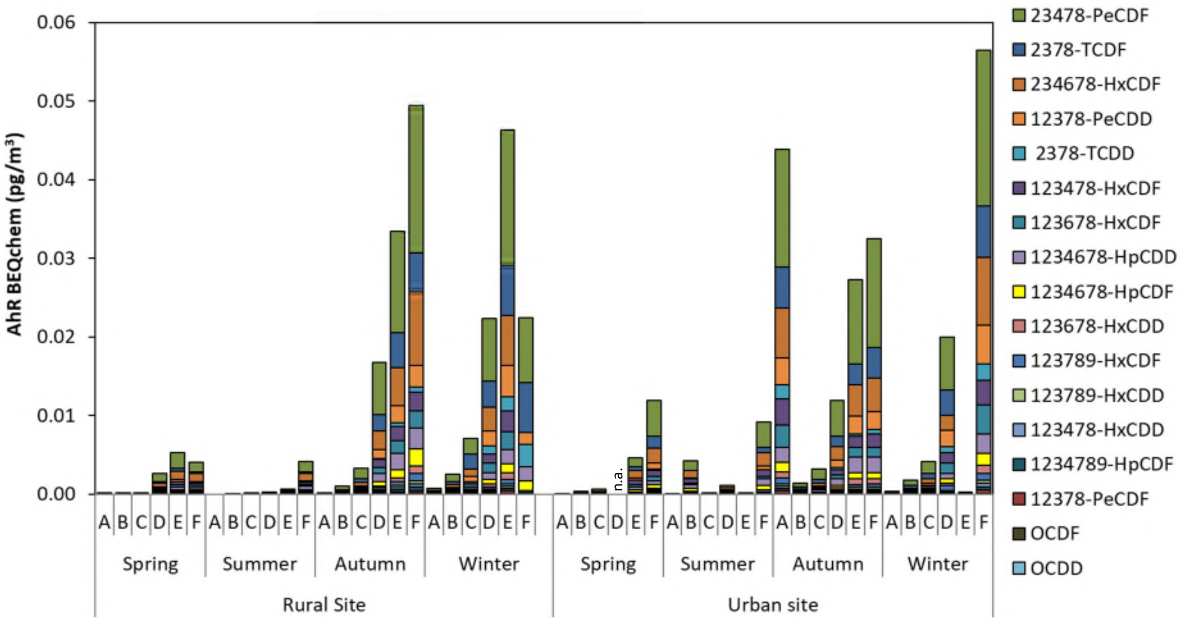

Figure S1.4 Contribution of PCDD/Fs congeners to calculated AhR-mediated bioanalytical equivalent BEQ$_{chem}$; A-F: size fractions of PM (A: 7.2-10; B: 3-7.2; C: 1.5-3; D: 0.95-1.5; E: 0.49-0.95 and F: < 0.49µm). Concentrations of chemicals used for the BEQ$_{chem}$ modeling were taken from Degrendele et al. (2016, 2014). n.a. – sample was not analyzed.

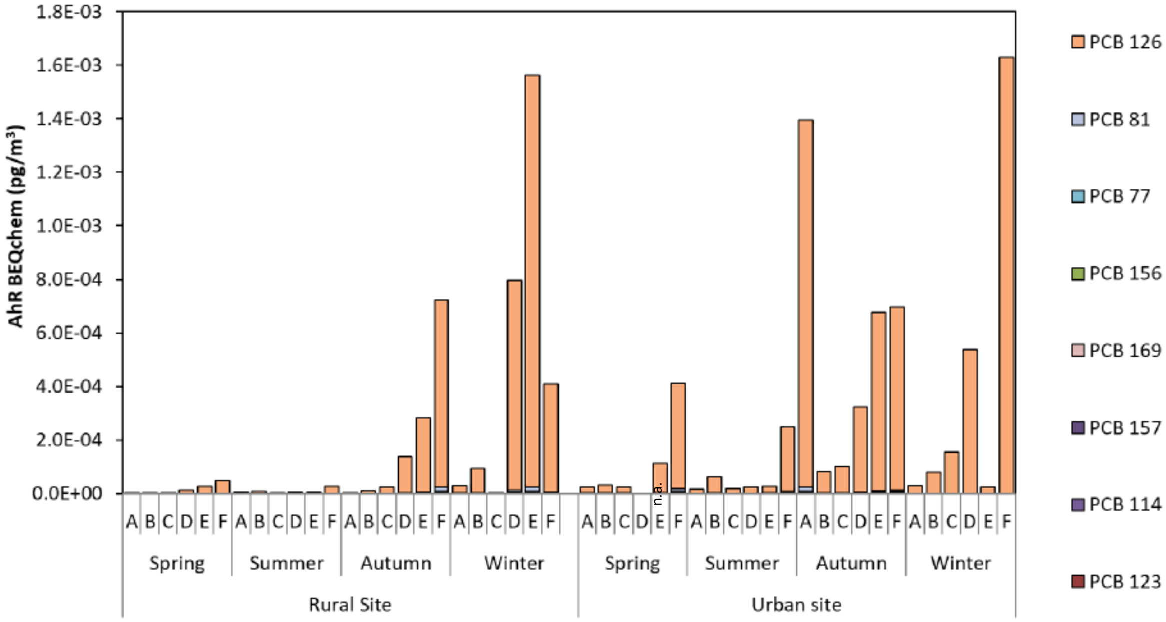

Figure S1.5 Contribution of PCBs congeners to calculated AhR-mediated bioanalytical equivalent BEQ$_{chem}$; A-F: size fractions of PM (A: 7.2-10; B: 3-7.2; C: 1.5-3; D: 0.95-1.5; E: 0.49-0.95 and F: < 0.49µm). Concentrations of chemicals used for the BEQ$_{chem}$ modeling were taken from Degrendele et al. (2016, 2014). n.a. – sample was not analyzed.

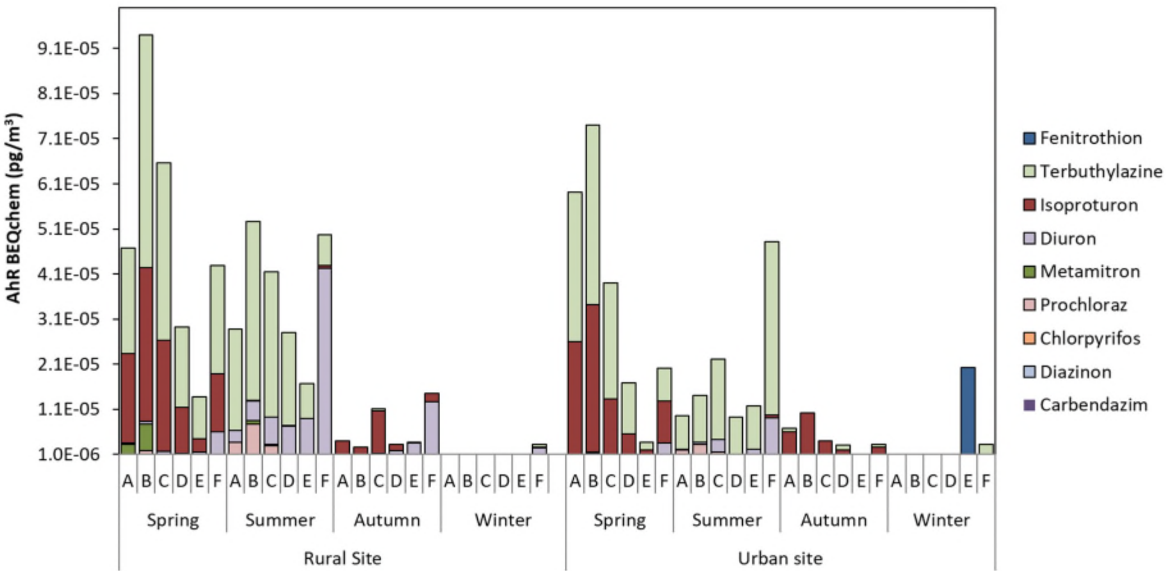

Figure S1.6 Contribution of CUPs to calculated AhR-mediated bioanalytical equivalent BEQ$_{chem}$; A-F: size fractions of PM (A: 7.2-10; B: 3-7.2; C: 1.5-3; D: 0.95-1.5; E: 0.49-0.95 and F: < 0.49µm). Concentrations of chemicals used for the BEQ$_{chem}$ modeling were taken from Degrendele et al. (2016, 2014).

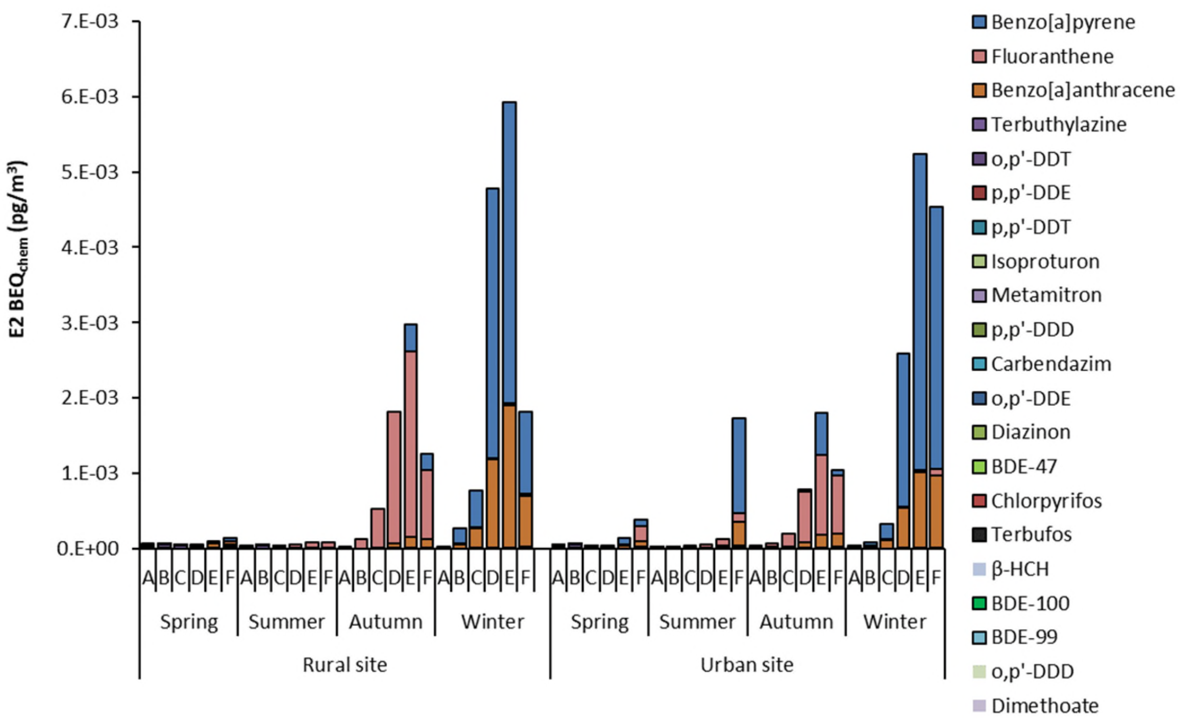

Figure S1.7 Contribution of pesticides, BDEs and PAHs to calculated estrogen bioanalytical equivalent BEQ_{chem}; A-F: size fractions of PM (A: 7.2-10; B: 3-7.2; C: 1.5-3; D: 0.95-1.5; E: 0.49-0.95 and F: < 0.49µm). Concentrations of chemicals used for the BEQ_{chem} modeling were taken from Degrendele et al. (2016, 2014) and (Okonski et al., 2014).

