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Fast empirical lab method for performance projections of large-scale powdered activated carbon re-circulation plants

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Abstract

Powdered activated carbon (PAC) for organic micro-pollutant (OMP) removal can be applied effectively on wastewater treatment plant (WWTP) effluents by using re-circulation schemes, accumulating the PAC in the system. This technique is complex because several factors are unknown: (i) the PAC concentration in the system, (ii) specific and average contact times of PAC particles, and (iii) PAC particle loadings with target compounds/competing water constituents. Thus, performance projections (e.g. in the lab) are very challenging. We sampled large-scale PAC plants with PAC sludge re-circulation on eight different WWTPs. The PAC plant-induced OMP removals were notably different, even when considering PAC concentrations in proportion to background organic sum parameters. The variability is likely caused by differing PAC products, varying water composition, differently effective plant/re-circulation operation, and variable biodegradation. Plant PAC samples and parts of the PAC plant influent samples were used in laboratory tests, applying multiples (0.5, 1, 2, 4) of the respective large-scale “fresh” PAC doses, and several fixed contact times (0.5, 1, 2, 4, 48 h). The aim was to empirically identify suitable combinations of lab PAC dose (as multiples of the plant PAC dose) and contact time, which represent the PAC plant performances in removing OMPs (for specific OMPs at single locations, and for averages of different OMPs at all locations). E.g., for five well adsorbing, little biodegradable OMPs, plant performances can be projected by using a lab PAC dose of twice the respective full-scale PAC dose and 4 h lab contact time (standard deviation of 13 %-points).

Keywords

adsorption; powdered activated carbon; organic micro-pollutant; trace organic contaminant; powdered activated carbon recirculation; wastewater treatment plant

Highlights

- Variable org. micropollutant (OMP) removal by powdered activated carbon at 8 plants
- Development of lab test predicting large-scale OMP removals at different locations
- Lab dose/time combinations identified to project specific & average OMP removals
- Acceptable scattering; literature comparison reveals transferability

1 Introduction

Adsorption onto powdered activated carbon (PAC) as an advanced step for the removal of organic micro-pollutants (OMPs) is currently being integrated into an increasing number of wastewater treatment plants (WWTPs) in several countries like Switzerland (Boehler et al. 2012), France (Mailler et al. 2015), and Germany (Metzger 2010). Among different design options the most simple ones are (option A) dosing PAC directly into existing secondary treatment steps/biology (Boehler et al. 2012; Evers et al. 2017) or (option B) into secondary effluents/rapid filtration influents (Ruhl et al. 2014; Altmann et al. 2015a; Altmann et al. 2015b; Loewenberg et al. 2016). A more complex option (C) is to build additional tertiary contactor basins which receive secondary effluent and which are followed by tertiary sedimentation/rapid filtration, with re-circulation of the PAC sludge (Garland & Beebe 1970; Nicolet & Rott 1999; Metzger 2010; Boehler et al. 2012; Margot et al. 2013; Mailler et al. 2015; Meinel et al. 2016a; Evers et al. 2017; Karelid et al. 2017a). The higher complexity of option C is usually outweighed by its better performance (Boehler et al. 2012; Evers et al. 2017), ultimately translating into substantially reduced operational costs (Nicolet-Misslbeck 2014).

Compared to primary effluents (option A), secondary effluents (options B & C) contain less adsorption-competitive background organic matter (BOM), thus reducing adverse BOM competitive effects on OMP removals (Najm et al. 1991; Karanfil et al. 1999; Kilduff & Wigton 1999; Graham et al. 2000; Cook et al. 2001; Matsui et al. 2003; Nowotny et al. 2007; Shimabuku et al. 2014; Zietzschmann et al. 2015b; Hu et al. 2016; Streicher et al. 2016; Zietzschmann et al. 2016a; Shimabuku et al. 2017). Compared to option B, option C substantially increases the residence time of PAC in the system due to the re-circulation design, resulting in very high PAC concentrations (g/L range) during continuous operation (Meinel et al. 2016a) and thus increasing the usage of the PAC capacity. The technique of PAC re-circulation is often termed “two step treatment” which can be somewhat misleading as the PAC is kept continuously in the system while only a small portion of the PAC particles is removed as excess PAC. Thus, PAC particles will be in contact with secondary effluent repeatedly rather than twice (cf. Figure 1). Pilot studies clearly showed the advantage of PAC-recirculation over single-step treatment without re-circulation (Meinel et al. 2016a; Karelid et al. 2017a). Therefore, the current study only examines such PAC plants with PAC sludge re-circulation for PAC enrichment in the adsorption reactor (option C).

Typical PAC re-circulation schemes in WWTPs consist of one or more contactors, a separation step, and a pumping system allowing for re-cycling the PAC sludge. Relatively small amounts (mg/L range) of fresh PAC are dosed to the adsorption step influent (effluent from clarification after mechanical-biological treatment). Subsequently, the PAC/water slurry is separated, e.g. via sedimentation (Mailler et al. 2015; Karelid et al. 2017b), hydrocyclones (Meinel et al. 2016a), and/or filtration (Boehler et al. 2012; Loewenberg et al. 2014; Ruhl et al. 2014; Altmann et al. 2015a; Altmann et al. 2015b; Krahnstöver & Wintgens 2018). The separation of the PAC/water suspension is enhanced by adding flocculant and polymer at one or more points within the PAC plant. It was shown that dosage of flocculant/coagulant does not affect adsorptive OMP removals (Altmann et al. 2015c). The separated PAC sludge is then re-introduced into the adsorption step influent.

In terms of the occurring processes, PAC plants with re-circulation setups are difficult to characterize. The PAC in the re-circulation sludge is normally accumulated over several weeks, to reach the envisaged high PAC concentrations in the g/L range. The differentiation between the sludge components (flocculant/biomass/PAC/inorganic particles) in re-circulation systems is difficult (Dittmann et al. 2018) and the exact PAC concentrations are usually not known (Meinel et al. 2016a); the only known process parameter in this respect is the dose of fresh PAC. Also, an exact contact time cannot be specified. The loading of the PAC (with OMP and BOM) in the system cannot be specified either, because of the different PAC particle residence times within the re-circulation system. In addition, changing water composition may induce partially dynamic competition between OMP and BOM. Therefore the OMP removal performances of large-scale PAC re-circulation setups are difficult to assess without using pilot/demonstration plants. Lab tests with pure water cannot be extrapolated to WWTP effluent applications (Alves et al. 2018). Also, lab tests are largely limited in their capabilities to reproduce the “black box” of large-scale PAC re-circulation because PAC-water separation and PAC re-suspension are elaborate. (Centrifugation of relatively high batch volumes (e.g. 100 mL) is required whilst PAC loss during supernatant removal must be minimized.) An approach using large centrifuge beakers was developed for repeated reuse of PAC (Zietzschmann et al. 2015a) and adopted for PAC reuse with addition of fresh PAC, simulating the start-up phase of a re-circulation system with increasing PAC concentrations (Meinel et al. 2016b).

