QUANTIFICATION OF NONPOLAR ORGANIC MICROPOLLUTANTS IN A WASTEWATER TREATMENT PLANT BY GC×GC: METHOD DEVELOPMENT, OCCURRENCE, AND ASSESSMENT OF PARTITIONING

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ABSTRACT

This paper presents the development and validation of a method of extraction and quantification of various nonpolar organic micropollutants in wastewater treatment plant (WWTP) influent, effluent, primary sludge, and secondary sludge matrices (including the liquid and particle phases). Analysis was performed by a comprehensive two-dimensional gas chromatograph (GC×GC) coupled to micro-electron capture detector (µECD). The 59 target analytes included polychlorinated naphthalenes, toxaphenes, organochlorine pesticides, polybrominated diphenyl ethers (PBDEs), and polychlorinated biphenyls (PCBs), as well as emerging persistent and bioaccumulative nonpolar chemicals. Quantification of analyte concentrations in sample extracts involved: the use of the internal standard method; a correction using compound- and matrix-specific recoveries; and a peak volume correction based on method blanks. The method is reliable for a wide range of nonpolar micropollutants in all matrices, as indicated by the good intra-day precision, inter-day precision, and relative recovery values. Specifically, for most of the analytes, relative recovery fell between 70% and 130% in all matrix types. Analysis of influent, effluent, primary sludge and secondary sludge samples revealed the occurrence of the following less-studied wastewater micropollutants: PBDE-10, PBDE-116, and pentachloronitrobenzene. Based on measured concentrations we used a three-way partitioning model between the aqueous phase, particulate organic matter (POM), and dissolved organic matter (DOM) to quantify apparent organic solid-water partition coefficients (K_p) of target micropollutants in the WWTP samples. Our findings indicate that sorption to DOM can contribute significantly to the apparent solid-liquid distribution of nonpolar organic micropollutants.

Keywords: wastewater, nonpolar micropollutants, GC×GC, dissolved organic matter (DOM)

1. Introduction

Wastewater, sewage sludge, and wastewater treatment plant (WWTP) effluent contain numerous organic micropollutants, which are potentially toxic. It is believed that nonpolar wastewater micropollutants "tend to partition mainly on the particulate phase and end up that way in the final sludge" (Ratola *et al.*, 2012), due to their high hydrophobicity. However, this model of partitioning to particulate organic matter (POM) often underestimates the levels of nonpolar micropollutants remaining in the effluent and the role that dissolved organic matter (DOM) plays in the micropollutant fate and behavior (Katsoyiannis and Samara, 2007; Barret *et al.*, 2010).

Comprehensive two-dimensional gas chromatography (GC×GC) provides expanded possibilities to detect and quantify nonpolar micropollutants in complex matrices (Murray, 2012). However, no studies exist on its use for a multi-residue analysis of all WWTP samples of interest.

The objective of this study was to develop and validate a quantification method by GC×GC coupled to micro-electron capture detector (µECD) for a wide range of nonpolar micropollutants

in WWTP influent, effluent, and sludge samples, including the liquid and particle phases of the influent and effluent. We used this method to quantify target analytes in samples from the Lausanne municipal WWTP in Switzerland. The results enabled us to characterize micropollutant occurrence and concentrations in the major WWTP streams and also provided a basis to evaluate liquid-solids partition coefficients in those streams.

2. Materials and methods

The target analytes of this study included persistent organic pollutants (POPs), as well as congeners from their chemical families: organochlorine pesticides (OCPs), toxaphenes, PCBs, and polybrominated diphenyl ethers (PBDEs). The target analytes also included polychlorinated naphthalenes (PCNs) and emerging persistent and bioaccumulative nonpolar commercial chemicals from a recent chemical prioritization study (Howard and Muir, 2011). Chemical standards of 59 of these analytes were used for calibration curve construction and GCxGC retention time matching.

Method validation included spiking samples from the WWTP with known amounts of the target analytes and calculating the relative recovery of extraction of each analyte, and the matrix-specific limit of quantification (LOQ). Validation also involved determination of the intra-day instrument precision and the inter-day analytical precision.