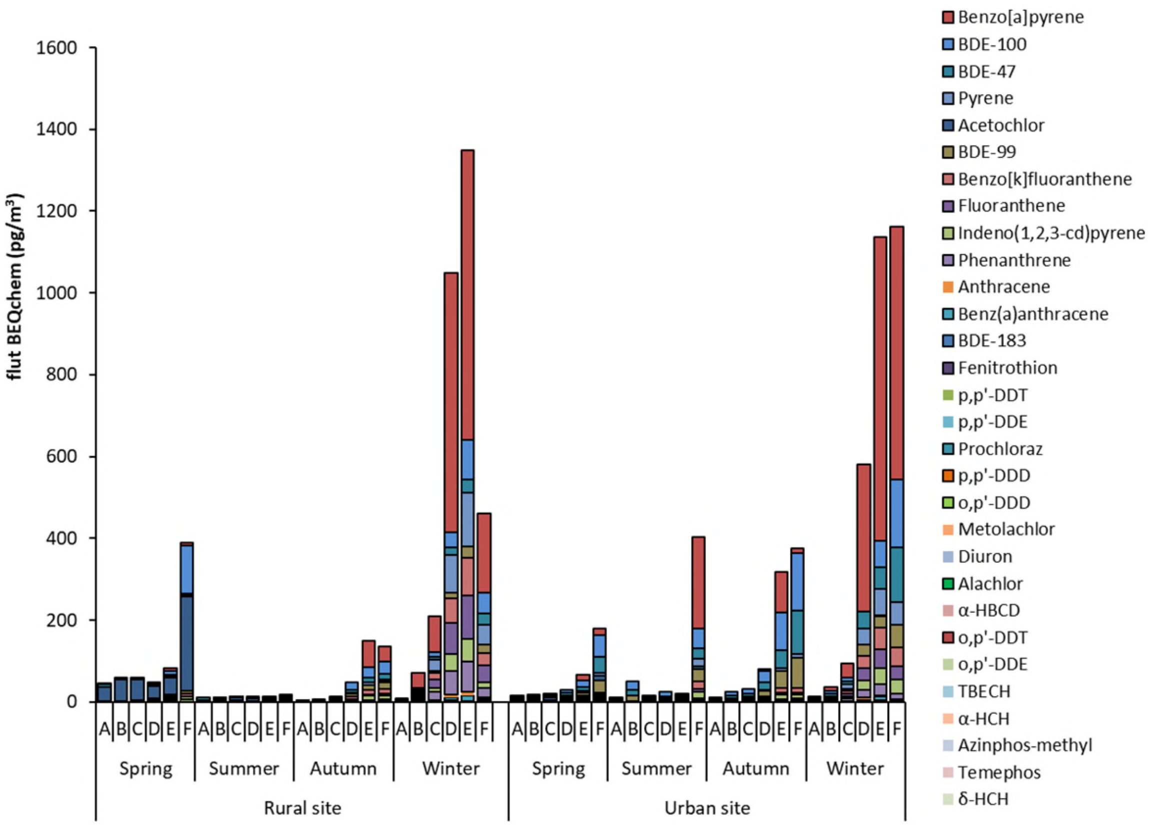

Figure S1.8 Contribution of chemicals to calculated anti-androgenic bioanalytical equivalent BEQ_{chem} A-F: size fractions of PM (A: 7.2-10; B: 3-7.2; C: 1.5-3; D: 0.95-1.5; E: 0.49-0.95 and F: < 0.49µm). Concentrations of chemicals used for the BEQchem modeling were taken from Degrendele et al. (2016, 2014) and Okonski et al. (2014).

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Table S2 -1:Contribution of individual analyzed compounds to calculated AhR-mediated bioanalytical e

Site	Season	Particle size (μm)	Acenaphthylen	Fluoranthe	Pyrene	Benzo(a)a	Chrysene	Benzo(b+j)
Rural Site	Spring	7.2-10.0	<LOD	9.80E-06	2.75E-05	2.56E-03	5.31E-04	5.53E-04
		3.0-7.2	<LOD	1.84E-05	5.02E-05	2.25E-04	1.04E-03	1.55E-03
		1.5-3.0	<LOD	2.71E-05	8.42E-05	4.62E-04	2.01E-03	3.20E-03
		0.95-1.5	<LOD	6.45E-05	2.02E-04	1.55E-03	6.30E-03	1.03E-02
		0.49-0.95	2.56241E-06	1.19E-04	4.23E-04	4.71E-03	1.69E-02	2.51E-02
		<0.49	2.78204E-06	1.15E-04	4.60E-04	3.71E-03	1.36E-02	3.34E-02
	Summer	7.2-10.0	<LOD	3.38E-06	1.44E-05	<LOD	<LOD	<LOD
		3.0-7.2	<LOD	1.10E-05	3.83E-05	2.18E-04	8.62E-04	1.26E-03
		1.5-3.0	<LOD	2.98E-05	8.48E-05	6.54E-04	2.64E-03	3.62E-03
		0.95-1.5	<LOD	1.23E-05	3.68E-05	1.67E-04	8.76E-04	1.53E-03
		0.49-0.95	<LOD	1.08E-05	3.51E-05	1.83E-04	8.93E-04	2.34E-03
		<0.49	<LOD	2.15E-05	9.27E-05	4.38E-04	1.82E-03	4.65E-03
	Autumn	7.2-10.0	<LOD	4.40E-06	1.81E-05	<LOD	2.52E-04	<LOD
		3.0-7.2	<LOD	1.54E-05	4.26E-05	2.19E-04	8.56E-04	1.42E-03
		1.5-3.0	<LOD	3.38E-05	9.53E-05	7.72E-04	2.92E-03	3.96E-03
		0.95-1.5	1.7766E-06	1.75E-04	4.16E-04	6.60E-03	1.96E-02	2.54E-02
		0.49-0.95	7.54079E-06	3.22E-04	1.38E-03	1.39E-02	4.19E-02	6.09E-02
		<0.49	6.58904E-06	2.64E-04	1.23E-03	1.05E-02	3.54E-02	7.46E-02
	Winter	7.2-10.0	<LOD	9.28E-05	1.94E-04	8.72E-04	3.22E-03	3.34E-03
		3.0-7.2	1.74E-05	5.13E-04	1.39E-03	5.76E-03	1.91E-02	1.83E-02
		1.5-3.0	8.93181E-05	2.25E-03	6.00E-03	2.69E-02	8.20E-02	7.91E-02
		0.95-1.5	0.000273323	7.57E-03	2.13E-02	1.17E-01	3.12E-01	3.22E-01
		0.49-0.95	0.000148131	1.07E-02	3.05E-02	1.89E-01	4.61E-01	4.69E-01
		<0.49	2.25736E-05	4.03E-03	1.12E-02	6.72E-02	2.10E-01	1.69E-01
Urban site	Spring	7.2-10.0	<LOD	3.78E-05	1.38E-04	3.50E-04	1.42E-03	1.60E-03
		3.0-7.2	<LOD	5.07E-05	1.64E-04	4.97E-04	2.40E-03	2.59E-03
		1.5-3.0	<LOD	7.46E-05	1.85E-04	5.80E-04	2.82E-03	3.39E-03
		0.95-1.5	<LOD	1.08E-04	3.02E-04	1.50E-03	5.92E-03	8.34E-03
		0.49-0.95	4.31948E-06	1.38E-04	5.25E-04	4.04E-03	1.40E-02	2.34E-02
		<0.49	1.11038E-05	3.71E-04	1.71E-03	8.02E-03	3.12E-02	3.60E-02
	Summer	7.2-10.0	<LOD	1.79E-05	7.44E-05	<LOD	5.71E-04	<LOD
		3.0-7.2	<LOD	2.25E-05	9.40E-05	2.37E-04	1.09E-03	1.05E-03
		1.5-3.0	<LOD	2.16E-05	8.68E-05	<LOD	9.02E-04	1.47E-03
		0.95-1.5	<LOD	4.61E-05	1.79E-04	6.16E-04	2.40E-03	2.85E-03
		0.49-0.95	<LOD	6.64E-05	3.23E-04	1.53E-03	5.01E-03	6.43E-03
		<0.49	1.8791E-05	8.30E-04	4.49E-03	3.07E-02	1.00E-01	1.00E-01
	Autumn	7.2-10.0	<LOD	1.50E-05	6.79E-05	3.36E-04	9.60E-04	2.55E-03
		3.0-7.2	<LOD	4.27E-05	1.83E-04	9.38E-04	3.34E-03	4.20E-03
		1.5-3.0	<LOD	6.63E-05	2.53E-04	1.94E-03	6.86E-03	6.88E-02
		0.95-1.5	<LOD	1.93E-04	7.11E-04	7.31E-03	2.21E-02	2.65E-02
		0.49-0.95	6.88189E-06	3.63E-04	1.62E-03	1.61E-02	4.75E-02	7.05E-02
		<0.49	1.56673E-05	5.25E-04	2.45E-03	1.76E-02	6.06E-02	5.68E-02
	Winter	7.2-10.0	2.63562E-06	8.05E-05	2.51E-04	6.78E-04	2.56E-03	2.68E-03
		3.0-7.2	7.51639E-06	1.93E-04	6.04E-04	2.18E-03	7.34E-03	7.14E-03
		1.5-3.0	2.40866E-05	7.47E-04	2.35E-03	1.09E-02	3.38E-02	3.49E-02
		0.95-1.5	0.000100544	2.95E-03	9.27E-03	5.31E-02	1.48E-01	1.60E-01

	0.49-0.95	0.000120311	4.62E-03	1.55E-02	1.01E-01	2.54E-01	2.88E-01
	<0.49	5.32004E-05	3.39E-03	1.29E-02	9.54E-02	2.64E-01	2.60E-01

quivalent BEQchem; A-F: size fractions of PM (A:7.2-10; B: 3-7.2; C 1.5-3; D: 0.95-1.5; E: 0.49-0.95 a

