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ACTIVE INDOOR AIR SAMPLING OF ORGANOCHLORINATED PERSISTENT POLLUTANTS AND POLYCYCLIC AROMATIC HYDROCARBONS

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Introduction

The German guideline VDI 2464 Part 4[1] targets the sampling and measurement of organochlorinated persistent pollutants (OCPP) and polycyclic aromatic hydrocarbons (PAH) in outdoor and indoor air. Outdoor air measurements are typically based on sampling volumes of several hundred cubic meters in contrast to indoor measurements which are normally based on several tenths of cubic meters due to the dimension of the location and the compliance with inhabitants of the facilities. In addition, the determination of compounds susceptible to reaction, resp. oxidation, such as benzo-a-pyrene is critical in case of long term sampling and related to the underestimation of educts such as benzo(a)pyrene[2]. Therefore repetitive trials of indoor air sampling on the basis of VDI 2464 Part 4 were executed to gain information about the quality of determination of OCPP and PAH.

Materials and Methods

Sampling

The sampling campaign was performed in the period from July 7th to 10th 2015 in a building of about 600 m³ volume, employing two low volume samplers (LVS) in parallel. The sampling train consists of a filter unit and XAD-2 (Sigma, Germany) resin as described in VDI 2464 Part 4[1]. In addition, a second backup cartridge filled with XAD -2 was connected behind the master cartridge. Three trials in series were executed with sampling volumes of about 55 m³ during 27h, each. Temperature was in the range of 19 to 25 °C for the inlet air. The outlet air was directed to the outdoor environment to avoid any influence from the sampling train on the air measurement. Field blanks for filter and XAD-2 were utilized to judge the possible quality of the results. For quality control the master cartridge was spiked with 16 ^{13}C-labelled EPA-PAH (see table 1) as sampling standards.

Determination of OCP and PAH levels

The sample pretreatment and analysis was executed according to VDI 2464 Part 4, but separately for the filter and the cartridges. In brief, XAD-2 cartridges and filters were Soxhlet extracted with a mixture of n-hexane/acetone (3:1) after spiking with PAH (Napthalene-D_8, Acenaphthylene-D_8, Acenaphthene-D_{10}, Fluorene-D_{10}, Phenanthene-D_{10}, Anthracene-D_{10}, Fluoranthene-D_{10}, Pyrene-D_{10}, Benzo(a)anthracene-D_{12}, Chrysene-D_{12}, Benzo(b)fluoranthene-D_{12}, Benzo(k)fluoranthene-D_{12}, Benzo(a)pyrene-D_{12}, Indeno(1,2,3-c,d)pyrene-D_{12}, Benzo(g,h,i)-perylene-D_{12}, Dibenzo(a,h)anthracene-D_{14}) and OCPP (Pentachlorobenzene $^{13}C_6$, alpha-HCH $^{13}C_6$, gamma-HCH $^{13}C_6$, beta-HCH $^{13}C_6$, delta-HCH $^{13}C_6$, Pentachloroanisole $^{13}C_6$, Hexachlorobutadiene $^{13}C_4$, Hexachlorobenzene $^{13}C_6$, Heptachlor $^{13}C_6$, Aldrin $^{13}C_{12}$, Octachlorostyrene $^{13}C_6$, oxy-Chlordane $^{13}C_{10}$, Heptachloroepoxide $^{13}C_{10}$, 2,4'-DDE $^{13}C_{12}$, 4,4'-DDE $^{13}C_{12}$, trans-Chlordane $^{13}C_{12}$, Endosulfan-I $^{13}C_9$, Endosulfan-II $^{13}C_9$, Endosulfan sulfate $^{13}C_9$, 4,4'-DDD D_8, Dieldrin $^{13}C_{12}$, 2,4'-DDT $^{13}C_{12}$, 4,4'-DDT $^{13}C_{12}$, Methoxychlor $^{13}C_{12}$, Mirex $^{13}C_{10}$) in nonane to monitor the extraction and cleanup procedures. The volume of the extracts was reduced and split into two halves. One half was stored as backup at -20 °C; the other half underwent several clean-up steps.

