The effect of sample filtration prior to analysis of organic micropollutants in wastewater

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INTRODUCTION

Wastewater treatment plants (WWTPs) represent the main entry pathway of organic micropollutants (OMPs) in the aquatic environment. The development of advanced instrumental analytics allows for the detection and quantification of a variety of these compounds in concentration levels of µg/L to ng/L in wastewater discharges and adjacent water bodies. The proper analysis of wastewater samples is of great importance for a representative monitoring of these compounds in a WWTP. Numerous studies [1] [2] report results for micropollutants in the influent and effluent of WWTPs after filtrating the samples prior to analysis. This study examines the effect of sample filtration on the concentration levels of selected micropollutants and on the calculated removal efficiency of the treatment plant.

Objective: Are filtrated samples representative for monitoring micropollutants in a wastewater treatment plant?

METHODS

Sampling location:
3 municipal WWTPs: LFKW (Germany),PE= 9660, WWTP1(Spain),PE= 58469 , WWTP2 (Spain),PE= 31915

Sampling period: November 2015

Sampling points: Influent (post primary treatment) and final effluent (effluent microsieve after secondary treatment for LFKW, effluent secondary treatment for WWTP1 and WWTP2)

- Over 3 consecutive days (24h composite samples for LFKW, grab samples for WWTP1 and WWTP2)
- 13 micropollutants (MPs) analyzed: carbamazepine (CBZ), diclofenac (DCF), ibuprofen (IBU), venlafaxine, Tonalide (AHTN), Galaxolide (HHCB), triclosan (TCS), mecoprop (MECO), terbutryne, caffeine (CAFF) , Isocyclemone E (OTNE), bisphenol A, Tris(2-chloroethyl)phosphate (TCEP)

MPs analysis procedure: Liquid/liquid extraction of samples in acidic and neutral fractions coupled with GC-MS

❑ **Samples analyzed non-filtrated (NF) and filtrated (F)** (with 0.45 µm cellulose membrane)

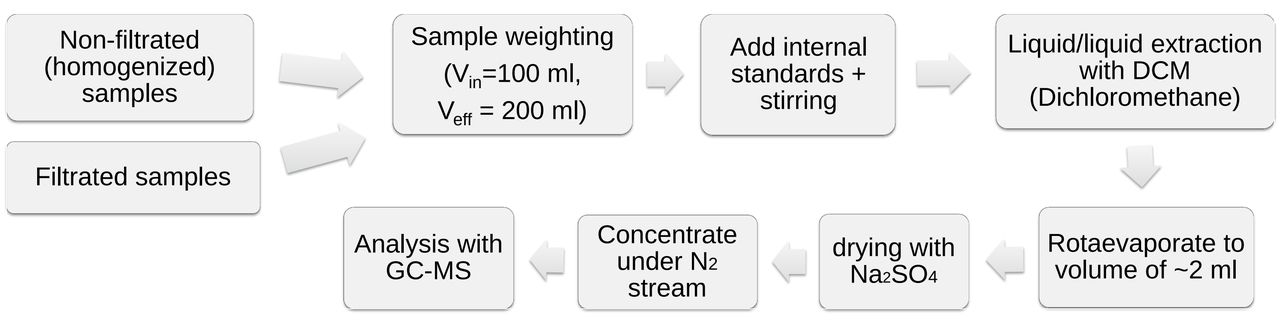


Figure 1. MP analysis procedure-diagram

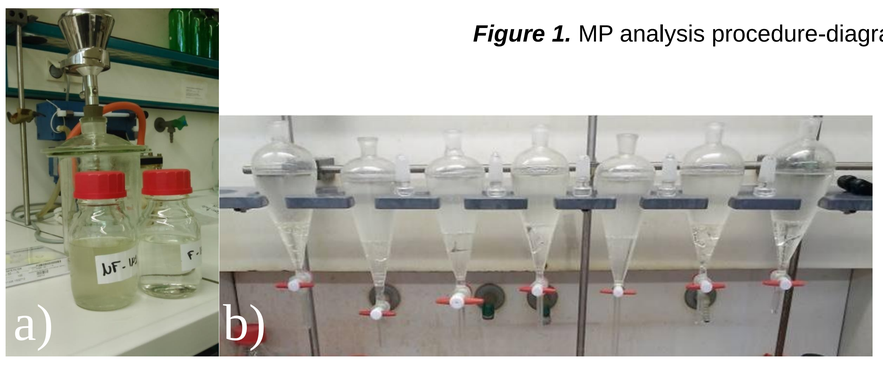


Figure 2.
a) Influent sample filtrated (F) and non-filtrated (NF)
b) Liquid/Liquid extraction