Benzo(k)fl	Benzo(a)p	Indeno(12	Dibenz(ah	Benzo(ghi)per	2378-TCDF	12378-PeC	23478-PeC	123478-Hx
4.26E-03	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOQ	<LOQ	<LOQ
1.04E-02	<LOD	3.00E-03	<LOD	6.08E-06	<LOQ	<LOQ	<LOQ	<LOQ
2.36E-02	<LOD	8.04E-03	<LOD	2.49E-05	<LOQ	1.23E-06	<LOQ	<LOQ
7.86E-02	<LOD	2.46E-02	5.14E-03	8.34E-05	2.30E-04	1.38E-05	1.05E-03	2.30E-04
1.84E-01	8.17E-04	4.51E-02	1.10E-02	1.35E-04	3.76E-04	2.65E-05	1.99E-03	3.92E-04
2.29E-01	8.89E-04	7.68E-02	1.54E-02	2.89E-04	2.16E-04	1.68E-05	1.22E-03	2.87E-04
<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOQ	<LOQ	<LOQ
1.13E-02	<LOD	3.15E-03	<LOD	9.75E-06	<LOQ	<LOQ	<LOQ	<LOQ
2.92E-02	<LOD	8.28E-03	<LOD	1.23E-05	<LOQ	<LOQ	<LOQ	<LOQ
1.18E-02	<LOD	3.74E-03	<LOD	8.59E-06	<LOQ	<LOQ	9.16E-05	<LOQ
1.89E-02	<LOD	7.24E-03	<LOD	1.61E-05	<LOQ	1.84E-06	2.28E-04	5.90E-05
3.56E-02	<LOD	1.12E-02	<LOD	5.23E-05	2.61E-04	1.40E-05	1.26E-03	2.70E-04
<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOQ	7.63E-05	<LOQ
1.17E-02	<LOD	2.89E-03	<LOD	<LOD	1.50E-04	2.97E-06	4.78E-04	1.00E-04
3.43E-02	<LOD	9.15E-03	<LOD	8.50E-06	4.36E-04	1.25E-05	1.37E-03	2.10E-04
1.86E-01	<LOD	3.49E-02	9.11E-03	8.44E-05	2.14E-03	9.10E-05	6.64E-03	1.05E-03
4.48E-01	8.07E-03	1.53E-01	3.09E-02	5.93E-04	4.45E-03	1.82E-04	1.29E-02	1.80E-03
4.78E-01	4.60E-03	1.63E-01	3.24E-02	6.48E-04	4.89E-03	2.42E-04	1.88E-02	2.30E-03
2.53E-02	<LOD	6.58E-03	<LOD	1.77E-05	1.30E-04	5.32E-06	2.80E-04	4.50E-05
1.42E-01	4.50E-03	3.99E-02	1.06E-02	1.60E-04	3.98E-04	1.60E-05	9.11E-04	1.43E-04
5.60E-01	1.08E-02	1.44E-01	4.03E-02	5.29E-04	1.86E-03	5.35E-05	1.97E-03	3.58E-04
2.25E+00	7.83E-02	6.10E-01	1.42E-01	2.00E-03	3.38E-03	1.83E-04	7.90E-03	1.17E-03
3.41E+00	8.74E-02	8.36E-01	1.89E-01	2.55E-03	6.38E-03	3.54E-04	1.73E-02	2.57E-03
1.14E+00	2.37E-02	2.25E-01	5.94E-02	6.42E-04	6.31E-03	1.13E-04	8.28E-03	<LOQ
1.31E-02	<LOD	3.62E-03	<LOD	2.61E-05	<LOQ	<LOQ	<LOQ	<LOQ
1.93E-02	<LOD	6.58E-03	<LOD	3.30E-05	3.82E-05	3.31E-06	1.79E-04	1.99E-05
2.54E-02	<LOD	7.60E-03	<LOD	1.60E-05	<LOQ	2.76E-06	2.15E-04	5.83E-05
7.04E-02	<LOD	2.09E-02	4.99E-03	4.86E-05	<LOQ	<LOQ	<LOQ	<LOQ
1.60E-01	1.78E-03	5.93E-02	1.41E-02	2.47E-04	4.33E-04	2.74E-05	1.12E-03	5.22E-04
2.36E-01	1.98E-03	7.59E-02	1.43E-02	4.22E-04	1.51E-03	8.06E-05	4.52E-03	7.95E-04
<LOD	<LOD	<LOD	<LOD	1.23E-05	<LOQ	<LOQ	<LOQ	<LOQ
8.19E-03	<LOD	<LOD	<LOD	1.45E-05	<LOQ	7.09E-06	1.20E-03	5.26E-04
<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOQ	<LOQ	<LOQ
1.78E-02	<LOD	6.23E-03	<LOD	2.64E-05	<LOQ	2.42E-06	2.81E-04	1.25E-04
4.97E-02	<LOD	1.69E-02	<LOD	8.71E-05	<LOQ	<LOQ	8.28E-05	<LOQ
6.74E-01	2.75E-02	2.30E-01	4.03E-02	1.37E-03	6.60E-04	3.86E-05	3.24E-03	8.04E-04
7.49E-03	<LOD	3.56E-03	<LOD	2.06E-05	5.15E-03	3.31E-04	1.50E-02	3.31E-03
2.45E-02	<LOD	9.23E-03	<LOD	4.52E-05	2.65E-04	6.74E-06	5.41E-04	8.51E-05
7.56E-02	<LOD	2.41E-02	5.48E-03	9.63E-05	4.45E-04	1.66E-05	1.33E-03	1.83E-04
1.98E-01	5.75E-04	4.91E-02	1.16E-02	1.60E-04	1.35E-03	6.96E-05	4.56E-03	6.48E-04
4.89E-01	1.23E-02	1.69E-01	3.63E-02	6.69E-04	2.71E-03	1.45E-04	1.07E-02	1.43E-03
3.57E-01	1.43E-03	1.28E-01	2.42E-02	7.15E-04	3.91E-03	1.81E-04	1.38E-02	1.68E-03
1.83E-02	1.29E-04	5.84E-03	<LOD	3.01E-05	<LOQ	2.42E-06	1.50E-04	3.16E-05
5.04E-02	9.38E-04	1.62E-02	4.30E-03	7.52E-05	3.25E-04	1.45E-05	6.53E-04	9.51E-05
2.34E-01	4.24E-03	7.04E-02	1.65E-02	2.84E-04	6.72E-04	3.16E-05	1.52E-03	2.64E-04
1.12E+00	4.44E-02	3.44E-01	7.30E-02	1.25E-03	3.25E-03	1.38E-04	6.69E-03	1.32E-03

1.92E+00	9.17E-02	6.10E-01	1.23E-01	2.18E-03	5.40E-05	1.15E-06	1.03E-04	1.81E-05
1.71E+00	7.63E-02	5.13E-01	9.41E-02	2.13E-03	6.50E-03	4.20E-04	1.99E-02	3.19E-03

and F: < 0.49µm); Concentrations of chemicals used for the BEQchem modeling were taken fror

123678-Hx	234678-Hx	123789-Hx	1234678-H	1234789-H	OCDF	2378-TCDI	12378-PeC	123478-Hx
3.63E-06	1.52E-05	<LOQ	2.66E-06	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
6.34E-06	2.77E-05	<LOQ	5.82E-06	<LOQ	2.65E-07	<LOQ	<LOQ	<LOQ
3.61E-06	6.63E-05	<LOQ	1.57E-05	2.44E-06	8.21E-07	<LOQ	<LOQ	<LOQ
1.40E-04	4.31E-04	5.09E-05	8.74E-05	2.42E-05	3.36E-06	<LOQ	1.68E-04	1.61E-05
3.22E-04	1.01E-03	1.10E-04	1.98E-04	5.30E-05	7.40E-06	<LOQ	2.68E-04	4.05E-05
2.60E-04	1.01E-03	1.02E-04	2.04E-04	5.30E-05	7.06E-06	<LOQ	2.32E-04	3.33E-05
<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
<LOQ	<LOQ	<LOQ	6.08E-06	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
<LOQ	<LOQ	<LOQ	2.89E-05	1.85E-05	1.93E-06	<LOQ	<LOQ	<LOQ
1.88E-05	6.34E-05	6.26E-06	2.08E-05	5.88E-06	1.16E-06	<LOQ	<LOQ	<LOQ
3.67E-05	1.63E-04	2.18E-05	5.63E-05	1.64E-05	3.00E-06	<LOQ	<LOQ	<LOQ
2.16E-04	8.79E-04	9.43E-05	2.23E-04	7.03E-05	1.22E-05	<LOQ	1.87E-04	2.71E-05
9.72E-06	2.47E-05	<LOQ	6.72E-06	6.96E-07	3.19E-07	<LOQ	<LOQ	<LOQ
4.35E-05	1.53E-04	1.30E-05	3.21E-05	5.43E-06	1.61E-06	<LOQ	<LOQ	<LOQ
1.52E-04	4.31E-04	4.79E-05	1.01E-04	2.49E-05	4.40E-06	<LOQ	1.91E-04	1.94E-05
7.30E-04	2.38E-03	2.28E-04	5.00E-04	1.19E-04	2.37E-05	1.27E-04	1.09E-03	1.17E-04
1.59E-03	4.79E-03	4.57E-04	1.06E-03	2.62E-04	5.83E-05	4.82E-04	2.22E-03	2.32E-04
2.22E-03	9.43E-03	8.59E-04	2.25E-03	4.95E-04	1.32E-04	6.52E-04	2.78E-03	3.46E-04
3.11E-05	7.99E-05	1.01E-05	1.45E-05	3.02E-06	5.79E-07	<LOQ	8.57E-05	6.67E-06
1.23E-04	3.54E-04	3.71E-05	6.53E-05	1.46E-05	2.64E-06	1.01E-04	1.81E-04	3.47E-05
3.58E-04	9.48E-04	1.09E-04	1.64E-04	5.09E-05	5.97E-06	<LOQ	6.52E-04	5.99E-05
1.19E-03	2.98E-03	3.02E-04	5.76E-04	1.46E-04	1.94E-05	1.06E-03	1.88E-03	1.40E-04
2.35E-03	6.31E-03	5.77E-04	1.13E-03	3.02E-04	3.82E-05	1.83E-03	4.01E-03	2.60E-04
<LOQ	<LOQ	<LOQ	1.17E-03	2.73E-04	3.82E-05	2.91E-03	1.52E-03	<LOQ
<LOQ	<LOQ	<LOQ	4.38E-06	<LOQ	2.03E-07	<LOQ	<LOQ	<LOQ
3.31E-05	5.99E-05	<LOQ	1.78E-05	3.95E-06	7.27E-07	<LOQ	<LOQ	<LOQ
3.88E-05	1.00E-04	1.58E-05	3.15E-05	6.44E-06	9.03E-07	<LOQ	8.90E-05	<LOQ
<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
3.04E-04	9.35E-04	1.19E-04	2.81E-04	7.72E-05	9.58E-06	<LOQ	3.19E-04	<LOQ
5.27E-04	1.88E-03	2.05E-04	3.93E-04	9.52E-05	1.30E-05	1.73E-04	7.78E-04	8.40E-05
<LOQ	<LOQ	<LOQ	1.96E-06	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
2.16E-04	9.21E-04	1.94E-04	3.25E-04	1.35E-04	2.71E-05	<LOQ	1.64E-04	<LOQ
<LOQ	<LOQ	<LOQ	2.76E-05	1.23E-05	2.66E-06	<LOQ	<LOQ	<LOQ
6.35E-05	2.25E-04	4.98E-05	8.69E-05	2.96E-05	8.15E-06	<LOQ	6.04E-05	<LOQ
1.16E-05	3.89E-05	7.65E-06	1.20E-05	1.81E-06	8.53E-07	<LOQ	<LOQ	<LOQ
3.45E-04	1.69E-03	2.93E-04	4.87E-04	1.84E-04	3.09E-05	7.59E-05	4.66E-04	<LOQ
2.90E-03	6.39E-03	7.06E-04	1.23E-03	3.43E-04	4.05E-05	1.80E-03	3.38E-03	2.95E-04
5.86E-05	1.51E-04	1.50E-05	3.46E-05	6.40E-06	1.16E-06	<LOQ	1.41E-04	1.82E-05
1.38E-04	3.86E-04	4.04E-05	8.86E-05	2.08E-05	2.81E-06	<LOQ	2.07E-04	2.35E-05
4.76E-04	1.73E-03	1.49E-04	3.36E-04	7.79E-05	1.12E-05	2.67E-04	9.37E-04	1.07E-04
1.20E-03	3.97E-03	3.58E-04	7.55E-04	2.13E-04	2.32E-05	2.71E-04	2.30E-03	2.07E-04
1.23E-03	4.26E-03	3.95E-04	7.59E-04	1.89E-04	1.95E-05	6.36E-04	2.26E-03	2.23E-04
1.36E-05	6.12E-05	8.53E-06	1.15E-05	3.05E-06	4.90E-07	<LOQ	<LOQ	<LOQ
6.96E-05	2.28E-04	2.88E-05	5.15E-05	1.15E-05	1.74E-06	4.31E-05	1.17E-04	1.14E-05
2.10E-04	5.62E-04	6.45E-05	1.13E-04	2.76E-05	3.97E-06	6.68E-05	2.98E-04	2.62E-05
1.35E-03	1.85E-03	6.17E-04	4.85E-04	1.50E-04	1.83E-05	7.66E-04	2.12E-03	1.54E-04

8.49E-06	2.31E-05	<LOQ	5.85E-06	<LOQ	2.81E-07	<LOQ	<LOQ	<LOQ
3.64E-03	8.60E-03	8.57E-04	1.53E-03	4.12E-04	5.06E-05	2.02E-03	4.99E-03	4.34E-04

n Degrendele et al. (2016, 2014) and (Okonski et al., 2014).