Although this approach allows for detailed examination of the process, it is laborious and time consuming due to repeated PAC-water separation followed by re-suspension and dosage of fresh PAC. Thus, this lab procedure is not useful for scientists and practitioners in need for rapid projections. Therefore, a more practical empirical lab test would be desirable, allowing for quick (several hours) and easy estimation of the adsorptive performance of large-scale PAC re-circulation plants. The assessment of such tests should mainly focus on refractory/poorly biodegradable OMPs: The additional retention time in PAC stages, in combination with favorable conditions for microorganisms, would complicate a concise differentiation of adsorptive/biodegradative removals of biodegradable compounds at different WWTPs/operating conditions.

In the present study, large-scale PAC plants equipped with PAC re-circulation, operated on eight WWTPs in the state of Baden-Württemberg (Figure S1 in the Supporting Information, SI), Germany, were sampled and examined regarding OMP removals. The OMP removals at different locations can be compared directly since in real waters (e.g. WWTP effluents), OMP removals are generally independent of the initial OMP concentration (Knappe et al. 1998; Westerhoff et al. 2005; Altmann et al. 2014; Zietzschmann et al. 2016a). Firstly, the similarities and differences of the plant performances in removing several OMPs should be assessed. Secondly, the large-scale OMP removals were compared to OMP removals on the lab-scale – in batch-tests using the sampled large-scale PAC plant influents and the corresponding sampled PACs, with different combinations of PAC doses (as multiples of the respective plant “fresh” PAC doses) and fixed adsorption times. The lab tests were conducted as single-step batches (without PAC-water separation & subsequent PAC re-suspension), in order to use a simple and quick lab procedure. The aim was to identify one or several combinations of lab PAC dose/adsorption time which satisfactorily reproduce the OMP removals reached on the sampled large-scale PAC re-circulation plants. To date, such PAC performance projections are barely examined and the current work targets this gap to facilitate more rapid assessments of PAC as an advanced WWTP effluent treatment step.

2 Materials and Methods

2.1 PAC plants

The large majority of PAC plants in Germany are operated in the state of Baden-Württemberg which pursues an initiative for advanced OMP removal on WWTPs. Most of these plants are equipped with PAC sludge re-circulation systems (currently 12 full-scale plants). Eight PAC re-circulation plants were included in the tests (map in Figure S1), of which seven are full-scale (Böblingen-Sindelfingen, Kressbronn-Langenargen, Lahr, Laichingen, Mannheim, Neu-Ulm/Steinhäule, Ravensburg/Langwiese) and one is pilot-scale (Kompetenzzentrum Spurenstoffe, Stuttgart). The examined WWTPs, the volumetric flows treated in the respective PAC plants, the water residence times in the adsorption steps, the applied PAC products and doses, the points of PAC sludge re-circulation in the respective plants, and the sampling dates are given in Table 1; PAC manufacturer data are reported in Table S1 in the SI. A general scheme of the PAC adsorption plants amended to the WWTPs is given in Figure 1. In most cases, the adsorption step follows the biological treatment train and receives effluent from the secondary sedimentation/clarifier. (Note that secondary treatment on most plants contains a biological phosphorous removal stage prior to the denitrification which is not shown in Figure 1.) Typically, PAC is dosed into the influent of the adsorption step, flocculant/coagulant is dosed into the adsorption reactor and to the sedimentation basin, and polymer is dosed into the effluent of the adsorption step. In Böblingen-Sindelfingen, PAC is dosed into the secondary effluent; in Lahr, PAC and flocculant are dosed into the secondary effluent; in Laichingen and Ravensburg, flocculant is dosed into the adsorption step and into the effluent of the sedimentation basin, and polymer is dosed into the adsorption step. In all plants, PAC is accumulated in the adsorption reactor, by re-circulating PAC from the sedimentation to the adsorption step influent; excess PAC is returned to the secondary treatment (denitrification/aeration/sedimentation); in Böblingen-Sindelfingen and Mannheim, excess PAC is withdrawn from the adsorption basin and returned to the oxic tank/aeration; at the KomS pilot, excess PAC is discarded. More detailed schemes of most plants can be retrieved via KomS (2017).

Table 1: Overview of the examined WWTPs and PAC plants, PE – population equivalent, $Q_{max,ads}$ – maximum volumetric flow treated, $t_{resid.water}$ – water residence time in adsorption step, exc. – excess, DOC – dissolved organic carbon.

	Acronym	Size [PE]	$Q_{max,ads}$ [L/s]	$t_{resid.water}$ [min]	PAC re-circulated to	Applied PAC product	"fresh" PAC dose on sampling day [mg/L]	PAC/DOC [mg/mg]	Day of sampling
Böblingen-Sindelfingen	BöSi	250,000	1,000	30	· adsorption · aeration (exc. PAC)	Cabot Norit SAE Super	12	1.0	18 May 2017
KomS-Pilot (Stuttgart)	KomS	(pilot)	-		· adsorption · (exc. PAC discarded)	Donaucarbon Carbopal AP	10	1.5	16 Nov 2016
Kressbronn-Langenargen	Kress	24,000	250	35	· adsorption · denitrific. (exc. PAC)	Donaucarbon Carbopal AP	5.2	0.7	18 May 2017
Lahr	Lahr	100,000	350	47	· adsorption · denitrific. (exc. PAC)	Carbotech PAK C 880 SR	11	1.4	29 May 2017
Laichingen	Laich	29,200	150	45	· adsorption · denitrific. (exc. PAC)	Carbotech PAK C 880 SR	6	1.3	16 Nov 2016
Mannheim	Mann	725,000	1,500	40	· adsorption · aeration (exc. PAC)	CSC pharmA-Clean	10	1.3	19 Jun 2017
Neu-Ulm/ Steinhäule	NUlm	445,000	1,600	34	· adsorption · aeration (exc. PAC)	Chemviron Pulsorb WP 235	15	2.7	15 Nov 2016
Ravensburg/ Langwiese	Rav	184,000	1,100	57	· adsorption · $2^{nd.}$ sedi. (exc. PAC)	CSC pharmA-Clean	8.5	1.5	15 Nov 2016