DISCUSSION

- The outcoming phase distribution (PD) is comparable among the three studied WWTPs for most of the examined MPs. Moreover, they are similar to reported results in the literature [3]. This implies the validity of the conclusions when referring to a municipal WWTP.
- The phase distribution varies among substances (Fig. 3-4). Some substances showed significant tendency to sorb on particles (HHCB: $PD_{aqueous,inf}$ <25%, $PD_{aqueous,eff}$ >85%) while others had low distribution in the particle phase (ibuprofen: $PD_{aqueous,inf} \approx PD_{aqueous,eff}$ >90%).
- For most MPs (especially lipophilic): $PD_{aqueous,effluent} > PD_{aqueous,influent}$ ➔ Reduction of suspended solids after secondary treatment explains the higher fraction of substance present in the aqueous phase (Fig. 6).
- The calculated removal efficiency of the WWTP:LFKW differs in filtrated and non-filtrated samples, which results from phase distribution differences between influent and effluent wastewater samples (Fig. 5.)
- The difference of the substances' phase distribution between influent and effluent showed strong correlation with their logD value, which describes hydrophobicity (R^2: 0.79-0.82). The more lipophilic MPs sorb on particles and show significant difference when determined in filtrated samples.

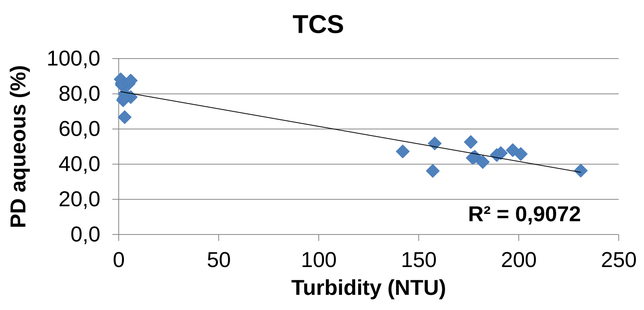
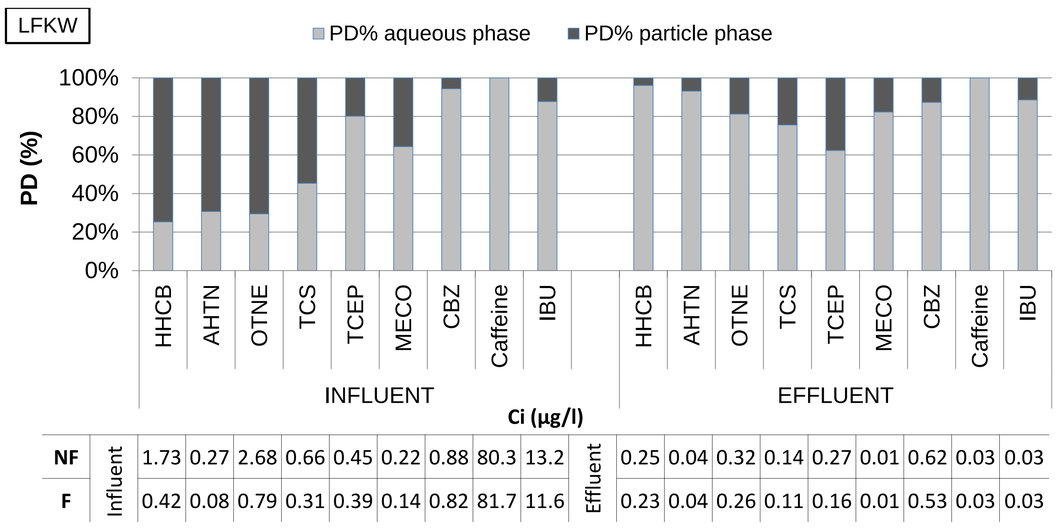


Figure 6. Correlation turbidity (NTU) – PD aqueous % of TCS for influent+effluent, all WWTPs

RESULTS

$$Phase\ distribution_{aqueous\ phase}, PD\% = \frac{Concentration\ in\ aqueous\ phase, F\ [\mu g/L]}{Concentration\ in\ homogenized\ phase, NF\ [\mu g/L]} x100$$



		HHCB	AHTN	OTNE	TCS	TCEP	MECO	CBZ	Caffeine	IBU
NF	Influent	1.73	0.27	2.68	0.66	0.45	0.22	0.88	80.3	13.2
F	Influent	0.42	0.08	0.79	0.31	0.39	0.14	0.82	81.7	11.6
NF	Effluent	0.25	0.04	0.32	0.14	0.27	0.01	0.62	0.03	0.03
F	Effluent	0.23	0.04	0.26	0.11	0.16	0.01	0.53	0.03	0.03

Figure 3. Mean phase distribution, PD% (particle phase = homogenized (NF) - aqueous (F) phase of MPs with mean concentration levels in Influent and Effluent samples