A glass column was filled (from bottom to top) with 10 g silica gel (LGC Standards, Wesel, Germany) and 5 g alumina B (LGC Standards, Wesel, Germany, deactivated with 3% distilled water). In order to eliminate impurities, the packed column was rinsed with 60 mL of n-hexane:dichloromethane (1:1, v/v). The extract, reduced to a volume of approximately 0.5 mL, was transferred onto the column and was eluted with 100 mL n-hexane:dichloromethane (1:1, v/v)). To the concentrated sample (1–2 mL), 0.5 mL acetonitrile was added and evaporated by a gentle stream of nitrogen to 0.5 mL. A SPE glass column was filled with 1 g of C18-modified silica gel (Chromabond C18 ec, Macherey-Nagel, Düren, Germany) and conditioned with 5 mL acetonitrile. After transferring the sample onto the column it was eluted with 5 mL of acetonitrile. Finally, the eluate was concentrated to 0.5 mL and transferred to a 2 mL auto-sampler vial with micro-insert, spiked with a recovery standard (pentachlorotoluene, 1,2,3,7,8,9-hexachlorodibenzo-p-dioxin $^{13}C_{12}$). The eluate was further evaporated by a gentle stream of nitrogen to a final volume of 20 µL and stored at –20 °C until analysis. OCPP and PAH were measured using a gas chromatograph (Agilent, 5890 Series II) coupled to a high resolution mass spectrometer (GC–HRMS). The mass spectrometer (Thermo, MAT 95S) was operated in single ion monitoring mode and the two most intense ions of the molecular ion cluster or of an abundant fragment ion cluster were monitored. The detailed GC-MS conditions are given in VDI 2464 Part 4[1].

Results and Discussion

Recoveries of sampling standards are listed in table 1. All in all, the recoveries are sufficient for all compounds (some values are not available due to problems within the analysis procedure). Both LVS perform very similarly. Recovery values lower than 70 % only occur for benzo(a)pyrene (BaP). However, losses were not dramatic when BaP is trapped by the XAD instead of the filter. BaP losses at the filter as described previously by Schauer et al.[2] could not be investigated in this study.

Concentrations of OCPP and PAH are shown in table 2. Since the first trial was executed after a period of weeks not using the building facility, the concentrations of the target compounds are higher than those observed for the following trials at normal ventilation conditions contamination with gamma-HCH is likely in combination with pentachlorophenol, which is converted biologically to pentachloroanisole. Backup values are often 10% or less, which confirms a quantitative sampling. On filters, concentrations above the LOQ are only detectable for compounds with lower vapor pressure and high affinity to filter trapped aerosols (eg. DDTs). However, the filter values indicate that aerosol bound compounds are not abundant in the indoor air sampled. Concentrations of less volatile PAH and OCPP are mainly in the range of the field blank values. The field blank situation allows to determine benzo(a)pyrene at the limit of 1000 pg/Nm^3, which is the target value in outdoor air in the European Union[3]. As well, all other compounds are detectable at reasonable limits of quantification.

Conclusions

Low volume sampling of OCPP and PAH in indoor environments can be successfully executed at sampling volumes of about 55 Nm^3. The LOQ and LOD values are compliant with tentative limit values. Recoveries of sampling standards indicate an adequate quantitative performance of the sampling and were confirmed by the acceptable breakthrough percentages in the backup-cartridges. Only naphthalene data are not really reliable due to its high volatility and abundance in laboratory or field blanks in addition to potential losses during sample pretreatment.

The trials were executed during a few quite hot summer days with outdoor temperature >30 °C, but neither the recoveries nor the concentrations indicate a substantial influence of temperature and the method can be considered also reliable at such conditions.