123678-Hx	123789-Hx	1234678-H	OCDD	PCB 77	PCB 81	PCB 126	PCB 169
<LOQ	<LOQ	4.13E-06	2.50E-07	1.95E-08	<LOQ	1.75E-06	<LOQ
<LOQ	<LOQ	8.12E-06	1.97E-07	<LOQ	1.69E-08	2.78E-06	<LOQ
<LOQ	<LOQ	2.12E-05	6.22E-07	<LOQ	1.48E-08	3.21E-06	3.59E-09
3.52E-05	2.61E-05	1.32E-04	3.17E-06	2.37E-08	6.15E-08	1.32E-05	1.31E-08
8.80E-05	4.56E-05	3.03E-04	7.12E-06	4.04E-08	1.63E-07	2.58E-05	3.21E-08
8.32E-05	3.97E-05	2.77E-04	5.52E-06	1.78E-07	3.90E-07	4.99E-05	6.88E-08
<LOQ	<LOQ	<LOQ	1.20E-07	1.20E-07	<LOQ	5.33E-06	<LOQ
<LOQ	<LOQ	6.24E-06	2.17E-07	1.10E-07	4.47E-08	6.84E-06	<LOQ
<LOQ	<LOQ	3.92E-05	8.98E-07	<LOQ	2.16E-08	<LOQ	<LOQ
<LOQ	<LOQ	2.15E-05	6.98E-07	<LOQ	3.54E-08	5.66E-06	<LOQ
<LOQ	<LOQ	6.97E-05	2.64E-06	2.47E-08	4.10E-08	4.63E-06	4.59E-09
6.95E-05	3.76E-05	4.53E-04	1.44E-05	1.26E-07	2.32E-07	2.58E-05	2.45E-08
<LOQ	<LOQ	1.11E-05	6.86E-07	1.57E-08	3.22E-08	2.36E-06	2.36E-09
<LOQ	<LOQ	4.30E-05	1.96E-06	1.16E-07	1.44E-07	9.67E-06	8.77E-09
5.16E-05	3.02E-05	1.91E-04	5.79E-06	1.10E-07	2.38E-07	2.32E-05	2.52E-08
2.65E-04	1.65E-04	1.08E-03	2.76E-05	5.29E-07	1.10E-06	1.35E-04	1.35E-07
5.44E-04	2.87E-04	2.03E-03	5.10E-05	1.53E-06	2.99E-06	2.78E-04	2.92E-07
9.69E-04	4.40E-04	2.61E-03	5.41E-05	6.63E-06	1.40E-05	6.99E-04	9.69E-07
7.91E-06	<LOQ	1.97E-05	4.05E-07	3.13E-07	5.96E-07	2.88E-05	1.99E-08
2.07E-05	1.56E-05	8.17E-05	1.48E-06	4.31E-07	1.09E-06	9.17E-05	6.69E-08
1.21E-04	5.78E-05	2.61E-04	4.45E-06	9.22E-07	<LOQ	<LOQ	<LOQ
3.21E-04	1.27E-04	8.90E-04	1.62E-05	2.25E-06	9.13E-06	7.82E-04	6.05E-07
8.48E-04	3.28E-04	1.76E-03	3.14E-05	4.31E-06	1.67E-05	1.54E-03	1.24E-06
<LOQ	<LOQ	1.80E-03	3.62E-05	1.04E-06	3.51E-06	4.05E-04	<LOQ
<LOQ	<LOQ	5.82E-06	6.64E-07	5.99E-07	7.68E-07	2.17E-05	8.31E-09
<LOQ	<LOQ	2.00E-05	4.55E-07	7.54E-07	1.10E-06	3.12E-05	<LOQ
<LOQ	<LOQ	3.85E-05	1.20E-06	5.54E-07	5.86E-07	2.26E-05	1.76E-08
<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
<LOQ	<LOQ	3.99E-04	9.10E-06	1.28E-06	1.99E-06	1.09E-04	1.09E-07
1.95E-04	7.04E-05	5.59E-04	1.20E-05	7.18E-06	1.00E-05	3.95E-04	3.40E-07
<LOQ	<LOQ	6.95E-06	1.01E-06	3.16E-07	4.10E-07	1.57E-05	6.05E-09
<LOQ	<LOQ	4.72E-04	1.26E-05	7.37E-07	9.66E-07	6.25E-05	7.64E-08
<LOQ	<LOQ	3.31E-05	8.00E-07	2.43E-07	3.51E-07	1.72E-05	<LOQ
<LOQ	<LOQ	1.16E-04	3.50E-06	3.09E-07	3.64E-07	2.46E-05	2.61E-08
<LOQ	<LOQ	1.44E-05	1.22E-06	4.43E-07	5.13E-07	2.48E-05	1.34E-08
<LOQ	<LOQ	8.50E-04	2.25E-05	3.36E-06	4.33E-06	2.41E-04	2.12E-07
7.74E-04	2.53E-04	1.89E-03	3.74E-05	4.89E-06	1.70E-05	1.37E-03	1.11E-06
2.23E-05	<LOQ	7.30E-05	1.69E-06	1.19E-06	1.68E-06	8.01E-05	4.94E-08
6.84E-05	2.28E-05	2.06E-04	5.86E-06	6.65E-07	1.07E-06	1.01E-04	8.53E-08
2.65E-04	8.84E-05	8.54E-04	1.93E-05	1.22E-06	2.52E-06	3.19E-04	3.08E-07
7.12E-04	2.44E-04	1.99E-03	4.45E-05	2.35E-06	5.16E-06	6.68E-04	6.91E-07
6.62E-04	2.46E-04	1.99E-03	4.55E-05	4.26E-06	7.31E-06	6.82E-04	7.05E-07
<LOQ	<LOQ	1.66E-05	6.98E-07	4.53E-07	7.87E-07	3.08E-05	1.44E-08
1.41E-05	9.60E-06	5.94E-05	1.57E-06	9.00E-07	2.16E-06	8.06E-05	4.29E-08
6.47E-05	3.11E-05	1.55E-04	3.29E-06	9.11E-07	2.47E-06	1.56E-04	1.06E-07
3.36E-04	<LOQ	6.76E-04	1.23E-05	2.14E-06	6.91E-06	5.38E-04	4.16E-07

<LOQ	<LOQ	1.38E-05	5.55E-07	8.26E-07	1.01E-06	2.57E-05	1.40E-08
1.03E-03	3.92E-04	2.49E-03	4.79E-05	7.07E-06	1.87E-05	1.63E-03	1.95E-06

PCB 114	**PCB 123**	**PCB 156**	**PCB 157**	**Chlorpyrif**	**Diazinon**	**Diuron**	**Prochloraz**	**Terbuthyla**
6.31E-10	<LOQ	5.84E-09	2.66E-09	2.74E-08	1.30E-08	2.74E-07	8.06E-07	2.34E-05
1.22E-10	<LOQ	6.32E-09	1.86E-09	1.52E-08	2.02E-08	5.97E-07	1.81E-06	5.15E-05
3.92E-10	<LOQ	6.09E-09	2.09E-09	2.84E-08	7.68E-09	9.20E-07	7.08E-07	3.93E-05
6.17E-10	<LOQ	1.46E-08	6.00E-09	2.03E-08	3.24E-09	8.45E-07	3.74E-07	1.77E-05
8.43E-10	<LOQ	2.73E-08	9.92E-09	2.43E-08	2.70E-09	1.29E-06	2.75E-07	9.34E-06
1.50E-09	<LOQ	5.80E-08	1.93E-08	6.79E-08	1.03E-08	5.69E-06	2.95E-07	2.40E-05
1.38E-09	<LOQ	2.52E-08	7.75E-09	<LOQ	1.70E-08	2.61E-06	3.62E-06	2.25E-05
<LOQ	<LOQ	2.41E-08	6.00E-09	<LOQ	8.65E-09	4.30E-06	7.73E-06	3.97E-05
<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1.42E-08	5.97E-06	2.87E-06	3.22E-05
3.68E-10	<LOQ	1.18E-08	3.09E-09	<LOQ	1.89E-08	6.29E-06	9.44E-07	2.06E-05
<LOQ	4.56E-10	5.76E-09	1.77E-09	<LOQ	9.52E-09	8.45E-06	4.33E-07	7.82E-06
9.32E-10	<LOQ	2.61E-08	7.71E-09	1.12E-08	3.14E-09	4.16E-05	6.29E-07	6.86E-06
1.41E-10	<LOQ	5.32E-09	1.74E-09	<LOQ	7.46E-09	3.98E-07	2.16E-07	LOQ
4.63E-10	<LOQ	2.44E-08	5.96E-09	<LOQ	5.52E-09	6.22E-07	2.56E-07	LOQ
6.31E-10	<LOQ	4.37E-08	1.34E-08	<LOQ	1.03E-08	8.95E-07	3.34E-07	3.81E-07
3.12E-09	<LOQ	2.07E-07	6.25E-08	<LOQ	1.25E-08	1.89E-06	<LOQ	<LOQ
8.93E-09	8.61E-09	4.12E-07	1.24E-07	<LOQ	<LOQ	3.51E-06	<LOQ	<LOQ
2.46E-08	<LOQ	1.18E-06	3.19E-07	<LOQ	3.56E-08	1.27E-05	<LOQ	<LOQ
2.26E-09	<LOQ	5.80E-08	1.62E-08	<LOQ	1.02E-08	<LOQ	<LOQ	<LOQ
3.85E-09	3.34E-09	1.19E-07	3.42E-08	<LOQ	8.22E-09	1.49E-07	1.57E-07	<LOQ
<LOQ	<LOQ	5.18E-07	<LOQ	<LOQ	2.92E-09	<LOQ	<LOQ	<LOQ
3.22E-08	<LOQ	6.62E-07	2.25E-07	<LOQ	3.46E-09	5.22E-07	<LOQ	<LOQ
8.14E-08	<LOQ	1.40E-06	4.46E-07	<LOQ	<LOQ	7.21E-07	<LOQ	<LOQ
2.10E-08	<LOQ	3.66E-07	1.39E-07	1.52E-08	<LOQ	2.39E-06	<LOQ	5.72E-07
2.84E-09	<LOQ	8.46E-08	1.82E-08	LOQ	6.60E-09	2.24E-07	3.93E-07	3.32E-05
2.33E-09	<LOQ	1.01E-07	2.30E-08	LOQ	5.41E-10	3.48E-07	4.33E-07	3.98E-05
1.93E-09	<LOQ	5.55E-08	1.48E-08	1.12E-08	1.28E-08	3.23E-07	3.74E-07	2.57E-05
<LOQ	<LOQ	<LOQ	<LOQ	3.14E-08	4.76E-09	2.49E-07	2.95E-07	1.12E-05
4.45E-09	<LOQ	1.36E-07	3.85E-08	1.72E-08	<LOQ	3.98E-07	1.77E-07	1.72E-06
1.77E-08	9.96E-09	9.55E-07	9.96E-08	3.04E-08	<LOQ	3.46E-06	<LOQ	7.24E-06
1.49E-09	<LOQ	5.48E-08	1.13E-08	LOQ	1.51E-08	1.49E-07	1.95E-06	7.43E-06
2.24E-09	<LOQ	1.04E-07	2.44E-08	1.12E-08	1.04E-08	4.23E-07	3.24E-06	1.03E-05
<LOQ	<LOQ	3.27E-08	<LOQ	1.22E-08	1.28E-08	2.88E-06	1.44E-06	1.77E-05
1.27E-09	<LOQ	4.35E-08	1.11E-08	6.08E-09	5.95E-09	5.22E-07	2.95E-07	8.39E-06
1.94E-09	<LOQ	6.94E-08	1.46E-08	1.07E-07	8.87E-09	1.67E-06	3.54E-07	9.53E-06
7.45E-09	<LOQ	2.84E-07	5.75E-08	3.14E-08	2.31E-08	8.73E-06	3.15E-07	3.85E-05
1.56E-07	<LOQ	1.38E-06	3.85E-07	<LOQ	1.09E-08	1.24E-07	2.56E-07	7.63E-07
4.76E-09	<LOQ	2.61E-07	5.32E-08	<LOQ	<LOQ	3.73E-07	5.51E-07	<LOQ
6.21E-09	<LOQ	2.30E-07	5.57E-08	<LOQ	1.59E-08	<LOQ	2.95E-07	<LOQ
8.48E-09	<LOQ	5.80E-07	1.67E-07	<LOQ	1.46E-08	<LOQ	2.95E-07	1.14E-06
2.45E-08	<LOQ	1.14E-06	3.27E-07	<LOQ	<LOQ	6.46E-07	<LOQ	<LOQ
2.77E-08	<LOQ	1.35E-06	3.51E-07	<LOQ	8.54E-09	7.21E-07	<LOQ	5.72E-07
2.73E-09	<LOQ	1.06E-07	2.02E-08	<LOQ	9.73E-09	<LOQ	9.83E-08	<LOQ
5.18E-09	<LOQ	1.91E-07	4.10E-08	<LOQ	7.57E-10	7.46E-08	<LOQ	<LOQ
8.24E-09	<LOQ	1.75E-07	4.96E-08	<LOQ	<LOQ	1.74E-07	<LOQ	<LOQ
5.03E-08	<LOQ	4.30E-07	1.30E-07	<LOQ	2.49E-09	<LOQ	<LOQ	<LOQ