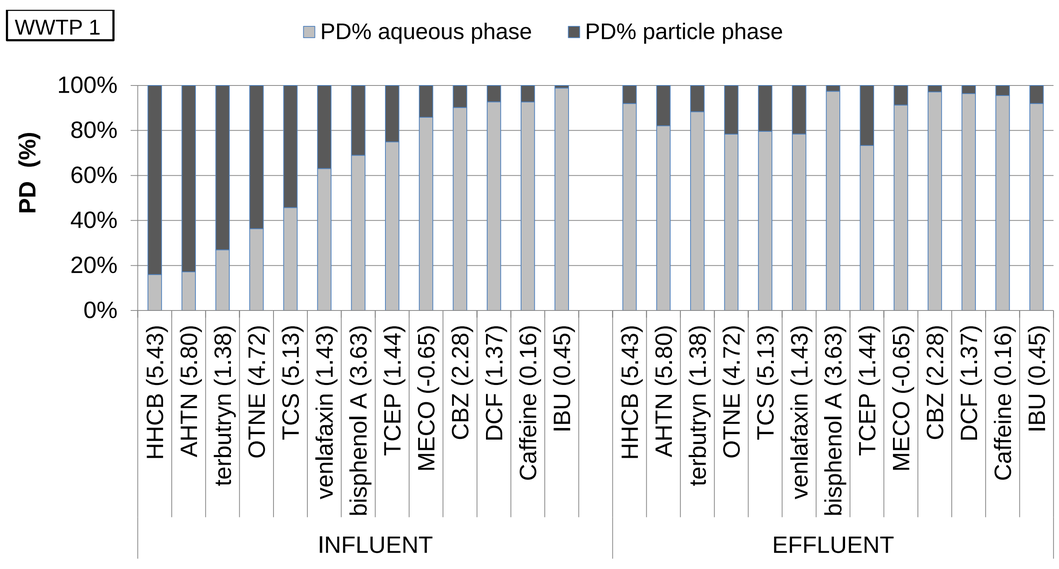


Figure 4. Mean phase distribution, PD (%) of MPs in Influent and Effluent samples of WWTP1 with logD pH=7.4 in ()

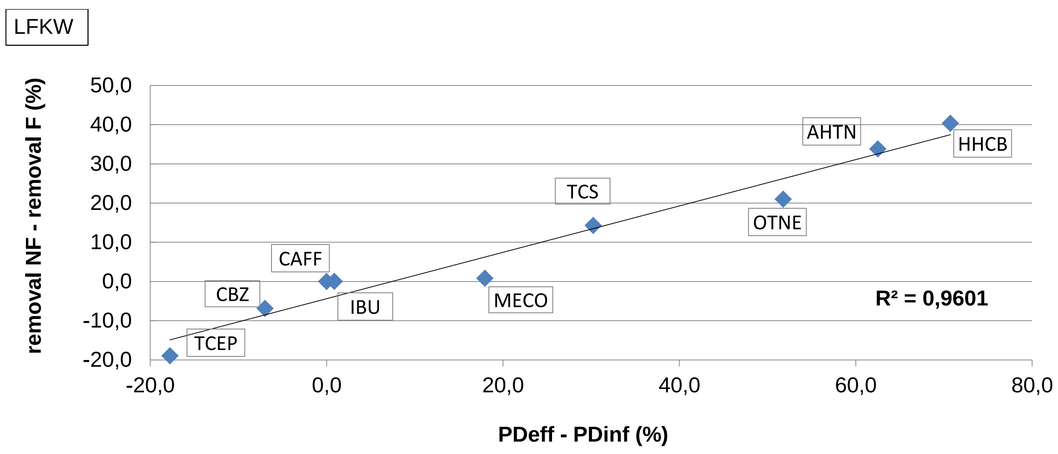


Figure 5. Correlation of difference in PD,aqueous(%) (effluent-influent) - difference in calculated mean removal efficiency of LFKW for MPs with non-filtrated (NF) and filtrated (F) samples

CONCLUSIONS

- Depending on substance physicochemical properties, the micropollutants showed variant phase distributions
- The phase distribution of more lipophilic micropollutants differed significantly between influent and effluent samples, which can be attributed to differences in the solids content
- For accurate reporting concentration levels for a wide range of micropollutants, their determination in non-filtrated samples is essential
- The complete mass balance of micropollutants in a WWTP should consider both aqueous and particle fractions
- The practiced analysis method of liquid/liquid extraction coupled with GC/MS performed with non-filtrated samples (which consider both aqueous and particle phases) is recommended for determination of a wide range of micropollutants in influent (heterogeneous/heavy matrix) and effluent samples of WWTPs

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