References

1. VDI 2464 Part 4 (2015): Ambient air measurement – Outdoor and indoor air measurement – Measurement of semivolatile and persistent organic pollutants (POPs) with GC/HRMS
2. Schauer, C., Niessner, R., Pöschl, U. (2003): Polycyclic aromatic hydrocarbons in urban air particulate matter: decadal and seasonal trends, chemical degradation and sampling artefacts. Environmental Science and Technology 37, 2861-2868
3. Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32004L0107

Table 1: Total recoveries of ^{13}C-labelled PAH sampling standards for all periods and LVS trials

Recovery PRC	2159	2152	2159	2152	2159	2152
	07.07.-08.07.15	07.07.-08.07.15	09.07.-10.07.15	09.07.-10.07.15	11.07.-12.07.15	11.07.-12.07.15
Naphthalene-13C6	98%		80%	79%		110%
Acenaphthylene-13C6	81%	73%	87%	85%	83%	80%
Acenaphthene-13C6	106%	113%	96%	95%	109%	109%
Fluorene-13C6			95%	91%	108%	92%
Phenanthrene-13C6	104%	107%	103%	92%	113%	104%
Anthracene-13C6*	97%	100%	96%	89%	91%	79%
Fluoranthene-13C6	101%	96%	101%	95%	98%	102%
Pyrene-13C3	102%	103%	97%	96%	110%	106%
Benzo(a)anthracene- 13C6*	90%	90%	102%	102%	78%	81%
Chrysene-13C6	89%	87%	105%	103%	93%	89%
Benzo(b)fluoranthene-13C6	94%	85%	112%	104%	91%	81%
Benzo(k)fluoranthene-13C6	87%	86%	109%	89%	92%	81%
Benzo(a)pyrene-13C4*	80%	82%	87%	84%	68%	49%
Indeno(1,2,3-cd)pyrene-13C 6	90%	77%	98%	88%	90%	71%
Benzo(g,h,i)perylen-13C12	94%	83%	80%	75%	86%	67%
Dibenz(a,h)anthracen-13C6	102%	89%	116%	98%	96%	79%

No value: quantification was not possible, because of lock mass loss or low recovery
*** Compounds, which are prone to oxidation or semiquinone formation during sampling**

Table 2: Indoor concentrations of OCPP and PAH: field blanks, filter, master- and backup-cartridges. Missing values not available due to interferences, n.d. not detectable, values in brackets = LOQ