2.80E-09	<LOQ	1.12E-07	1.71E-08	<LOQ	<LOQ	1.49E-07	7.86E-08	<LOQ
1.87E-07	<LOQ	1.63E-06	4.89E-07	6.69E-08	<LOQ	4.97E-07	2.16E-07	2.29E-06

Carbendaz	Fenitrothi	Isoproturo	Metamitron
8.9E-09	LOQ	1.98E-05	2.37E-06
2.79E-08	LOQ	3.41E-05	5.88E-06
1.19E-08	LOQ	2.46E-05	LOQ
3.84E-09	LOQ	1.02E-05	LOQ
LOQ	LOQ	2.82E-06	LOQ
LOQ	LOQ	1.28E-05	LOQ
1.66E-08	LOQ	LOQ	LOQ
4.13E-08	LOQ	1.57E-07	6.89E-07
1.76E-08	LOQ	LOQ	3.9E-07
8.09E-09	LOQ	2.09E-07	LOQ
8.09E-09	LOQ	LOQ	LOQ
1.27E-08	LOQ	5.75E-07	LOQ
2.43E-09	LOQ	3.4E-06	LOQ
2.02E-10	LOQ	1.73E-06	LOQ
2.99E-08	LOQ	9.46E-06	LOQ
LOQ	LOQ	1.31E-06	LOQ
LOQ	LOQ	2.61E-07	LOQ
5.06E-09	LOQ	1.78E-06	LOQ
LOQ	LOQ	1.57E-07	LOQ
LOQ	LOQ	5.75E-07	LOQ
LOQ	LOQ	LOQ	4.8E-07
LOQ	LOQ	LOQ	LOQ
LOQ	LOQ	LOQ	LOQ
LOQ	LOQ	2.61E-07	LOQ
1.44E-08	LOQ	2.53E-05	LOQ
2.12E-08	LOQ	3.27E-05	6.89E-07
1.25E-08	LOQ	1.25E-05	LOQ
LOQ	LOQ	4.97E-06	LOQ
LOQ	LOQ	1.46E-06	LOQ
3.03E-09	LOQ	9.36E-06	LOQ
2.45E-08	LOQ	LOQ	LOQ
1.98E-08	LOQ	LOQ	LOQ
1.42E-08	LOQ	LOQ	LOQ
4.05E-09	LOQ	LOQ	LOQ
3.36E-08	LOQ	LOQ	LOQ
LOQ	LOQ	5.75E-07	LOQ
1.21E-09	LOQ	5.7E-06	LOQ
7.28E-09	LOQ	9.26E-06	LOQ
4.25E-09	LOQ	3.71E-06	LOQ
LOQ	LOQ	1.67E-06	LOQ
2.02E-10	LOQ	1.05E-07	LOQ
LOQ	LOQ	1.93E-06	LOQ
LOQ	LOQ	2.09E-07	LOQ
LOQ	LOQ	5.75E-07	LOQ
LOQ	LOQ	LOQ	LOQ
LOQ	LOQ	LOQ	LOQ

LOQ	2E-05	LOQ	LOQ
LOQ	LOQ	2.09E-07	LOQ

Table S2 -2: Contribution of individual analyzed compounds to calculated ER-mediated bioanalytical e
modeling were taken from Degrendele et al. (2016, 2014) and (Okonski et al., 2014).

Site	Season	Particle size (μm)	β-HCH	o,p'-DDE	p,p'-DDE	o,p'-DDD	p,p'-DDD	o,p	p,p'-DDT
Rural Site	Spring	7.2-10.0	5.61E-07	2.69E-07	7.48E-07	3.29E-07	6.36E-08	0	5.59E-07
		3.0-7.2	LOD	1.08E-07	5.51E-07	1.65E-07	6.94E-08	##	4.97E-07
		1.5-3.0	LOD	1.62E-07	7.01E-07	2.47E-07	8.67E-08	##	7.14E-07
		0.95-1.5	2.81E-07	2.16E-07	9.88E-07	7.40E-07	1.45E-07	##	1.77E-06
		0.49-0.95	8.42E-07	2.69E-07	1.45E-06	6.58E-07	2.66E-07	##	2.68E-06
		<0.49	1.78E-05	3.23E-07	1.16E-06	1.32E-06	1.33E-07	##	4.85E-06
	Summer	7.2-10.0	LOD	1.62E-07	7.01E-07	1.07E-06	2.43E-07	##	<LOD
		3.0-7.2	LOD	1.62E-07	6.05E-07	1.07E-06	2.89E-07	##	9.32E-08
		1.5-3.0	1.4E-07	1.08E-07	4.37E-07	6.58E-07	2.14E-07	<L(	<LOD
		0.95-1.5	LOD	5.39E-08	3.89E-07	6.58E-07	2.02E-07	<L(	2.07E-08
		0.49-0.95	1.96E-06	1.08E-07	6.65E-07	1.07E-06	2.83E-07	##	2.38E-07
		<0.49	5.61E-06	3.77E-07	1.35E-06	1.23E-06	4.45E-07	##	3.62E-07
	Autumn	7.2-10.0	4.21E-07	5.39E-08	3.89E-07	5.76E-07	1.50E-07	##	<LOD
		3.0-7.2	LOD	1.62E-07	9.40E-07	1.07E-06	4.05E-07	##	<LOD
		1.5-3.0	2.81E-06	2.16E-07	1.31E-06	1.48E-06	5.95E-07	<L(	0.00E+00
		0.95-1.5	2.25E-06	5.39E-07	3.18E-06	3.37E-06	1.52E-06	##	1.86E-07
		0.49-0.95	1.68E-06	7.01E-07	4.89E-06	4.94E-06	2.43E-06	##	5.38E-07
		<0.49	1.26E-06	5.39E-07	3.66E-06	3.87E-06	2.04E-06	##	1.44E-06
	Winter	7.2-10.0	7.02E-07	2.69E-07	4.01E-07	2.47E-07	1.10E-07	##	1.52E-06
		3.0-7.2	2.81E-07	2.69E-07	5.45E-07	4.94E-07	2.14E-07	##	1.43E-06
		1.5-3.0	1.82E-06	4.31E-07	6.05E-07	4.94E-07	2.49E-07	##	1.56E-06
		0.95-1.5	1.26E-06	9.16E-07	1.62E-06	2.22E-06	1.00E-06	##	3.41E-06
		0.49-0.95	8.42E-07	1.29E-06	2.39E-06	2.63E-06	1.29E-06	##	4.18E-06
		<0.49	2.53E-06	9.7E-07	2.20E-06	2.22E-06	1.18E-06	##	1.02E-05
Urban site	Spring	7.2-10.0	7.86E-06	2.69E-07	4.07E-07	1.32E-06	3.35E-07	##	6.21E-08
		3.0-7.2	1.05E-05	3.77E-07	5.57E-07	1.65E-06	4.10E-07	##	7.25E-08
		1.5-3.0	LOD	2.16E-07	4.07E-07	1.32E-06	3.24E-07	##	3.11E-08
		0.95-1.5	1.12E-06	2.69E-07	4.61E-07	1.48E-06	3.76E-07	##	6.21E-08
		0.49-0.95	LOD	4.31E-07	7.90E-07	2.55E-06	6.94E-07	##	1.45E-07
		<0.49	7.3E-06	7.01E-07	1.23E-06	3.78E-06	1.09E-06	##	4.76E-07
	Summer	7.2-10.0	6.74E-06	2.69E-07	4.07E-07	1.40E-06	3.29E-07	##	6.21E-08
		3.0-7.2	5.61E-07	3.77E-07	6.65E-07	2.22E-06	6.18E-07	##	2.17E-07
		1.5-3.0	2.25E-06	2.69E-07	4.13E-07	1.48E-06	3.81E-07	##	2.59E-07
		0.95-1.5	9.82E-07	3.23E-07	4.79E-07	1.81E-06	4.62E-07	##	1.24E-07
		0.49-0.95	1.38E-05	3.77E-07	5.63E-07	1.97E-06	5.72E-07	##	2.59E-07
		<0.49	5.75E-06	7.54E-07	1.17E-06	3.54E-06	9.02E-07	##	4.04E-07
	Autumn	7.2-10.0	6.88E-06	5.39E-07	1.24E-06	2.30E-06	7.28E-07	##	3.42E-07
		3.0-7.2	6.6E-06	6.47E-07	1.25E-06	2.63E-06	6.65E-07	##	2.48E-07
		1.5-3.0	4.91E-06	5.39E-07	1.08E-06	2.71E-06	7.17E-07	##	2.90E-07
		0.95-1.5	2.81E-07	8.08E-07	1.66E-06	3.70E-06	1.25E-06	##	5.18E-07
		0.49-0.95	4.21E-07	1.19E-06	2.43E-06	5.59E-06	2.02E-06	##	1.18E-06
		<0.49	2.81E-07	1.19E-06	2.86E-06	7.57E-06	2.27E-06	##	1.31E-06
	nter	7.2-10.0	1.25E-05	3.77E-07	3.83E-07	1.07E-06	2.31E-07	##	LOD
		3.0-7.2	7.44E-06	4.31E-07	4.49E-07	1.23E-06	2.25E-07	##	8.28E-08
		1.5-3.0	3.37E-06	6.47E-07	6.71E-07	1.56E-06	3.35E-07	##	1.14E-07

Wir	0.95-1.5	2.81E-06	8.62E-07	1.05E-06	2.39E-06	5.90E-07	##	1.35E-07
	0.49-0.95	1.68E-06	1.02E-06	1.15E-06	2.88E-06	7.92E-07	##	1.55E-07
	<0.49	2.39E-06	1.02E-06	1.37E-06	4.03E-06	1.07E-06	##	4.14E-07

quivalent BEQchem; A-F: size fractions of PM (A: 7.2-10.0; B: 3-7.2; C 1.5-3; D: 0.95-1.5; E: (