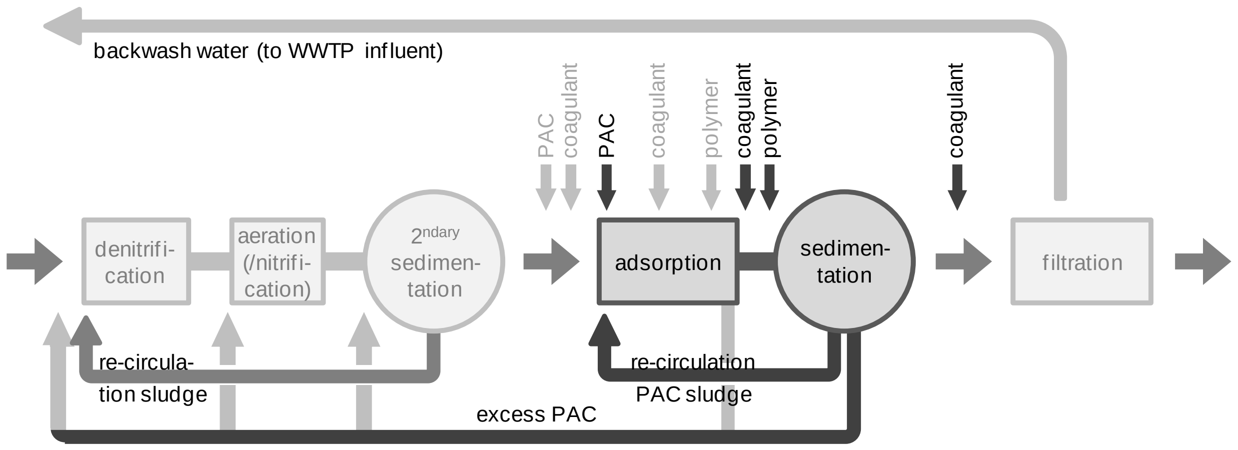


Figure 1: General plant scheme for the tested PAC re-circulation plants; PAC, coagulant, and polymer dosing points: dark grey – standard, light grey – optional; excess PAC withdrawal in Böblingen-Sindelfingen and Mannheim from adsorption basin – light grey; excess PAC re-circulation points variable – light grey; KomS pilot: excess PAC discarded.

2.2 Sampling

24 h composite samples were taken from the influents and effluents of the PAC plants. At the KomS pilot, Laichingen, Neu-Ulm, and Ravensburg samples were taken, 0.45 µm-filtered, cooled, and used in the laboratory tests within 24 h. The samples of Böblingen-Sindelfingen, Kressbronn, Lahr, and Mannheim were kept frozen until the day before laboratory testing. The effluent samples and parts of the influent samples were analyzed to determine the plant performances in removing DOC, ultraviolet absorption at 254 nm (UV_{254}), and OMPs. The influent samples were further used for the batch tests. Samples of the PACs were obtained directly from the dosing systems of the examined PAC plants on the day of water sampling.

2.3 Batch tests

PAC batch tests were conducted in a typical bottle point method, using 50 mL of the respective water in 300 mL glass bottles in which the desired PAC doses were adjusted by pipetting from PAC stock suspensions, made from dried PAC and ultra pure water (resistivity >17 MΩ cm, *ELGA Berkefeld*, Germany). The adjusted PAC concentrations in the batches were multiples (0.5, 1, 2, and 4) of the dosed "fresh" PAC concentration of the respective PAC plant. The PAC stock suspension volumes added to the batches were 100, 200, 400, and 800 µL for all tested waters, by using differently concentrated stock suspensions of the respective sampled PAC (g/L): 3.00 (BöSi), 2.50 (KomS), 1.31 (Kress), 2.75 (Lahr), 1.50 (Laich), 2.50 (Mann), 3.75 (NUlm), and 2.13 (Ravensburg), resulting in water dilutions ≤ 1.6% (max. 0.8 mL PAC stock suspension per 50 mL batch volume). Upon dosage, the batches were closed and put on a one-dimensional horizontal shaker for thorough mixing (note the impacts of different mixing techniques on OMP removals at short timescales shown in the SI). The tested adsorption times were 0.5, 1, 2, 4, and 48 h; for each dose/time combination, a separate batch was used. When finished, the batch waters were filtered through 0.45 µm regenerated cellulose membrane syringe filters (*Chromafil X-tra RC 25/45*, *Macherey-Nagel*, Germany), previously rinsed with ultra pure water. Due to an experimental error, the Böblingen-Sindelfingen batch with a lab dose of 4 times the plant dose and an adsorption time of 0.5 h could not be utilized.

Additional data for verification was obtained from preliminary tests which were conducted with additional samples, in an analogous test procedure as described above but with less lab dose/time combinations: (1) Böblingen-Sindelfingen (sampled in May 2014, lab PAC dose multiple of plant PAC dose: 1, i.e. 10 mg/L, SAE Super/Norit Germany, 24 h), (2) Berlin pilot plant at phosphorous elimination plant Tegel (lab PAC dose multiple of plant PAC dose: 1, i.e. 20 mg/L, Aquasorb 5000 P-s/Jacobi Germany, 0.5 & 1 h, cf. Meinel et al. 2016a).

2.4 Water quality analysis

High performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS) was used for the quantification of OMP, based on an established multi-method (Zietzschmann et al. 2015a; Zietzschmann et al. 2015b; Zietzschmann et al. 2016a); details are given in the SI (HPLC conditions, limits of quantification (LoQs), …). OMPs were only considered if they were detected at all 8 sampled locations. DOC was measured in triplicate by catalytic combustion on a *varioTOC cube* (*elementar Analysensysteme*, Germany). UV_{254} was measured in 1 cm *Suprasil* quartz cuvettes (*Hellma*, Germany) on a *Lambda 12* (*Perkin-Elmer*, USA); specific ultraviolet absorbance (SUVA) was calculated as UV_{254} [1/m] divided by DOC [mg/L]. Fractionized DOC and UV_{254} were measured on a liquid chromatography with online organic carbon detection (LC-OCD, *DOC-Labor Huber*, Germany) with a *HW50S* size exclusion LC column (*Toyopearl*, Japan); data were evaluated using the software *Chromcalc* (*DOC-Labor Huber*, Germany), with typical peak allocation (Huber et al. 2011); the local chromatogram minimum between the fractions of the building blocks and the low molecular weight acids was taken as the integration limit between high/low molecular weight organic compounds (cf. Zietzschmann et al. 2014; Zietzschmann et al. 2016a; Zietzschmann et al. 2016b).