Sampling period			07.07.-08.07.15	07.07.-08.07.15	07.07.-08.07.15	07.07.-08.07.15	09.07.-10.07.15	09.07.-10.07.15	09.07.-10.07.15	09.07.-10.07.15	09.07.-10.07.15	09.07.-10.07.15	11.07.-12.07.15	11.07.-12.07.15	11.07.-12.07.15	11.07.-12.07.15	11.07.-12.07.15	11.07.-12.07.15
Sampling volume (Nm³)	55 (fictional)	55 (fictional)	54.32	54.32	53.99	53.99	55.21	55.21	55.21	54.87	54.87	54.87	55.08	55.08	55.08	62.06	62.06	62.06
Sampling device	Field blank XAD	Field blank Filter	Backup 2159	Master 2159	Backup 2152	Master 2152	Filter 2159	Backup 2159	Master 2159	Filter 2152	Backup 2152	Master 2152	Filter 2159	Backup 2159	Master 2159	Filter 2152	Backup 2152	Master 2152
	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³
alpha-Hexachlorocyclohexane	n.d. (1.3)	0.31	1.2	192	n.d. (1.0)	216	0.66	0.48	146	n.d. (1.3)	n.d. (3.0)	135	n.d. (1.4)	n.d. (3.6)	146	0.84	0.44	126
beta-Hexachlorocyclohexane	n.d. (1.6)	0.65	n.d. (1.4)	18.5	n.d. (1.4)	n.d. (16.2)	1.4	0.67	n.d. (10.3)	n.d. (1.8)	n.d. (3.6)	18.6	n.d. (2.3)	n.d. (5.6)	25.3	n.d. (2.2)	0.25	24.5
gamma-Hexachlorocyclohexane	10.0	15.9	330	107858	31.5	100806	2.5	40.8	57028	3.2	46.8	55659	4.7	22.6	57180	14.4	24.5	63968
delta-Hexachlorocyclohexane	n.d. (1.8)	0.26	n.d. (1.0)	10.5	n.d. (1.2)	11.0	n.d. (2.4)	n.d. (1.3)	9.8	n.d. (1.9)	n.d. (4.3)	8.1	n.d. (2.3)	n.d. (5.8)	10.3	n.d. (2.0)	0.22	6.9
epsilon-Hexachlorocyclohexane	n.d. (2.3)	0.12	n.d. (1.3)	10.1	n.d. (1.6)	n.d. (15.0)	n.d. (3.1)	n.d. (1.6)	n.d. (9.6)	n.d. (2.5)	n.d. (5.3)	2.3	n.d. (2.9)	n.d. (7.0)	n.d. (7.5)	n.d. (2.7)	n.d. (0.5)	n.d. (6.2)
Hexachlorobutadiene	33.2	n.d. (0.4)		1106	25.2	1127	n.d. (1.5)	n.d. (0.8)	1354	n.d. (0.9)	n.d. (4.7)	1330	n.d. (0.6)	n.d. (2.0)	1128	n.d. (0.5)	n.d. (1.7)	1059
Pentachlorobenzene	2.7	0.52	2.7	1464	1.7	1460	0.79	2.4	1352	0.71	3.0	1068	0.70	2.7	1020	3.2	1.5	912
Hexachlorobenzene	8.4	2.5	3.4	622	2.9	639	3.8	2.9	409	4.5	4.3	384	2.6	3.4	405	2.6	2.3	331
Pentachloroanisole	2.2	1.4	24.5	10514	n.d. (0.3)	10779	n.d. (0.2)	2.6	4669	0.92	4.2	4365	n.d. (0.3)	n.d. (1.0)	6135	n.d. (0.2)	2.3	4526
Octachlorostyrene	n.d. (0.8)	n.d. (0.5)	n.d. (0.3)	3.0	n.d. (0.5)	2.6	n.d. (0.3)	n.d. (0.4)	2.0	n.d. (0.6)	n.d. (1.4)	2.5	n.d. (0.7)	n.d. (1.8)	1.8	n.d. (0.5)	n.d. (1.7)	n.d. (0.8)
4,4’-Dichlorodiphenyltrichloroethane	1.1	20.5	0.89	61.3	0.55	68.2	16.2	2.6	43.4	18.2	3.2	49.3	19.6	7.2	69.8	16.1	2.0	50.6