Dimethoat	Benzo[a]a	Benzo[a]p	Chlorpyrifo	Diazinon	Terbuthyla	Carbendaz	BDE-47	Fluoranthe
<LOD	2.55E-05	<LOD	5.906E-08	3.16E-07	1.98E-05	<LOD	3.05E-08	7.76E-07
<LOD	2.24E-06	<LOD	3.28E-08	4.92E-07	4.35E-05	<LOD	7.77E-09	2.53E-06
1.01E-11	4.60E-06	<LOD	6.12E-08	1.87E-07	3.32E-05	<LOD	8.31E-09	6.84E-06
9.10E-11	1.54E-05	<LOD	4.37E-08	7.90E-08	1.50E-05	<LOD	1.65E-08	2.82E-06
2.63E-10	4.69E-05	3.73E-05	5.25E-08	6.58E-08	7.89E-06	<LOD	2.36E-08	2.49E-06
5.36E-10	3.70E-05	4.06E-05	1.47E-07	2.50E-07	2.03E-05	<LOD	1.94E-08	4.93E-06
<LOD	<LOD	<LOD	<LOD	4.13E-07	1.90E-05	3.33E-07	2.89E-08	1.01E-06
<LOD	2.17E-06	LOD	<LOD	2.11E-07	3.35E-05	1.05E-06	1.13E-08	3.54E-06
<LOD	6.51E-06	LOD	<LOD	3.45E-07	2.72E-05	4.47E-07	4.32E-09	7.76E-06
<LOD	1.67E-06	LOD	<LOD	4.61E-07	1.74E-05	1.44E-07	4.63E-09	4.01E-05
<LOD	1.83E-06	LOD	<LOD	2.32E-07	6.60E-06	<LOD	1.61E-08	7.38E-05
<LOD	4.36E-06	LOD	2.41E-08	7.63E-08	5.80E-06	<LOD	1.17E-08	6.06E-05
<LOD	<LOD	LOD	<LOD	1.82E-07	<LOD	6.21E-07	2.01E-09	2.13E-05
<LOD	2.18E-06	LOD	<LOD	1.34E-07	<LOD	1.55E-06	5.62E-09	1.18E-04
<LOD	7.69E-06	LOD	<LOD	2.50E-07	3.22E-07	6.59E-07	1.22E-08	5.17E-04
<LOD	6.57E-05	LOD	<LOD	3.05E-07	<LOD	3.03E-07	3.75E-08	1.74E-03
<LOD	1.38E-04	3.68E-04	<LOD	<LOD	<LOD	3.03E-07	5.37E-08	2.46E-03
<LOD	1.04E-04	2.10E-04	<LOD	8.66E-07	<LOD	4.77E-07	6.41E-08	9.25E-04
<LOD	8.69E-06	LOD	<LOD	2.47E-07	<LOD	9.09E-08	1.01E-08	2.25E-06
<LOD	5.74E-05	2.05E-04	<LOD	2.00E-07	<LOD	7.58E-09	1.59E-08	4.22E-06
<LOD	2.68E-04	4.95E-04	<LOD	7.11E-08	<LOD	1.12E-06	3.58E-08	6.23E-06
<LOD	1.17E-03	3.58E-03	<LOD	8.42E-08	<LOD	<LOD	9.81E-08	1.48E-05
<LOD	1.88E-03	3.99E-03	<LOD	LOD	<LOD	<LOD	1.58E-07	2.72E-05
<LOD	6.69E-04	1.08E-03	3.28E-08	LOD	4.83E-07	1.89E-07	1.35E-07	2.63E-05

<LOD	3.48E-06	<LOD	<LOD	1.61E-07	2.80E-05	<LOD	1.94E-08	4.12E-06
<LOD	4.95E-06	<LOD	<LOD	1.32E-08	3.37E-05	<LOD	2.23E-08	5.17E-06
<LOD	5.78E-06	<LOD	2.41E-08	3.11E-07	2.17E-05	<LOD	1.78E-08	4.97E-06
<LOD	1.50E-05	<LOD	6.78E-08	1.16E-07	9.50E-06	<LOD	2.42E-08	1.06E-05
<LOD	4.02E-05	8.12E-05	3.72E-08	<LOD	1.45E-06	<LOD	4.53E-08	1.52E-05
<LOD	7.99E-05	9.04E-05	6.56E-08	<LOD	6.12E-06	<LOD	1.83E-07	1.90E-04
<LOD	<LOD	<LOD	<LOD	3.68E-07	6.28E-06	5.38E-07	1.82E-08	3.44E-06
<LOD	2.36E-06	<LOD	2.41E-08	2.53E-07	8.70E-06	7.96E-07	6.26E-08	9.80E-06
<LOD	<LOD	<LOD	2.62E-08	3.11E-07	1.50E-05	4.70E-07	2.12E-08	1.52E-05
<LOD	6.14E-06	<LOD	1.31E-08	1.45E-07	7.09E-06	<LOD	2.53E-08	4.42E-05
<LOD	1.52E-05	<LOD	2.32E-07	2.16E-07	8.05E-06	<LOD	2.48E-08	8.33E-05
<LOD	3.06E-04	1.26E-03	6.78E-08	5.63E-07	3.25E-05	1.14E-07	1.27E-07	1.20E-04
<LOD	3.35E-06	<LOD	<LOD	2.66E-07	6.44E-07	9.17E-07	1.66E-08	1.85E-05
<LOD	9.35E-06	<LOD	<LOD	<LOD	<LOD	7.43E-07	3.04E-08	4.42E-05
<LOD	1.93E-05	<LOD	<LOD	3.87E-07	<LOD	5.30E-07	3.58E-08	1.71E-04
<LOD	7.29E-05	2.63E-05	<LOD	3.55E-07	9.66E-07	1.52E-07	8.23E-08	6.77E-04
<LOD	1.60E-04	5.62E-04	<LOD	<LOD	<LOD	1.26E-06	2.18E-07	1.06E-03
<LOD	1.75E-04	6.54E-05	<LOD	2.08E-07	4.83E-07	<LOD	5.07E-07	7.79E-04
2.02E-11	6.75E-06	5.88E-06	<LOD	2.37E-07	<LOD	4.55E-08	1.35E-08	8.67E-06
<LOD	2.17E-05	4.28E-05	<LOD	1.84E-08	<LOD	2.73E-07	2.77E-08	1.16E-05
<LOD	1.08E-04	1.94E-04	<LOD	<LOD	<LOD	1.59E-07	3.77E-08	1.71E-05

<LOD	5.29E-04	2.03E-03	<LOD	6.05E-08	<LOD	<LOD	2.01E-07	2.48E-05
<LOD	1.01E-03	4.18E-03	<LOD	<LOD	<LOD	7.58E-09	2.47E-07	3.17E-05
<LOD	9.51E-04	3.48E-03	1.44E-07	<LOD	1.93E-06	<LOD	6.44E-07	8.50E-05

).49-0.95 and F: < 0.49µm); Concentrations of chemicals used for the BEQchem

Isoproturo	Metamitrc	BDE-99	Terbufos	BDE-100
2.7E-06	8.88E-07	2.63E-10	<LOD	1.45E-09
4.65E-06	2.20E-06	9.79E-11	3.06E-08	5.40E-10
3.36E-06	<LOD	1.33E-10	3.06E-08	7.35E-10
1.40E-06	<LOD	5.43E-10	3.93E-08	2.99E-09
3.85E-07	<LOD	9.44E-10	<LOD	5.20E-09
1.75E-06	<LOD	1.36E-08	5.24E-08	7.50E-08
<LOD	<LOD	6.42E-12	<LOD	3.54E-11
2.14E-08	2.58E-07	6.42E-12	3.49E-08	3.54E-11
<LOD	1.46E-07	6.42E-12	3.49E-08	3.54E-11
2.85E-08	<LOD	1.27E-10	3.49E-08	6.99E-10
<LOD	<LOD	3.13E-10	3.49E-08	1.73E-09
7.85E-08	<LOD	4.98E-10	4.37E-08	2.74E-09
4.64E-07	<LOD	6.26E-11	<LOD	3.45E-10
2.35E-07	<LOD	2.28E-10	<LOD	1.26E-09
1.29E-06	<LOD	5.33E-10	2.18E-08	2.94E-09
1.78E-07	<LOD	2.06E-09	<LOD	1.13E-08
3.57E-08	<LOD	3.03E-09	3.49E-08	1.67E-08
2.43E-07	<LOD	3.58E-09	7.42E-08	1.97E-08
2.14E-08	<LOD	1.73E-10	<LOD	9.56E-10
7.85E-08	<LOD	6.00E-10	3.93E-08	3.31E-09
<LOD	1.80E-07	1.36E-09	<LOD	7.52E-09
<LOD	<LOD	4.09E-09	<LOD	2.26E-08
<LOD	<LOD	1.14E-08	<LOD	6.28E-08
3.57E-08	<LOD	5.94E-09	6.55E-08	3.27E-08
3.45E-06	<LOD	1.89E-09	<LOD	2.61E-09
4.47E-06	2.58E-07	2.59E-09	<LOD	3.02E-09
1.71E-06	<LOD	2.01E-09	<LOD	3.10E-09
6.78E-07	<LOD	3.95E-09	<LOD	5.14E-09
2.00E-07	<LOD	9.73E-09	<LOD	1.02E-08
1.28E-06	<LOD	3.40E-08	<LOD	3.44E-08
<LOD	<LOD	2.18E-09	<LOD	2.28E-09
<LOD	<LOD	1.55E-08	<LOD	1.29E-08
<LOD	<LOD	3.31E-09	<LOD	3.08E-09
<LOD	<LOD	5.78E-09	<LOD	6.59E-09
<LOD	<LOD	3.61E-09	<LOD	3.91E-09
7.85E-08	<LOD	3.44E-08	<LOD	3.12E-08
7.78E-07	<LOD	2.23E-09	1.31E-08	2.26E-09
1.26E-06	<LOD	4.03E-09	<LOD	5.75E-09
5.07E-07	<LOD	6.05E-09	<LOD	6.88E-09
2.28E-07	<LOD	1.53E-08	1.75E-08	1.79E-08
1.43E-08	<LOD	4.64E-08	8.73E-09	5.83E-08
2.64E-07	<LOD	8.57E-08	2.18E-08	9.06E-08
2.85E-08	<LOD	2.01E-09	<LOD	1.96E-09
7.85E-08	<LOD	4.64E-09	<LOD	5.74E-09
<LOD	<LOD	6.90E-09	1.31E-08	6.53E-09

<LOD	<LOD	3.29E-08	<LOD	2.66E-11
<LOD	<LOD	3.37E-08	<LOD	4.17E-08
2.85E-08	<LOD	6.22E-08	5.24E-08	1.07E-07

Table S2 -3: Contribution of individual analyzed compounds to calculated antiAR-mediated bioana
0.49µm); Concentrations of chemicals used for the BEQchem modeling were taken from Degrendel