2.5 Calculations

To determine the combination of lab PAC dose and adsorption time ("lab dose/time combination") which best represents PAC plant OMP removals, several calculations were conducted, as outlined in the following; a corresponding scheme is included in Table S2. Firstly, differences of the OMP removals achieved in the lab and in the PAC plants were calculated as shown in Equation 1.

$$RD_{X,i,k} = R_{X,i,lab,k} - R_{X,i,plant} \qquad \textbf{Equation 1}$$

where *X* is the index for the respective location, *i* is the index for the OMP under consideration, *k* is the index for the lab dose/time combination, $RD_{X,i,k}$ is the removal difference in percentage points, $R_{X,i,lab,k}$ is the lab removal in % at dose/time combination *k*, and $R_{X,i,plant}$ is the PAC plant removal in %, respectively.

For each location and OMP (indices *X* and *i* in Equation 1), 20 removal differences were calculated as 20 lab dose/time combinations *k* were tested (whereas there is only 1 PAC plant removal for each location and OMP). Negative removal differences mean that the respective plant removal is higher than the lab removal, while positive values mean higher lab than plant removals. Values equal to zero mean that lab and plant removals were the same.

For comparisons of average OMP removals, the removal differences $RD_{X,i,k}$ from Equation 1 were averaged over different OMPs *i*, as shown in Equation 2. This was done for the 10 OMPs found at all plants, and a subset of 5 poorly biodegradable, well adsorbable OMPs (benzotriazole, carbamazepine, diclofenac, methylbenzotriazole, metoprolol) with initial concentrations >4*LoQ.

$$RD_{X,av,k} = \frac{1}{n}\sum_{i=1}^{n} RD_{X,i,k} \qquad \textbf{Equation 2}$$

where $RD_{X,av,k}$ is the OMP-average removal difference at location X for lab dose/time combination k, n is the number of OMPs included in averaging, i is the index for the respective OMP, and $RD_{X,i,k}$ is the removal difference at location X for OMP i at lab dose/time combination k.

Also, averages over the 8 tested locations were calculated for single OMPs, by averaging the removal differences $RD_{X,i,k}$ from Equation 1 over all plants, as shown in Equation 3.

$$RD_{av,i,k} = \frac{1}{8}\sum_{X=1}^{8} RD_{X,i,k} \qquad \textbf{Equation 3}$$

where $RD_{av,i,k}$ is the plant-average removal difference for OMP i at lab dose/time combination k, 8 is the number of locations, X is the index for the respective location, and $RD_{X,i,k}$ is the removal difference at location X for OMP i at lab dose/time combination k.

Furthermore, averages over all plants were calculated of the OMP-average removals, by inserting the $RD_{X,av,k}$ from Equation 2 into the right side of Equation 3. Accordingly, plant-average OMP-average removal differences $RD_{av,av,k}$ were determined for all tested lab dose/time combinations k to find the overall best representation when several/all OMPs and all locations are included simultaneously.

To estimate scattering of the calculated removal differences, standard deviations were determined for all of the plant-average removal differences resulting when using Equation 3. (Calculating standard deviations from OMP-average removal differences does not make sense because of the strongly variable adsorbability and biodegradability of different OMPs.)

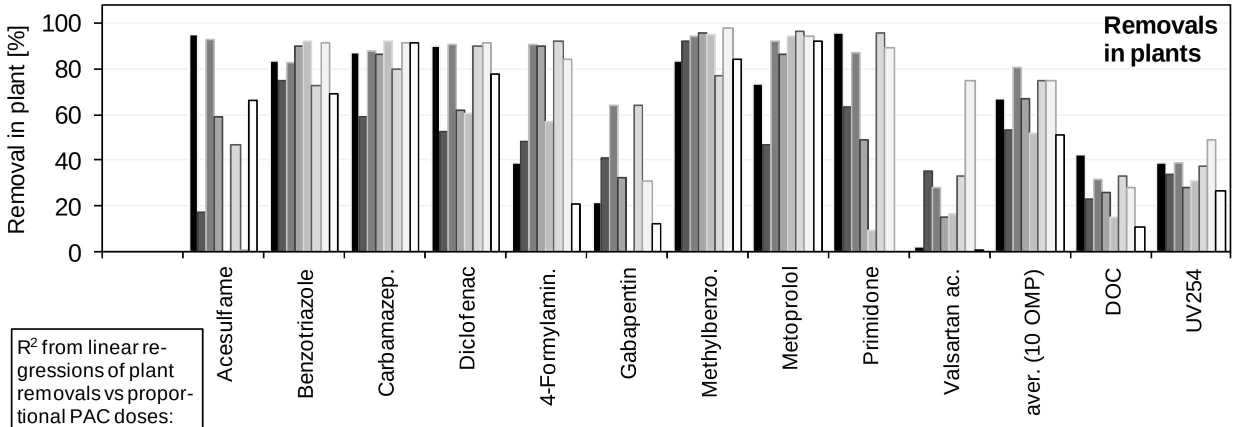
3 Results and Discussion

3.1 Water characterization and large-scale OMP removals

The DOC concentrations, UV_{254}, SUVAs, low molecular weight (LMW) DOC concentrations, and OMP concentrations are given in Table S3 (only those OMP that were quantifiable in all PAC plant influent samples are considered). The DOC concentrations range from 4.7 mg/L in Laichingen to 12.8 mg/L in Böblingen-Sindelfingen. The absolute values of UV_{254} are about twice as high as the corresponding DOC values, resulting in SUVAs of 2.1-2.3 L/m/mg, except for Böblingen-Sindelfingen with a lower SUVA of 1.4 L/m/mg. The LMW DOC concentrations are between 1.7-5.0 mg/L, making up a minimum of 31% (Neu-Ulm) and a maximum of 43% (KomS pilot) of the corresponding DOC concentrations. A more detailed insight into the BOM/DOC composition is given in the LC-OCD chromatograms of the tested WWTP effluents (Figure S2). Overall, the BOM/DOC of the tested waters exhibit similar compositions; the WWTP effluent Böblingen-Sindelfingen has an extraordinarily high biopolymer content. The OMP concentrations are in typical µg/L-ranges, with comparatively high values (>10 µg/L) for acesulfame (12.1 µg/L in Böblingen-Sindelfingen), benzotriazole (17.1 µg/L in Mannheim), and methylbenzotriazole (16.5 µg/L in Mannheim and 12.5 µg/L at the KomS pilot).