2,4’-Dichlorodiphenyltrichloroethane	1.4	2.5	0.61	67.6	0.59	75.9	2.7	1.0	54.2	2.2	1.5	50.6	3.6	2.7	54.1	2.6	1.2	52.5
4,4’-Dichlorodiphenyldichloroethane	0.66	0.94	0.45	2.4	0.38	1.7	0.94	0.58	2.4	0.92	0.63	2.8	1.0	n.d. (2.8)	3.0	0.85	n.d. (0.3)	2.1
2,4’-Dichlorodiphenyldichloroethane	0.71	0.23	0.11	2.1	n.d. (0.7)	2.4	0.06	0.21	1.6	0.35	n.d. (0.5)	1.6	0.43	n.d. (2.5)	1.6	0.39	n.d. (0.3)	1.3
4,4’-Dichlorodiphenyldichloroethene	1.7	1.3	0.73	108	0.68	119	1.9	1.4	68.3	2.8	2.4	75.3	3.5	1.6	92.4	2.3	1.7	75.5
2,4’-Dichlorodiphenyldichloroethene	0.33	0.13	0.14	16.0	0.22	17.7	0.16	0.19	10.5	0.31	0.38	10.0	n.d. (0.5)	n.d. (0.6)	13.2	0.18	n.d. (0.2)	10.0
trans-Chlordane	n.d. (0.8)	n.d. (0.2)	n.d. (0.4)	n.d. (2.9)	n.d. (0.5)	4.0	n.d. (0.5)	n.d. (0.4)	n.d. (1.9)	n.d. (0.7)	n.d. (1.4)	n.d. (2.4)	n.d. (1.4)	n.d. (2.1)	n.d. (5.4)	n.d. (0.7)	n.d. (0.5)	n.d. (1.9)
cis-Chlordane	n.d. (0.9)	n.d. (0.2)	n.d. (0.4)	n.d. (3.3)	n.d. (0.6)	3.9	n.d. (0.5)	n.d. (0.4)	n.d. (2.2)	n.d. (0.8)	n.d. (1.6)	n.d. (2.8)	n.d. (1.6)	n.d. (2.5)	n.d. (6.0)	n.d. (0.8)	n.d. (0.5)	n.d. (2.2)
oxy-Chlordane	n.d. (1.5)	n.d. (0.3)	n.d. (0.5)	n.d. (1.8)	n.d. (0.9)	n.d. (3.5)	n.d. (0.7)	n.d. (0.7)	n.d. (2.4)	n.d. (1.1)	n.d. (1.9)	n.d. (2.3)	n.d. (1.1)	n.d. (2.6)	n.d. (2.4)	n.d. (0.9)	n.d. (0.9)	n.d. (2.2)
Heptachlor	n.d. (0.8)	n.d. (0.1)	n.d. (0.2)	7.5	n.d. (0.4)	7.9	n.d. (0.2)	n.d. (0.3)	n.d. (0.4)	n.d. (0.3)	n.d. (1.0)	5.2	n.d. (0.4)	n.d. (1.7)	5.6	n.d. (0.3)	n.d. (0.4)	4.7
cis-Heptachloroepoxide	n.d. (1.5)	n.d. (0.2)	n.d. (0.6)	n.d. (2.0)	n.d. (0.9)	5.7	n.d. (0.8)	n.d. (0.7)	n.d. (2.5)	n.d. (1.1)	n.d. (2.1)	n.d. (2.4)	n.d. (1.2)	n.d. (2.9)	4.3	n.d. (1.0)	n.d. (0.5)	n.d. (2.6)
trans-Heptachloroepoxide	n.d. (1.1)	n.d. (0.2)	n.d. (0.4)	n.d. (1.4)	n.d. (0.6)	n.d. (2.6)	n.d. (0.5)	n.d. (0.5)	n.d. (1.8)	n.d. (0.8)	n.d. (1.4)	n.d. (1.7)	n.d. (0.8)	n.d. (2.0)	n.d. (1.7)	n.d. (0.7)	n.d. (0.4)	n.d. (1.8)
Dieldrin	3.8	0.84	n.d. (0.4)	30.6	n.d. (0.6)	37.4	n.d. (0.5)	n.d. (0.5)	27.3	n.d. (0.7)	n.d. (1.5)	23.7	1.8	n.d. (2.4)	24.7	n.d. (0.7)	n.d. (0.4)	21.4
Endrin	n.d. (1.7)	n.d. (0.1)	n.d. (0.7)	n.d. (2.1)	n.d. (1.1)	n.d. (5.2)	n.d. (0.7)	n.d. (0.9)	n.d. (2.6)	n.d. (1.0)	n.d. (2.6)	n.d. (2.2)	n.d. (0.9)	n.d. (3.6)	n.d. (0.7)	n.d. (0.9)	n.d. (0.6)	n.d. (2.4)