For analyte quantification we performed a sampling campaign, during which we took flow-proportioned 24-hour composite samples from the influent and effluent streams, and grab samples from the primary and secondary sludge streams. We separated the liquid phase from the solid phase of influent and effluent samples with filtration. Filtrates underwent solid phase extraction (SPE) using C_{18} extraction disks (USEPA, 2007a). Filter-retained particles and freeze-dried sludge samples underwent pressurized fluid extraction (PFE) (USEPA, 2007b), with in-line clean-up of matrix interferences.

Analysis of extracts and standards was performed on a GCxGC-µECD (Leco) with an Rxi-1ms column (30 m × 0.25 mm × 0.25 µm) as the first dimension, and a BPX-50 column (1.5 m × 0.10 mm × 0.10 µm) as the second dimension. Figure 1 shows a chromatogram of a liquid-phase effluent extract. Analyte quantification involved: external calibration curves; the internal standard method; a correction using the compound- and matrix-specific recoveries; and a peak volume correction based on method blanks. See Dimitriou-Christidis *et al.* (submitted) for details on sampling, extraction, quantification, and method validation.
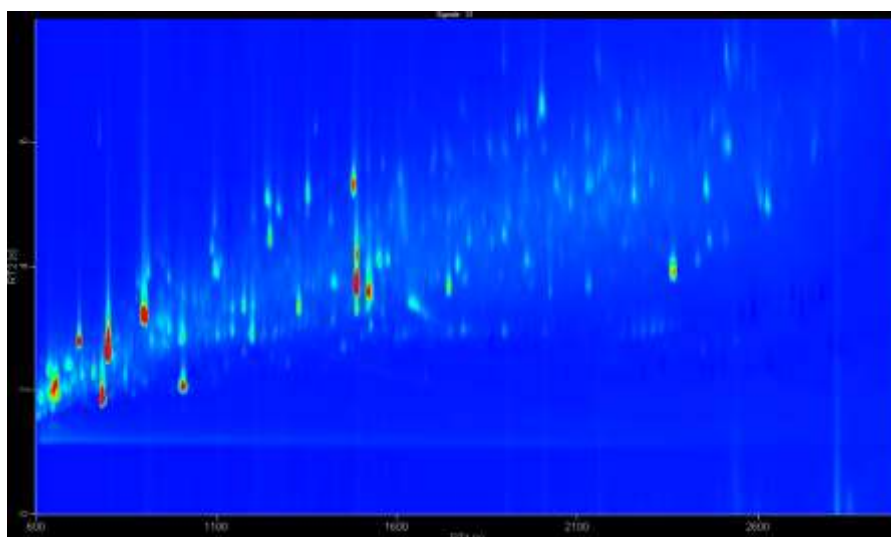

Figure 1: GCxGC-µECD chromatogram of a liquid-phase effluent sample extract.

3. Results

Method validation involved the measurement of matrix-specific relative recoveries, LOQs, and intra- and inter-day method precision for the 59 target analytes (see Table 1 for results for select

analytes). Of the mean relative recoveries for the 59 target analytes, 62%, 66%, and 61% of the values were within an acceptable 70%-130% range for the liquid, particle, and sludge matrices, respectively. For 80% of the target analytes for which an LOQ was determined, the LOQ was <10 ng/L in the liquid and particle matrices. For 67% of the analytes, the LOQ was <10 ng/g in the sludge matrix. The intraday precision of the measurements (expressed as the percent relative standard deviation, %RSD) was satisfactory, with 79% of the target analytes exhibiting %RSD<15%. The inter-day precision of the analytical method was also satisfactory, exhibiting %RSD for the liquid, particle, and sludge matrix, respectively, of: 29%, 13%, and 8% for one internal standard; and 20%, 20%, and 9% for the other internal standard. Therefore, the analytical method is robust and can reliably quantify a wide range of nonpolar analytes in the different wastewater matrices.

Table 1: Results of the method validation for a select subset of the 59 final analytes.