The large-scale PAC plant removals of the OMPs that were quantifiable in all of the WWTP effluents/PAC plant influents (cf. Table S3) are given in Figure 2 which also shows the average OMP removals (all 10 OMPs included), as well as the corresponding DOC and UV_{254} removals. (Figure 2 also includes information on proportional PAC doses, which is discussed further below.) Removals in the range of 50-100% are reached for the well adsorbing compounds benzotriazole, carbamazepine, diclofenac, methylbenzotriazole, and metoprolol. The removals of the moderately adsorbing compounds 4-formylaminoantipyrine and primidone show higher scattering and are generally lower. Acesulfame and gabapentin are generally considered to be poor adsorbates (e.g. Jekel et al. 2015; Zietzschmann et al. 2015b). Their partially high removals (up to 90%) are likely caused by biodegradation (Altmann et al. 2016; Falas et al. 2016; Müller et al. 2017; Kahl et al. 2018) as the biomass can adapt, being re-circulated with the PAC sludge. For valsartan acid, a metabolite of antihypertensive sartan compounds (valsartan, candesartan, olmesartan …), the removals are the lowest among the measured OMPs. However, slightly better adsorption of this compound as compared to gabapentin was observed in drinking water GAC filters (Sperlich et al. 2017). Although low removals during bank filtration were observed (Noedler et al. 2013), the biodegradability of valsartan acid in aerated technical systems was shown to be similar or even higher than that of gabapentin (Hellauer et al. 2017; Sperlich et al. 2017). Given the relatively low removals observed here, it is possible that some formation of valsartan acid from its precursors occurs in the PAC plants, as valsartan acid formation in WWTP activated sludge batch tests was reported (Kern et al. 2010).

Proportional PAC doses	■ Böbl.-Sindelf.	■ KomS-Pilot	▨ Kressbronn	▨ Lahr	▨ Laichingen	▨ Mannheim	☐ Neu-Ulm	☐ Ravensburg
PAC/DOC [mg/mg]	1.0	1.5	0.7	1.4	1.3	1.3	2.7	1.5
PAC/UV_{254} [mg/(1/m)]	0.7	0.7	0.4	0.7	0.6	0.6	1.2	0.6
PAC/DOC_{LMW} [mg/mg]	2.6	3.5	1.9	3.3	3.4	3.0	9.0	3.6



R^2 from linear regressions of plant removals vs proportional PAC doses:	Acesulfame	Benzotriazole	Carbamazep.	Diclofenac	4-Formylamin.	Gabapentin	Methylbenzo.	Metoprolol	Primidone	Valsartan ac.	aver. (10 OMP)	DOC	UV254
PAC/DOC:	0.5	0.1	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.6	0.0	0.0	0.2
PAC/UV_{254}:	0.3	0.1	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.4	0.0	0.0	0.2
PAC/DOC_{LMW}:	0.4	0.1	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.6	0.0	0.0	0.3

Figure 2: OMP, DOC, and UV_{254} removals achieved in the tested PAC plants, with $DOC/UV_{254}/DOC_{LMW}$ proportional PAC doses (top), and R^2 from linear regressions of removals vs. proportional PAC doses (bottom).

In order to obtain higher comparability between the OMP removals reached at different locations, using PAC doses in proportion to the respective influent DOCs of different PAC plants has been suggested (Boehler et al. 2012; Altmann et al. 2014). The $DOC/UV_{254}/DOC_{LMW}$-proportional PAC doses are included in Figure 2 (top), together with R^2 from linear correlations of the plant removals versus the proportional doses (bottom). The coefficients of determination are all (very) low, indicating no correlations between the proportional PAC doses and the removal of any of the parameters. (Corresponding graphs for some OMPs are included in Figure S3.) It is particularly noteworthy that not even the consideration of the LMW BOM compounds in the proportional PAC dose allows for inferring OMP removals. The LMW compounds have been identified as particularly competitive in OMP adsorption (e.g. Kilduff & Wigton 1999; Zietzschmann et al. 2014; Hu et al. 2016; Streicher et al. 2016). Accordingly, the proportional PAC doses do not suffice to estimate OMP or DOC/UV_{254} removals at different locations. This finding can be underlined by the fact that in Kressbronn, the OMP removals were overall the highest (cf. Figure 2), but the DOC-proportional PAC dose was the lowest. Likely, different PAC products, variable water characteristics, the location-specific process design, and varying biodegradation cause the observed disparities. The variable plant performances shown in Figure 2 demonstrate that strong OMP elimination is not always easily achieved. Plant operation should be thoroughly optimized, and PAC products should be well tested prior to selection (Karelid et al. 2017b).

3.2 OMP removals: Lab versus plant

Given the inability of the DOC-/UV_{254}/LMW-DOC-proportional PAC dose to project expected OMP removals in PAC plants, other means must be explored. Here, we aim at elucidating the empirical potential of lab batch tests to do so. In order to provide an approach which can be consistently applied to different locations, multiples of the respective plant PAC doses were used in the lab, and combined with fixed adsorption times. To identify the best-fitting combination of lab PAC dose (as a multiple of the respective large-scale PAC dose) and adsorption time, the respective large-scale removals were subtracted from the corresponding OMP removals at all tested lab dose/time combinations. As an example, the differences between the lab and plant benzotriazole removals for all tested lab PAC doses and all tested lab adsorption times at the sampled locations are given in Figure 3, showing four sets (lab doses as multiple of respective full-scale doses) of five columns (adsorption times) for each location. Note that the results directly depend on both, the plant OMP removals and lab OMP removals: For high plant OMP removals, the maximum attainable value of the difference (lab removal minus plant removal) is close to zero (e.g. 100% lab removal – 95% plant removal = 5%). It appears logical that the values of the subtractions grow for increasing lab doses and lab adsorption times in most cases, with some scattering around lower lab PAC doses.