Site	Season	Particle size (µm)	o,p'-DDD	p,p'-DDD	p,p'-DDT	o,p'-DDT	o,p'-DDE	p,p'-DDE
Rural Site	Spring	7.2-10.0	8.00E-03	1.28E-02	8.13E-01	5.16E-03	1.86E-03	1.18E-01
		3.0-7.2	1.60E-02	2.49E-02	7.63E-01	4.16E-03	7.43E-04	8.69E-02
		1.5-3.0	1.60E-02	2.90E-02	8.35E-01	4.00E-03	1.11E-03	1.11E-01
		0.95-1.5	7.20E-02	1.17E-01	1.82E+00	7.99E-03	1.49E-03	1.56E-01
		0.49-0.95	8.53E-02	1.51E-01	2.23E+00	9.16E-03	1.86E-03	2.30E-01
		<0.49	7.20E-02	1.37E-01	5.47E+00	1.70E-02	2.23E-03	1.83E-01
	Summer	7.2-10.0	1.07E-02	7.41E-03	2.99E-01	3.33E-03	1.11E-03	1.11E-01
		3.0-7.2	5.33E-03	8.08E-03	2.66E-01	2.33E-03	1.11E-03	9.54E-02
		1.5-3.0	8.00E-03	1.01E-02	3.82E-01	2.66E-03	7.43E-04	6.90E-02
		0.95-1.5	2.40E-02	1.68E-02	9.46E-01	5.00E-03	3.71E-04	6.14E-02
		0.49-0.95	2.13E-02	3.10E-02	1.43E+00	6.83E-03	7.43E-04	1.05E-01
		<0.49	4.26E-02	1.55E-02	2.59E+00	1.15E-02	2.60E-03	2.14E-01
	Autumn	7.2-10.0	3.47E-02	2.83E-02	LOD	9.99E-04	3.71E-04	6.14E-02
		3.0-7.2	3.47E-02	3.37E-02	4.98E-02	9.99E-04	1.11E-03	1.48E-01
		1.5-3.0	2.13E-02	2.49E-02	LOD	LOD	1.49E-03	2.06E-01
		0.95-1.5	2.13E-02	2.36E-02	1.11E-02	LOD	3.71E-03	5.02E-01
		0.49-0.95	3.47E-02	3.30E-02	1.27E-01	6.66E-04	4.83E-03	7.72E-01
		<0.49	4.00E-02	5.19E-02	1.94E-01	2.50E-03	3.71E-03	5.77E-01
	Winter	7.2-10.0	1.87E-02	1.75E-02	LOD	0.00E+00	1.86E-03	6.33E-02
		3.0-7.2	3.47E-02	4.72E-02	LOD	1.67E-04	1.86E-03	8.60E-02
		1.5-3.0	4.80E-02	6.94E-02	0.00E+00	LOD	2.97E-03	9.54E-02
		0.95-1.5	1.09E-01	1.77E-01	9.96E-02	1.17E-03	6.31E-03	2.56E-01
		0.49-0.95	1.60E-01	2.84E-01	2.88E-01	3.00E-03	8.91E-03	3.78E-01
		<0.49	1.25E-01	2.38E-01	7.69E-01	5.83E-03	6.68E-03	3.47E-01
Urban site	Spring	7.2-10.0	3.47E-02	2.69E-02	LOD	5.00E-04	1.86E-03	6.42E-02
		3.0-7.2	4.00E-02	2.63E-02	4.43E-02	8.33E-04	2.60E-03	8.79E-02
		1.5-3.0	5.06E-02	3.91E-02	6.09E-02	9.99E-04	1.49E-03	6.42E-02
		0.95-1.5	7.73E-02	6.87E-02	7.19E-02	2.17E-03	1.86E-03	7.27E-02
		0.49-0.95	9.33E-02	9.23E-02	8.30E-02	1.33E-03	2.97E-03	1.25E-01
		<0.49	1.31E-01	1.25E-01	2.21E-01	6.83E-03	4.83E-03	1.94E-01
	Summer	7.2-10.0	4.26E-02	3.91E-02	3.32E-02	9.99E-04	1.86E-03	6.42E-02
		3.0-7.2	5.33E-02	4.78E-02	3.87E-02	9.99E-04	2.60E-03	1.05E-01
		1.5-3.0	4.26E-02	3.77E-02	1.66E-02	6.66E-04	1.86E-03	6.52E-02
		0.95-1.5	4.80E-02	4.38E-02	3.32E-02	8.33E-04	2.23E-03	7.56E-02
		0.49-0.95	8.26E-02	8.08E-02	7.74E-02	1.50E-03	2.60E-03	8.88E-02
		<0.49	1.23E-01	1.27E-01	2.54E-01	4.16E-03	5.20E-03	1.84E-01
	Autumn	7.2-10.0	4.53E-02	3.84E-02	3.32E-02	1.17E-03	3.71E-03	1.96E-01
		3.0-7.2	7.20E-02	7.21E-02	1.16E-01	2.17E-03	4.46E-03	1.97E-01
		1.5-3.0	4.80E-02	4.45E-02	1.38E-01	2.00E-03	3.71E-03	1.71E-01
		0.95-1.5	5.86E-02	5.39E-02	6.64E-02	1.50E-03	5.57E-03	2.62E-01
		0.49-0.95	6.40E-02	6.67E-02	1.38E-01	2.17E-03	8.17E-03	3.84E-01
		<0.49	1.15E-01	1.05E-01	2.16E-01	5.00E-03	8.17E-03	4.51E-01
	nter	7.2-10.0	7.46E-02	8.49E-02	1.83E-01	2.83E-03	2.60E-03	6.05E-02
		3.0-7.2	8.53E-02	7.75E-02	1.33E-01	3.16E-03	2.97E-03	7.09E-02
		1.5-3.0	8.80E-02	8.35E-02	1.55E-01	2.00E-03	4.46E-03	1.06E-01

Wir	0.95-1.5	1.20E-01	1.46E-01	2.77E-01	3.33E-03	5.94E-03	1.65E-01
	0.49-0.95	1.81E-01	2.35E-01	6.31E-01	7.66E-03	7.05E-03	1.81E-01
	<0.49	2.45E-01	2.64E-01	7.03E-01	8.99E-03	7.05E-03	2.16E-01

ılytical equivalent BEQchem; A-F: size fractions of PM (A: 7.2-10.0; B: 3-7.2; C 1.5-3; D: 0.95-
le et al. (2016, 2014) and (Okonski et al., 2014).

Acetochlo	Alachlor	Azinphos-	Fenitrothio	Temephos	Prochloraz	BDE-47	BDE-99	BDE-100
33.57323	<LOD	0.000357	<LOD	<LOD	1.30E-01	6.30E+00	8.66E-01	2.26E+00
52.92079	<LOD	0.000429	<LOD	<LOD	2.92E-01	1.60E+00	4.56E-01	8.40E-01
50.84955	0.001506	0.000429	<LOD	<LOD	1.14E-01	1.72E+00	7.04E-01	1.14E+00
28.59585	<LOD	<LOD	<LOD	<LOD	6.04E-02	3.41E+00	2.38E+00	4.65E+00
42.27562	0.006024	<LOD	<LOD	<LOD	4.45E-02	4.88E+00	4.37E+00	8.09E+00
232.0262	<LOD	<LOD	<LOD	<LOD	4.77E-02	4.01E+00	6.95E+00	1.17E+02
3.195157	0.002886	<LOD	<LOD	<LOD	5.85E-01	5.97E+00	2.64E-02	<LOD
4.672315	0.001506	0.0005	<LOD	<LOD	1.25E+00	2.33E+00	1.00E+00	<LOD
6.839883	0.002259	<LOD	<LOD	<LOD	4.64E-01	8.92E-01	6.98E-01	<LOD
6.165529	0.003388	<LOD	<LOD	<LOD	1.53E-01	9.56E-01	6.53E-01	1.09E+00
2.023064	0.003765	<LOD	<LOD	<LOD	6.99E-02	3.32E+00	1.38E+00	2.68E+00
1.766167	0.009914	<LOD	<LOD	<LOD	1.02E-01	2.41E+00	2.39E+00	4.27E+00
0.642243	<LOD	<LOD	<LOD	<LOD	3.50E-02	4.16E-01	2.64E-01	5.37E-01
0.626186	<LOD	<LOD	<LOD	<LOD	4.13E-02	1.16E+00	9.27E-01	1.95E+00
0.915196	<LOD	0.000429	<LOD	<LOD	5.40E-02	2.53E+00	2.18E+00	4.57E+00
0.417458	<LOD	<LOD	<LOD	<LOD	<LOD	7.75E+00	7.73E+00	1.76E+01
0.337177	0.018448	<LOD	<LOD	2.43E-04	<LOD	1.11E+01	1.10E+01	2.60E+01
1.027588	<LOD	<LOD	<LOD	<LOD	<LOD	1.32E+01	1.65E+01	3.07E+01
0.08028	<LOD	<LOD	<LOD	1.46E-04	<LOD	2.08E+00	8.38E-01	1.49E+00
0.112392	0.002008	<LOD	<LOD	<LOD	2.54E-02	3.29E+00	2.21E+00	5.15E+00
0.096336	0.00389	<LOD	<LOD	<LOD	<LOD	7.39E+00	5.33E+00	1.17E+01
<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	2.03E+01	1.42E+01	3.51E+01
0.144505	<LOD	<LOD	<LOD	<LOD	<LOD	3.25E+01	2.76E+01	9.77E+01
0.417458	<LOD	<LOD	<LOD	<LOD	<LOD	2.79E+01	2.09E+01	5.09E+01
3.484166	0.002133	<LOD	<LOD	<LOD	6.36E-02	4.01E+00	1.64E+00	4.06E+00
2.552914	0.003137	<LOD	<LOD	1.46E-04	6.99E-02	4.61E+00	2.24E+00	4.69E+00
5.892575	0.002635	<LOD	<LOD	<LOD	6.04E-02	3.68E+00	1.74E+00	4.82E+00
4.190633	<LOD	<LOD	<LOD	<LOD	4.77E-02	5.00E+00	3.42E+00	8.00E+00
1.830391	<LOD	<LOD	<LOD	<LOD	2.86E-02	9.35E+00	8.43E+00	1.58E+01
11.15896	<LOD	<LOD	<LOD	<LOD	<LOD	3.78E+01	2.94E+01	5.35E+01
0.97942	<LOD	<LOD	<LOD	1.46E-04	3.15E-01	3.77E+00	1.89E+00	3.55E+00
0.706467	<LOD	<LOD	<LOD	<LOD	5.24E-01	1.29E+01	1.34E+01	2.01E+01
2.825867	<LOD	<LOD	<LOD	<LOD	2.32E-01	4.37E+00	2.86E+00	4.79E+00
0.995476	<LOD	<LOD	<LOD	<LOD	4.77E-02	5.22E+00	5.01E+00	1.02E+01
1.091812	<LOD	<LOD	<LOD	<LOD	5.72E-02	5.13E+00	3.13E+00	6.08E+00
5.667791	0.007655	<LOD	<LOD	<LOD	5.08E-02	2.63E+01	2.98E+01	4.84E+01
0.545906	0.003137	<LOD	<LOD	<LOD	4.13E-02	3.44E+00	1.93E+00	3.51E+00
0.754635	0.004643	<LOD	<LOD	<LOD	8.90E-02	6.27E+00	3.49E+00	8.95E+00
0.578018	<LOD	<LOD	<LOD	<LOD	4.77E-02	7.39E+00	5.24E+00	1.07E+01
0.385346	0.006651	<LOD	<LOD	<LOD	4.77E-02	1.70E+01	1.33E+01	2.78E+01
0.144505	0.011043	<LOD	<LOD	<LOD	<LOD	4.51E+01	4.02E+01	9.07E+01
0.353233	0.007655	<LOD	<LOD	<LOD	<LOD	1.05E+02	7.42E+01	1.41E+02
0.048168	0.006275	0.000357	<LOD	4.86E-05	1.59E-02	2.79E+00	1.74E+00	3.04E+00
0.064224	0.002635	<LOD	<LOD	<LOD	<LOD	5.73E+00	4.02E+00	8.93E+00
0.096336	<LOD	<LOD	<LOD	9.71E-05	<LOD	7.78E+00	5.98E+00	1.02E+01

0.128449	<LOD	<LOD	<LOD	<LOD	<LOD	4.14E+01	2.85E+01	<LOD
0.337177	<LOD	<LOD	9.99E-01	<LOD	1.27E-02	5.10E+01	2.92E+01	6.48E+01
0.626186	0.131392	<LOD	<LOD	1.94E-04	3.50E-02	1.33E+02	5.38E+01	1.67E+02