Analyte	Recovery (%) (mean ± RSD[1])			LOQ			Intraday precision (%RSD[1])
	Liquid	Particle	Sludge	Liquid (ng/L)	Particle (ng/L)	Sludge (ng/g)	
Octachloronaphthalene	92±18	107±11	73±15	0.3	0.2	0.4	16
PCB-153-2,2',4,4',5,5'-HexaCB	94±33	109±18	100±21	0.2	0.2	0.3	8
Heptachlor exo-epoxide	77±43	54±16	52±8	0.2	0.3	0.3	7
PBDE-10-2,6-DiBDE	60±7	90±30	85±35	6	2	6	8
PBDE-116-2,3,4,5,6-PentaBDE	49±34	127±36	122±8	9	9	0.7	22
Pentachloronitrobenzene	108±13	62±42	93±27	0.4	0.4	100	9

[1]Relative standard deviation.

We used the analytical method to quantify the concentrations of the 59 target analytes in influent, effluent, primary sludge, and secondary sludge samples from the sampling campaign. Detected micropollutants represented all chemical families analyzed. The following analytes exhibited a high frequency of occurrence above LOQ: octachloronaphthalene, PCB-44, PCB-52, PCB-153, PCB-180, several organochlorine pesticides, PBDE-10, PBDE-28, PBDE-116, musk tibetene, and pentachloronitrobenzene. Among these pollutants, PBDE-10, PBDE-116, and pentachloronitrobenzene are not frequently studied in wastewater. Occurrence of PBDE-10 and PBDE-116 was confirmed in the WWTP effluent by passive sampling and analysis by GC×GC coupled to electron capture negative chemical ionization–time-of-flight mass spectrometry (ENCI-TOFMS) (Dimitriou-Christidis *et al.*, submitted). Furthermore, occurrence of pentachloronitrobenzene was recently confirmed in the sediments of the Vidy Bay in Lake Geneva, the receiving water body of the WWTP (Samanipour *et al.*, in preparation).

We examined whether observed concentration trends of each micropollutant could be explained in terms of partitioning between the water, POM, and DOM phases based on the following model:

$$K_p=K_d(1+[DOC]K_{DOC}) \qquad (1)$$

where K_d (L/g VSS) is the organic solids-liquid partition coefficient, K_p (L/g VSS) is the organic solids-water partition coefficient, [*DOC*] is the concentration of the dissolved organic carbon (kg/L), and K_{DOC} is the dissolved organic carbon-water partition coefficient (L/kg DOC) (Schwarzenbach *et al.*, 2003). K_d values for each micropollutant were estimated in the influent, primary effluent, and effluent streams using the measured concentrations in the liquid (C_l) and particle phases (C_p). Unlike K_d, often reported in wastewater studies, K_p is independent of [*DOC*], allowing meaningful comparisons of K_p between different streams and studies. We estimated the K_{DOC} of each micropollutants as a function of the octanol-water partition coefficient, K_{ow}, for sorption to wastewater-derived DOM (Neale *et al.*, 2011):

$$\log K_{DOC} = 0.2 \log K_{ow} + 2.3 \qquad (2)$$

Table 2: Stream-specific K_p estimates (L/g VSS).

Analyte	logK_{ow}	Influent	Primary effluent	Secondary effluent	Mean	Standard error	Relative error (%)
PCB-18	5.5	18	25	36	27	6.8	25
PCB-52	6.1	170	7.9	12	55	48	86
PCB-153	7.7	2.8	ND[1]	130	69	38	56
PBDE-77	6.3	ND[1]	6.8	ND[1]	6.8	1.4	20
β-BHC	3.8	92	22	ND[1]	57	42	74
γ-BHC	3.8	20	230	ND[1]	160	100	64
Aldrin	6.5	7.0	15	ND[1]	11	3.8	35
Heptachlor exo-epoxide	5.0	61	18	ND[1]	39	27	68
Dieldrin	5.2	ND[1]	48	ND[1]	48	19	41
Endrin	5.2	270	130	ND[1]	150	90	60
β-Endosulfan	3.8	9.3	27	37	25	5.2	21
Pentachloro-nitrobenzene	4.6	11	20	64	30	10	34
Musk tibetene	3.5	23	150	ND[1]	97	40	41

[1]Not determined because the mean K_d value was not estimated from at least two pairs of liquid- and particle-phase concentration values.