Endosulfan-I	n.d. (2.1)	n.d. (0.6)	n.d. (0.8)	88.7	n.d. (1.2)	85.9	n.d. (1.2)	n.d. (1.0)	39.4	n.d. (1.7)	n.d. (2.8)	55.7	n.d. (3.1)	n.d. (3.9)	65.6	n.d. (1.8)	n.d. (0.8)	60.6
Endosulfan-II	n.d. (2.1)	n.d. (0.4)	n.d. (0.9)	9.1	n.d. (1.2)	15.1	n.d. (2.5)	n.d. (0.8)	n.d. (2.9)	n.d. (2.7)	n.d. (2.6)	5.4	n.d. (2.0)	n.d. (3.9)	6.9	n.d. (2.5)	n.d. (0.5)	7.2
Endosulfan-sulfate	n.d. (1.2)	n.d. (0.1)	n.d. (0.5)	n.d. (1.4)	n.d. (0.6)	n.d. (3.5)	n.d. (1.4)	n.d. (0.6)	n.d. (1.6)	n.d. (0.9)	n.d. (1.5)	n.d. (1.6)	n.d. (0.8)	n.d. (2.7)	n.d. (1.9)	n.d. (1.0)	n.d. (0.2)	n.d. (1.6)
Mirex	n.d. (0.1)	n.d. (0.1)	n.d. (0.1)	n.d. (0.2)	n.d. (0.1)	n.d. (0.3)	n.d. (0.1)	n.d. (0.1)	n.d. (0.2)	n.d. (0.1)	n.d. (0.3)	n.d. (0.2)	n.d. (0.1)	n.d. (0.4)	n.d. (0.1)	n.d. (0.1)	n.d. (0.3)	n.d. (0.1)
Naphthalene	997	180		467515	508		78.1	1529		54.3	1188		87.9	1441		76.8	958	212250
Acenaphthylene	103	12.0	136	15742	132	13568	8.3	28.3	3275	6.4	21.4	1259	11.8	18.6	5302	11.7	14.3	3765
Acenaphthene	18.3	10.7	83.9	24665	15.0	27125	7.4	25.7	8875	5.0	38.7	7662	11.0	56.8	11330	12.8	35.9	9551
Fluorene	53.1	22.7	113		33.7		17.6	55.6	17496	9.4	38.7	14658	21.8	39.3	20937	26.4	26.1	15599
Phenanthrene	123	68.0	188	96005	72.3	104553	41.6	143	40856	23.1	62.8	38699	50.3	89.0	48729	63.6	43.8	37587
Anthracene	44.1	3.7	32.3	3973	12.1	4626	56.7	32.7	2516	5.6	31.0	1859	11.1	14.2	1707	4.7	10.4	1286
Fluoranthene	44.7	20.1	35.1	6447	19.7	7778	28.5	166	4377	18.0	55.5	3700	51.0	19.4	4602	90.6	12.7	3938
Pyrene	23.6	12.6	45.1	4332	15.0	4808	23.1	128	3472	14.0	51.0	2686	50.0	13.5	3501	79.7	11.8	2827
Benzo(a)anthracene	9.4	2.1	5.7	49.4	9.7	77.1	12.5	15.1	46.7	8.1	13.3	37.7	27.2	5.1	34.3	20.6	6.2	35.6
Chrysene	16.8	5.3	10.9	96.1	13.1	135	23.9	30.4	83.5	16.2	24.1	87.5	42.0	10.0	75.8	41.3	9.4	69.2
Benzo(b)fluoranthene	45.2	2.8	28.4	39.8	43.4	40.3	49.5	40.5	40.3	33.8	36.6	36.8	62.5	34.0	14.2	67.9	30.3	9.5
Benzo(k)fluoranthene	34.2	1.4	22.1	27.1	34.6	37.4	37.7	26.8	26.4	23.0	29.5	27.6	56.2	25.7	6.9	52.7	21.9	4.9
Benzo(a)pyrene	76.8	1.4	47.9	22.5	76.5	31.1	45.1	57.5	54.0	36.8	51.8	49.8	77.1	49.5	6.1	78.9	47.7	6.0
Indeno(1,2,3-c,d)pyrene	91.3	2.9	53.5	62.5	94.6	74.1	80.3	88.1	77.8	65.6	89.9	76.6	109	66.2	20.5	115	67.4	24.0
Benzo(g,h,i)perylene	69.6	3.9	43.7	65.6	78.9	78.9	57.8	62.3	61.2	50.3	62.4	57.1	106	55.5	18.6	95.3	49.2	23.1
Dibenzo(a,h)anthracene	23.7	0.79	16.4	8.9	24.0	14.5	16.6	26.4	21.6	13.7	23.7	23.4	24.9	18.9	4.6	22.9	18.2	8.1