1.5; E: 0.49-0.95 and F: <

BDE-183	Fluoranthe	Benz(a)ant	Anthracen	Benzo[k]fl	Benzo[a]p	δ-HCH	Diuron	Fonofos
<LOD	9.72E-02	1.86E-01	<LOD	1.15E-01	<LOD	4.75E-06	2.40E-03	1.05E-03
<LOD	1.82E-01	1.63E-02	<LOD	2.80E-01	<LOD	3.17E-06	5.25E-03	1.05E-03
5.46E-02	2.69E-01	3.35E-02	<LOD	6.36E-01	<LOD	3.76E-06	8.09E-03	1.05E-03
4.12E-01	6.40E-01	1.12E-01	<LOD	2.11E+00	<LOD	4.75E-06	7.43E-03	1.40E-03
6.13E-01	1.18E+00	3.42E-01	8.94E-02	4.95E+00	6.62E+00	5.94E-07	1.14E-02	2.81E-03
<LOD	1.14E+00	2.70E-01	9.12E-02	6.15E+00	7.20E+00	3.36E-06	5.01E-02	2.11E-03
<LOD	3.35E-02	<LOD	<LOD	<LOD	<LOD	<LOD	2.30E-02	1.40E-03
<LOD	1.09E-01	1.58E-02	<LOD	3.05E-01	<LOD	<LOD	3.78E-02	1.40E-03
<LOD	2.96E-01	4.75E-02	<LOD	7.86E-01	<LOD	<LOD	5.25E-02	1.40E-03
7.89E-02	1.22E-01	1.21E-02	<LOD	3.18E-01	<LOD	9.90E-07	5.53E-02	1.40E-03
1.45E-01	1.08E-01	1.33E-02	<LOD	5.10E-01	<LOD	1.98E-06	7.43E-02	2.11E-03
7.03E-01	2.13E-01	3.18E-02	<LOD	9.58E-01	<LOD	1.19E-06	3.66E-01	1.75E-03
2.56E-02	4.37E-02	<LOD	<LOD	<LOD	<LOD	0.00E+00	3.50E-03	<LOD
4.02E-02	1.53E-01	1.59E-02	<LOD	3.16E-01	<LOD	<LOD	5.47E-03	<LOD
2.30E-01	3.35E-01	5.60E-02	<LOD	9.22E-01	<LOD	7.92E-07	7.87E-03	<LOD
1.29E+00	1.74E+00	4.79E-01	3.80E-01	5.00E+00	<LOD	2.18E-06	1.66E-02	<LOD
1.74E+00	3.19E+00	1.01E+00	2.08E-01	1.21E+01	6.54E+01	7.92E-07	3.08E-02	<LOD
3.04E+00	2.62E+00	7.61E-01	1.84E-01	1.29E+01	3.73E+01	<LOD	1.12E-01	5.26E-03
6.26E-02	9.21E-01	6.33E-02	6.66E-02	6.80E-01	<LOD	7.92E-07	1.31E-03	1.40E-03
3.12E-01	5.09E+00	4.18E-01	4.87E-01	3.82E+00	3.65E+01	1.58E-06	<LOD	1.75E-03
9.36E-01	2.24E+01	1.95E+00	1.79E+00	1.51E+01	8.79E+01	7.92E-07	4.59E-03	2.11E-03
2.32E+00	7.51E+01	8.50E+00	6.80E+00	6.05E+01	6.35E+02	1.98E-06	6.34E-03	2.81E-03
<LOD	1.06E+02	1.37E+01	1.02E+01	9.17E+01	7.08E+02	1.39E-06	2.10E-02	2.11E-03
2.29E+00	4.00E+01	4.88E+00	2.76E+00	3.06E+01	1.92E+02	7.13E-06	2.40E-03	2.46E-03
1.87E-01	3.75E-01	2.54E-02	<LOD	3.53E-01	<LOD	5.94E-07	1.97E-03	<LOD
5.94E-01	5.03E-01	3.61E-02	<LOD	5.19E-01	<LOD	1.19E-06	3.06E-03	<LOD
8.34E-01	7.40E-01	4.21E-02	<LOD	6.84E-01	<LOD	<LOD	2.84E-03	<LOD
2.37E+00	1.07E+00	1.09E-01	7.67E-02	1.89E+00	<LOD	<LOD	2.19E-03	<LOD
3.26E+00	1.37E+00	2.93E-01	1.29E-01	4.32E+00	1.44E+01	<LOD	3.50E-03	<LOD
4.56E+00	3.68E+00	5.82E-01	4.31E-01	6.35E+00	1.61E+01	<LOD	3.04E-02	<LOD
1.59E-01	1.78E-01	<LOD	<LOD	<LOD	<LOD	<LOD	1.31E-03	2.81E-03
5.91E-01	2.24E-01	1.72E-02	<LOD	2.20E-01	<LOD	<LOD	3.72E-03	<LOD
2.50E-01	2.15E-01	<LOD	<LOD	<LOD	<LOD	<LOD	2.54E-02	<LOD
1.66E-01	4.57E-01	4.47E-02	<LOD	4.80E-01	<LOD	<LOD	4.59E-03	<LOD
3.04E-01	6.59E-01	1.11E-01	1.01E-01	1.34E+00	<LOD	2.77E-06	1.46E-02	<LOD
1.21E+00	8.24E+00	2.23E+00	9.34E-01	1.81E+01	2.23E+02	4.55E-06	7.67E-02	<LOD
3.58E-01	1.49E-01	2.44E-02	<LOD	2.01E-01	<LOD	7.92E-07	1.09E-03	<LOD
1.06E+00	4.24E-01	6.81E-02	<LOD	6.59E-01	<LOD	<LOD	3.28E-03	<LOD
6.26E-01	6.57E-01	1.41E-01	<LOD	2.03E+00	<LOD	<LOD	<LOD	<LOD
1.32E+00	1.91E+00	5.31E-01	1.21E-01	5.33E+00	4.66E+00	<LOD	<LOD	<LOD
3.40E+00	3.60E+00	1.17E+00	3.07E-01	1.32E+01	9.98E+01	<LOD	5.68E-03	<LOD
4.01E+00	5.21E+00	1.28E+00	6.49E-01	9.61E+00	1.16E+01	1.19E-06	6.34E-03	<LOD
2.11E-01	7.99E-01	4.92E-02	5.74E-02	4.93E-01	1.04E+00	<LOD	<LOD	<LOD
4.47E-01	1.91E+00	1.58E-01	1.28E-01	1.36E+00	7.60E+00	<LOD	6.56E-04	3.51E-03
6.26E-01	7.41E+00	7.89E-01	6.09E-01	6.29E+00	3.44E+01	<LOD	1.53E-03	<LOD

2.67E+00	2.93E+01	3.85E+00	2.69E+00	3.02E+01	3.60E+02	3.96E-07	<LOD	<LOD
2.80E+00	4.59E+01	7.34E+00	4.37E+00	5.15E+01	7.43E+02	<LOD	1.31E-03	1.37E-02
3.14E+00	3.37E+01	6.93E+00	2.29E+00	4.60E+01	6.18E+02	3.56E-06	4.37E-03	<LOD

Indeno(1,2	Metolachl	Phenanthr	Pyrene	α-HBCD	TBECH	α-HCH
<LOD	2.31E-02	5.43E-02	1.19E-01	<LOD	1.69E-03	1.42E-03
1.98E-01	3.95E-02	8.93E-02	2.17E-01	6.49E-04	1.47E-03	7.12E-04
5.31E-01	4.65E-02	9.73E-02	3.63E-01	<LOD	8.64E-04	1.23E-03
1.63E+00	2.99E-02	2.71E-01	8.72E-01	5.01E-04	6.52E-04	2.14E-03
2.98E+00	4.77E-02	5.86E-01	1.83E+00	7.23E-04	9.49E-04	3.24E-04
5.07E+00	4.52E-01	4.99E-01	1.98E+00	1.17E-02	5.30E-04	2.59E-04
<LOD	1.78E-02	4.68E-04	6.22E-02	<LOD	7.66E-04	3.24E-04
2.08E-01	2.54E-02	1.77E-02	1.65E-01	6.49E-04	8.53E-04	4.53E-04
5.47E-01	3.75E-02	5.03E-02	3.66E-01	<LOD	9.55E-04	1.68E-03
2.47E-01	3.44E-02	<LOD	1.59E-01	6.30E-04	1.22E-03	6.47E-04
4.78E-01	1.60E-02	6.72E-03	1.51E-01	1.89E-03	1.63E-03	1.42E-03
7.40E-01	1.72E-02	1.02E-01	4.00E-01	6.38E-02	1.92E-03	5.82E-04
<LOD	<LOD	1.17E-03	7.82E-02	<LOD	4.71E-04	6.47E-05
1.91E-01	<LOD	5.05E-02	1.84E-01	<LOD	3.27E-04	6.47E-05
6.04E-01	<LOD	1.48E-01	4.11E-01	<LOD	3.01E-04	<LOD
2.30E+00	<LOD	7.13E-01	1.80E+00	1.34E-03	2.38E-04	8.41E-04
1.01E+01	<LOD	1.03E+00	5.94E+00	2.34E-03	4.32E-04	1.29E-04
1.08E+01	<LOD	7.37E-01	5.29E+00	1.44E-02	3.45E-04	3.24E-04
4.34E-01	<LOD	9.31E-01	8.39E-01	3.34E-04	6.33E-04	6.47E-05
2.64E+00	<LOD	4.40E+00	5.99E+00	1.43E-03	3.97E-04	1.04E-03
9.48E+00	<LOD	1.91E+01	2.59E+01	5.19E-04	5.67E-04	1.16E-03
4.03E+01	<LOD	5.84E+01	9.17E+01	6.12E-04	1.02E-03	5.82E-04
5.52E+01	<LOD	7.33E+01	1.31E+02	1.95E-03	7.48E-04	<LOD
1.48E+01	<LOD	2.28E+01	4.81E+01	5.79E-03	6.39E-04	2.85E-03
2.39E-01	1.17E-02	2.06E-01	5.94E-01	7.60E-04	2.64E-04	1.29E-04
4.34E-01	1.00E-02	3.01E-01	7.09E-01	1.08E-03	2.90E-04	6.47E-04
5.02E-01	2.66E-02	3.72E-01	7.99E-01	<LOD	2.14E-04	<LOD
1.38E+00	2.07E-02	5.05E-01	1.30E+00	5.19E-04	2.79E-04	<LOD
3.92E+00	4.30E-03	8.08E-01	2.26E+00	1.13E-03	2.29E-04	6.47E-05
5.01E+00	4.73E-02	2.12E+00	7.37E+00	2.43E-03	1.26E-03	4.53E-04
<LOD	1.09E-02	1.15E-01	3.21E-01	<LOD	1.17E-03	<LOD
<LOD	1.35E-02	1.20E-01	4.05E-01	<LOD	7.37E-04	3.24E-04
<LOD	1.80E-02	1.38E-01	3.74E-01	6.30E-04	1.00E-03	9.06E-04
4.11E-01	8.40E-03	2.18E-01	7.74E-01	8.71E-04	1.50E-03	7.12E-04
1.11E+00	1.31E-02	4.52E-01	1.39E+00	7.79E-04	2.40E-03	1.49E-03
1.52E+01	9.57E-02	3.88E+00	1.94E+01	6.88E-03	6.70E-03	1.23E-03
2.35E-01	<LOD	2.91E-02	2.93E-01	6.49E-04	2.12E-04	1.29E-04
6.09E-01	<LOD	2.06E-01	7.88E-01	3.24E-03	1.66E-04	<LOD
1.59E+00	2.05E-03	2.87E-01	1.09E+00	1.32E-03	2.51E-04	<LOD
3.24E+00	<LOD	7.88E-01	3.07E+00	1.39E-03	2.59E-04	<LOD
1.11E+01	<LOD	1.27E+00	7.01E+00	2.71E-03	7.96E-04	<LOD
8.44E+00	<LOD	2.85E+00	1.06E+01	5.88E-03	7.61E-04	<LOD
3.86E-01	<LOD	6.02E-01	1.08E+00	<LOD	2.40E-04	<LOD
1.07E+00	<LOD	1.25E+00	2.61E+00	1.17E-03	3.86E-04	<LOD
4.65E+00	<LOD	5.19E+00	1.01E+01	9.09E-04	3.58E-04	<LOD

2.27E+01	<LOD	1.96E+01	4.00E+01	8.90E-04	4.65E-04	<LOD
4.03E+01	<LOD	2.65E+01	6.67E+01	1.24E-03	7.79E-04	6.47E-05
3.39E+01	<LOD	1.33E+01	5.54E+01	3.24E-03	2.46E-03	1.42E-03