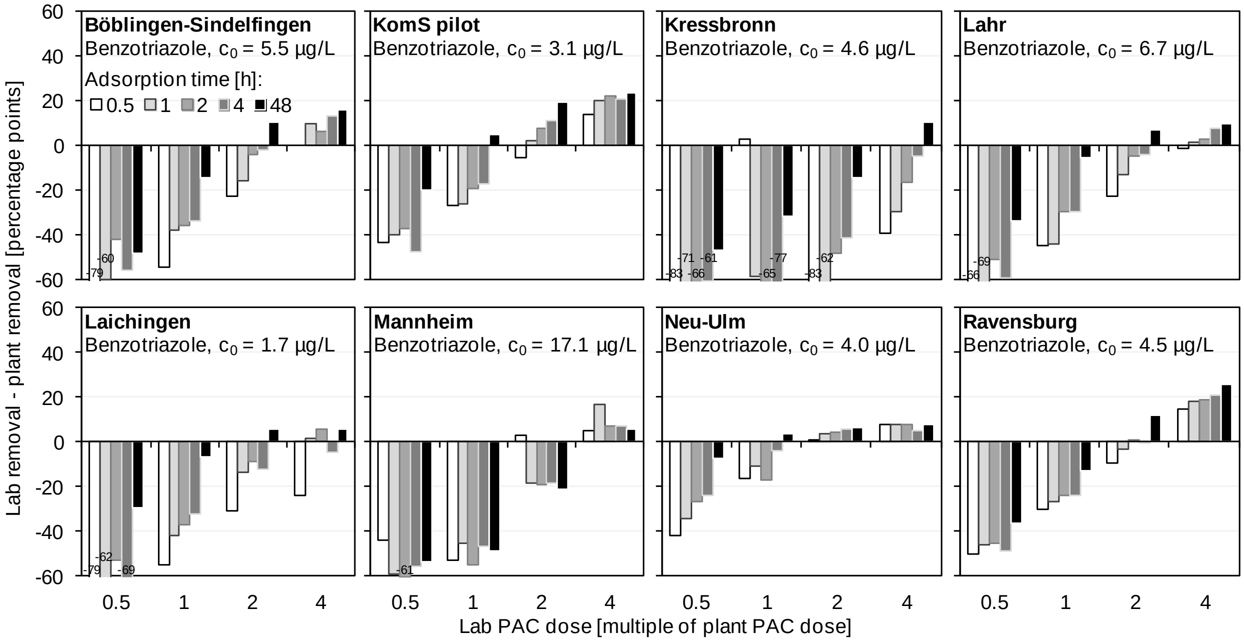
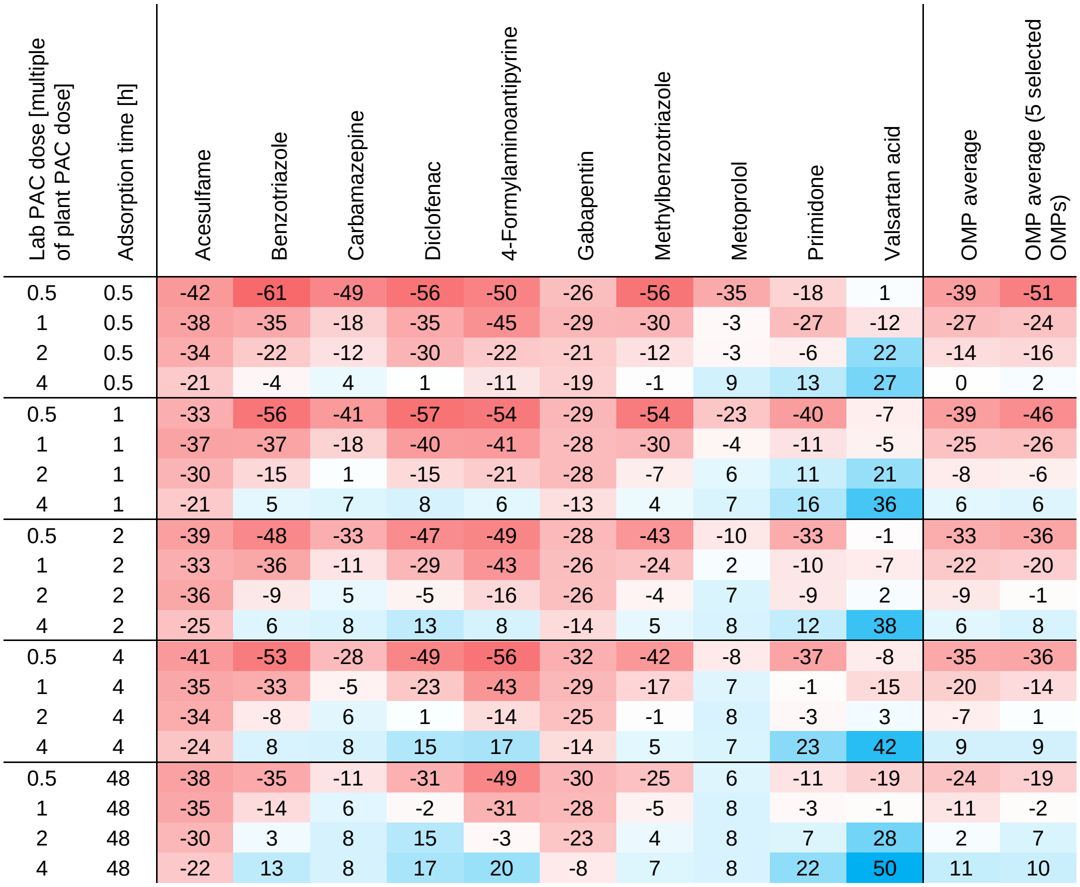


Figure 3: Differences between lab and plant removals of benzotriazole at the tested lab PAC doses (as multiples of plant PAC doses, cf. x-axis) and the tested adsorption times (grey shades) at the eight sampled locations, with initial concentrations c_0.

For all locations except Kressbronn and Mannheim, the batch tests with lab doses twice the plant doses and 2 h adsorption time result in average benzotriazole removal differences in the range of ±10%. In Kressbronn, a lab PAC dose of fourfold the large-scale dose results in the best reproduction of the large-scale OMP removals, and short lab adsorption times (0.5 h, 1 h) are clearly not sufficient to obtain similar removals as in the plant. According to these results, the benzotriazole removals in many large-scale PAC plants appear roughly predictable in a lab test by using twice the respective plant PAC dose and a fixed adsorption time of 2 h. Similar observations can be made for other OMPs, as shown in Figures S4 & S5. However, the congruency between different plants depends on the OMP under consideration, with more scattering occurring in the case of biodegradable OMPs (cf. Table S4). The likely reason is that their biodegradation is variable at different locations. With no considerable biodegradation occurring in the lab tests due to short batch adsorption times (meaning no opportunity for microbial build-up as in PAC re-circulation systems), the differences between lab and plant OMP removals are scattering stronger for biodegradable OMPs.