Stream-specific and mean K_p estimates are presented in Table 2 for the 13 of the 59 analytes for which stream-average K_d values were estimated from at least two pairs of C_p and C_l values. We used C_p and C_l pairs measured in the same sample, when available. Values of $[DOC]K_{DOC}$ (eq. 1) exhibit ranges of: 0.09 to 0.60 for the influent; 0.10 to 0.71 for the primary effluent; and 0.01 to 0.08 for the secondary effluent. This indicates that sorption to DOM may contribute significantly to the solid-liquid distribution of micropollutants in the influent and primary effluent streams, altering the apparent K_d value by up to 60%. Our data does not exhibit a strong linear relationship between logK_p and logK_{ow}, such as this reported by Dobbs *et al.* (1989) for polycyclic aromatic hydrocarbons (PAHs) and OCPs (although our K_p estimates fall in the same neighborhood as the Dobbs *et al.* (1989) relationship). The lack of a linear trend in our data could be indicative of measurement variability (e.g., the significant standard errors in K_p) or it could be due to the fact that the relationship that we used to estimate the K_{DOC} (eq. 2) is not appropriate for our system.

4. Conclusions

The analytical method presented in this paper is robust and can reliably quantify a wide range of nonpolar analytes in the different wastewater matrices. Analysis of samples from the Lausanne WWTP revealed the occurrence of PBDE-10, PBDE-116, and pentachloronitrobenzene, which are not frequently studied in wastewater. DOM plays an important role in the solids-liquid distribution of hydrophobic pollutants in WWTP streams, although the dependence of wastewater-specific K_p and K_{DOC} values on compound hydrophobicity remains unclear. Thus, the phenomenon of pollutant sorption to wastewater matrices deserves further investigation.

REFERENCES

1. Barret M., Patureau D., Latrille E. and Carrère H. (2010) A three-compartment model for micropollutants sorption in sludge: Methodological approach and insights. Water Res., **44**, 616-624.
2. Dimitriou-Christidis P., Bonvin A., Samanipour S., Hollender J., Rutler R., Westphale J., Gros J. and Arey J.S. (submitted) GCxGC quantification of priority and emerging nonpolar organic micropollutants in all types of wastewater streams: Analysis methodology, chemical occurrence, and partitioning.

3. Dobbs R.A., Wang L. and Govind R. (1989) Sorption of toxic organic compounds on wastewater solids: correlation with fundamental properties. Environ. Sci. Technol., **23**, 1092-1097.
4. Howard P.H. and Muir D.C. (2010) Identifying new persistent and bioaccumulative organics among chemicals in commerce. Environ. Sci. Technol., **44**, 2277-2285.
5. Katsoyiannis A. and Samara C. (2007) The fate of dissolved organic carbon (DOC) in the wastewater treatment process and its importance in the removal of wastewater contaminants. Environ. Sci. Pollut. R. Int., **14**, 284-292.
6. Murray J.A. (2012) Qualitative and quantitative approaches in comprehensive two-dimensional gas chromatography. J. Chromatogr. A, **1261**, 58-68.
7. Neale P.A., Antony A., Gernjak W., Leslie G. and Escher, B.I. (2011) Natural versus wastewater derived dissolved organic carbon: Implications for the environmental fate of organic micropollutants. Water Res., **45**, 4227-4237.
8. Ratola N., Cincinelli A., Alves A. and Katsoyiannis A. (2012) Occurrence of organic microcontaminants in the wastewater treatment process. A mini review. J. Hazard. Mater., **239**, 1-18.
9. Samanipour S., Trogolo, D. and Arey, J. S. In preparation.
10. Schwarzenbach R.P., Gschwend P.M. and Imboden D.M. (2003) Environmental Organic Chemistry. John Wiley & Sons Hoboken, New Jersey.
11. U.S. Environmental Protection Agency (USEPA) (2007a) Method 3535A: Solid-Phase Extraction (SPE), Revision 1.
12. U.S. Environmental Protection Agency (USEPA) (2007b) Method 3545A: Pressurized Fluid Extraction (PFE), Revision 1.