To determine which combination of plant PAC dose multiple/adsorption time should be used in the lab for plant OMP removal projections on all plants on average, the lab-minus-plant removal differences can be averaged over all tested plants, as shown in Table 2 (columns third from left to third from right). The lab PAC dose/time combinations which result in values close to zero are the most suitable to estimate OMP-specific plant performances at all tested locations. (Note that this approach does not account for scattering of the data, as will be discussed further below.) For example, in the case of metoprolol, a lab combination of a PAC dose equal to the plant PAC dose and 2 h adsorption time results in a removal difference of 2 percentage points on average over all plants.

Table 2: Averages of removal differences (lab removal – plant removal) over the eight tested locations in percentage points, with color intensity corresponding to deviation from zero ("5 selected OMPs": Benzotriazole, carbamazepine, diclofenac, methylbenzotriazole, metoprolol).



Lab PAC dose [multiple of plant PAC dose]	Adsorption time [h]	Acesulfame	Benzotriazole	Carbamazepine	Diclofenac	4-Formylaminoantipyrine	Gabapentin	Methylbenzotriazole	Metoprolol	Primidone	Valsartan acid	OMP average	OMP average (5 selected OMPs)
0.5	0.5	-42	-61	-49	-56	-50	-26	-56	-35	-18	1	-39	-51
1	0.5	-38	-35	-18	-35	-45	-29	-30	-3	-27	-12	-27	-24
2	0.5	-34	-22	-12	-30	-22	-21	-12	-3	-6	22	-14	-16
4	0.5	-21	-4	4	1	-11	-19	-1	9	13	27	0	2
0.5	1	-33	-56	-41	-57	-54	-29	-54	-23	-40	-7	-39	-46
1	1	-37	-37	-18	-40	-41	-28	-30	-4	-11	-5	-25	-26
2	1	-30	-15	1	-15	-21	-28	-7	6	11	21	-8	-6
4	1	-21	5	7	8	6	-13	4	7	16	36	6	6
0.5	2	-39	-48	-33	-47	-49	-28	-43	-10	-33	-1	-33	-36
1	2	-33	-36	-11	-29	-43	-26	-24	2	-10	-7	-22	-20
2	2	-36	-9	5	-5	-16	-26	-4	7	-9	2	-9	-1
4	2	-25	6	8	13	8	-14	5	8	12	38	6	8
0.5	4	-41	-53	-28	-49	-56	-32	-42	-8	-37	-8	-35	-36
1	4	-35	-33	-5	-23	-43	-29	-17	7	-1	-15	-20	-14
2	4	-34	-8	6	1	-14	-25	-1	8	-3	3	-7	1
4	4	-24	8	8	15	17	-14	5	7	23	42	9	9
0.5	48	-38	-35	-11	-31	-49	-30	-25	6	-11	-19	-24	-19
1	48	-35	-14	6	-2	-31	-28	-5	8	-3	-1	-11	-2
2	48	-30	3	8	15	-3	-23	4	8	7	28	2	7
4	48	-22	13	8	17	20	-8	7	8	22	50	11	10

To determine which lab combination (multiple of plant PAC dose & adsorption time) gives the best plant representation independent of the OMP, average OMP removals can be used for each plant, as shown in Figure 4. Only benzotriazole, carbamazepine, diclofenac, methylbenzotriazole, and metoprolol are included because of their comparatively low biodegradability and their initial concentrations being consistently high (≥4*LoQ; Figure S6 includes all OMP). Analogous to Figure 3, the determined lab OMP removals outweigh the observed plant removals with increasing lab PAC doses and adsorption times. Furthermore, the variation between the different adsorption times appears smaller for higher lab PAC doses. This implies that lab procedures applying higher PAC doses would be less prone to errors from variable adsorption times. In the cases of Böblingen-

Sindelfingen, Lahr, Laichingen, Mannheim, Neu-Ulm, and Ravensburg, lab PAC doses twice as high as the respective plant PAC doses, combined with an adsorption time of 2 h, reach overall the best results. For the KomS pilot, a lab PAC dose equal to the plant PAC dose, combined with 2 h adsorption time, achieves the best approximation of the plant performance. The fact that the plant performance of the KomS pilot is better represented by a lower lab dose than at the other locations could be related to this plant being pilot-scale. Possibly, the plant may not work as reliably as those at the other locations. In the case of Kressbronn, a lab combination of four times the plant PAC dose and 4 h reaches the best simulation of the measured average OMP removals in the plant. Accordingly, higher lab PAC doses/longer lab adsorption times are necessary to project the plant performance in this case compared to the other tested locations.

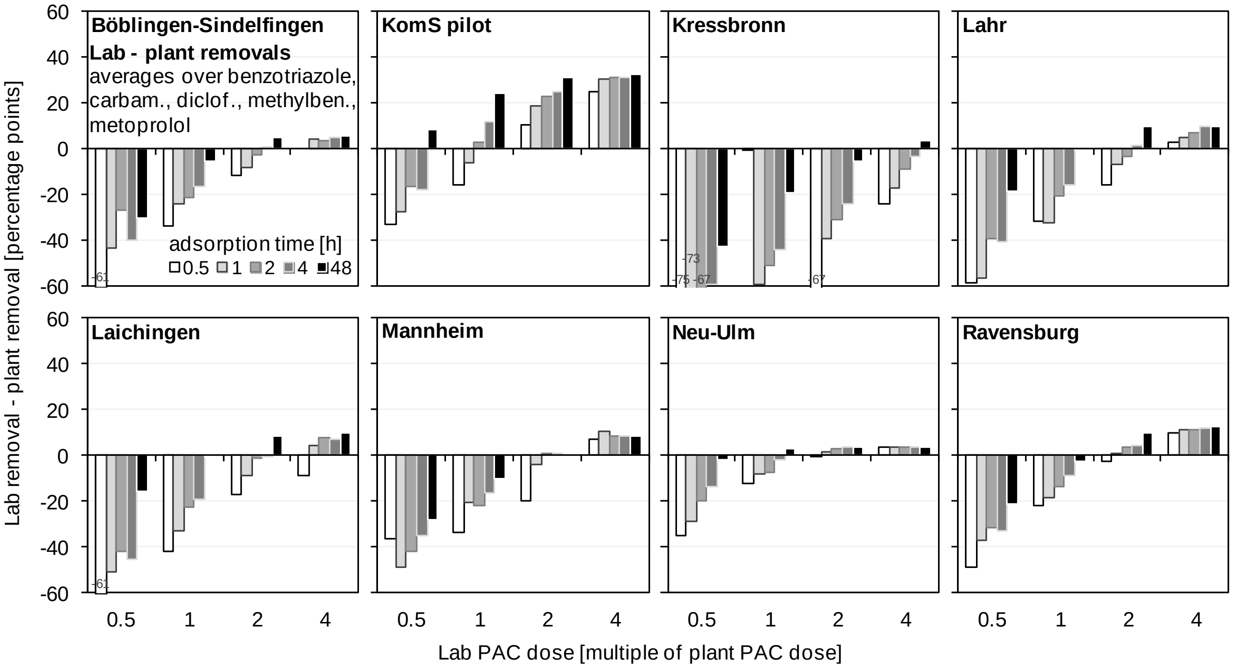


Figure 4: Differences between lab and plant OMP removals at varying lab PAC doses (as multiples of the respective full-scale PAC doses) & adsorption times, averaged over benzotriazole, carbamazepine, diclofenac, methylbenzotriazole, and metoprolol.

The data of Figure 4 can be averaged over all plants, as shown in the rightmost column of Table 2, providing the best suitable lab combination for projections of the tested plants on average. Two lab combinations of PAC dose and adsorption time are well suited to approximate the plant removals of the average of the five selected compounds on average over all plants (double the plant PAC dose and 2 h or 4 h of adsorption time). The average values of all ten measured OMPs are given in the column second from right in Table 2. Here, the best result is a removal difference of 0 percentage points, reached with a lab combination of 4 times the plant PAC dose and 0.5 h of adsorption time. Note that the values in the column first from right in Table 2 are generally slightly higher than those in the column second from right. The reason is that the column second from right includes more biodegradable OMPs whose plant removals are enhanced by biodegradation.

3.3 Scattering of data

According to the results shown in Figure 4, the performances of six out of eight plants can be described with accuracies within a range of ±5% with a lab combination of twice the plant PAC dose and 2 h adsorption time. At this combination however, two of the eight plants differ, by +23 (KomS pilot) and by -31 (Kressbronn) percentage points, respectively. To assess the precision of the suggested approach, Table 2 cannot be used as it does not include information on the scattering of the data. Therefore, the standard deviations associated with the plant averages given in Table 2 were calculated (cf. Table S4), for single OMPs as well as for OMP averages. Comparatively high scattering (up to 56 percentage points standard deviation) occurs for acesulfame, 4-formylaminoantipyrine, gabapentin, primidone, and valsartan acid. Except for primidone, these substances are biodegradable (Huebner et al. 2012; Altmann et al. 2016; Hellauer et al. 2017; Müller et al. 2017; Sperlich et al. 2017; Kahl et al. 2018) which can explain the strong variability. For primidone, the variability of the plant removals is already very high (cf. Figure 2) and the initial concentrations are low in many cases (cf. Table S3) making the data prone to systematic scattering (0.5*LoQ was taken for values <LoQ).

The scattering (i.e. standard deviation) for strongly adsorbing substances (benzotriazole, carbamazepine, diclofenac, methylbenzotriazole, metoprolol) declines with increasing lab PAC doses (adsorption times of 2, 4, and 48 h) and with increasing adsorption times. The maximum standard deviation is 30 percentage points (diclofenac, lab dose = 2*plant dose, 0.5 h), the minimum is 7 percentage points (methylbenzotriazole, lab dose = 2*plant dose, 48 h). For high lab doses and adsorption times, lab removals approach 100% and plant PAC removals are already relatively high (for strongly adsorbing OMPs), implying differences near zero. Accordingly, it would be advisable to use comparatively high lab PAC doses/adsorption times to reduce the scattering and increase the precision. However, the corresponding removal differences (cf. Table 2) may be above zero, resulting in over-estimations of the plant removals. (Since the over-estimations are known from Table 2, they could theoretically be subtracted.)

Considering Table 2, the most suitable lab combination for predicting the average plant removal of all included OMPs is four times plant PAC dose and 0.5 h adsorption time. The standard deviation for this combination is 18 percentage points (cf. Table S4), meaning that 68% of the tested plants fall in a range of ±18% average OMP removal (assuming normal distribution). The most suitable lab combination for predicting the average plant removal of the five selected well adsorbable/little biodegradable OMPs is twice plant PAC dose and 2 h (or 4 h) of adsorption time (cf. Table 2). The standard deviations of these cases are 15 and 13 percentage points, respectively, meaning that 68% of the tested plants fall in ranges of ±15% and ±13%, respectively. These data indicate that rough projections of the average plant performances at different locations are possible.

3.4 Comparison with additional data and other studies

The results of the current study were compared to those of preliminary experiments and other studies fulfilling the following criteria: (1) OMP removal data from both, lab tests and large-scale/pilot tests need to be available, (2) the examined OMPs should be among those found in the current study, (3) the lab tests need to be conducted with the same PAC as used on the respective plant, (4) the same water as tested in the plant should be used in the lab, (5) the lab tests should use adequate multiples of the respective plant doses, and (6) adequate contact times should be applied. The average removal differences (for benzotriazole, carbamazepine, diclofenac, and metoprolol) between lab tests/plants at the eight locations examined in the current study are compared to removal differences from preliminary experiments and from other studies in Figure 5. Despite some studies using PAC dose multiples and/or adsorption times which are not exactly consistent with the current study, they were included in the comparison, in order to give a broader view. Those cases are marked in Figure 5. The SI contains a detailed discussion on the data found in the cited studies. In most cases, the lab-vs.-plant removal differences observed in other studies are very similar to those of the current study. Deviations can be explained by lab dose multiples being slightly higher than in the current study (Margot et al. 2013), or by relatively short lab adsorption times for which results are more prone to systematic variations (e.g. exact length and thoroughness of shaking/mixture, duration of membrane filtration for PAC removal etc. – the dependence of OMP removals on mixing intensities in batch tests is demonstrated in Figure S7.) According to Figure 5, it is advisable to use at least 2 h as contact time in the lab in order to minimize the impacts of such systematic variability. Among the four OMPs shown in Figure 5, diclofenac shows the strongest variations, which is likely due to it being potentially more biodegradable than the other OMPs (Filter et al. 2017). For benzotriazole, carbamazepine, and metoprolol at high lab PAC doses (2 or 4 fold plant PAC dose) and longer lab adsorption times, the lab-plant removal differences from the preliminary tests and from other studies are very close to those observed in the current study (less than 10 percentage points). These comparisons show that large-scale PAC plant performance can be projected in the lab with the developed approach. Practitioners, engineers/planners, authorities, and researchers can use the proposed procedure to quickly assess OMP removal potentials by PAC re-circulation systems at various WWTP sites.

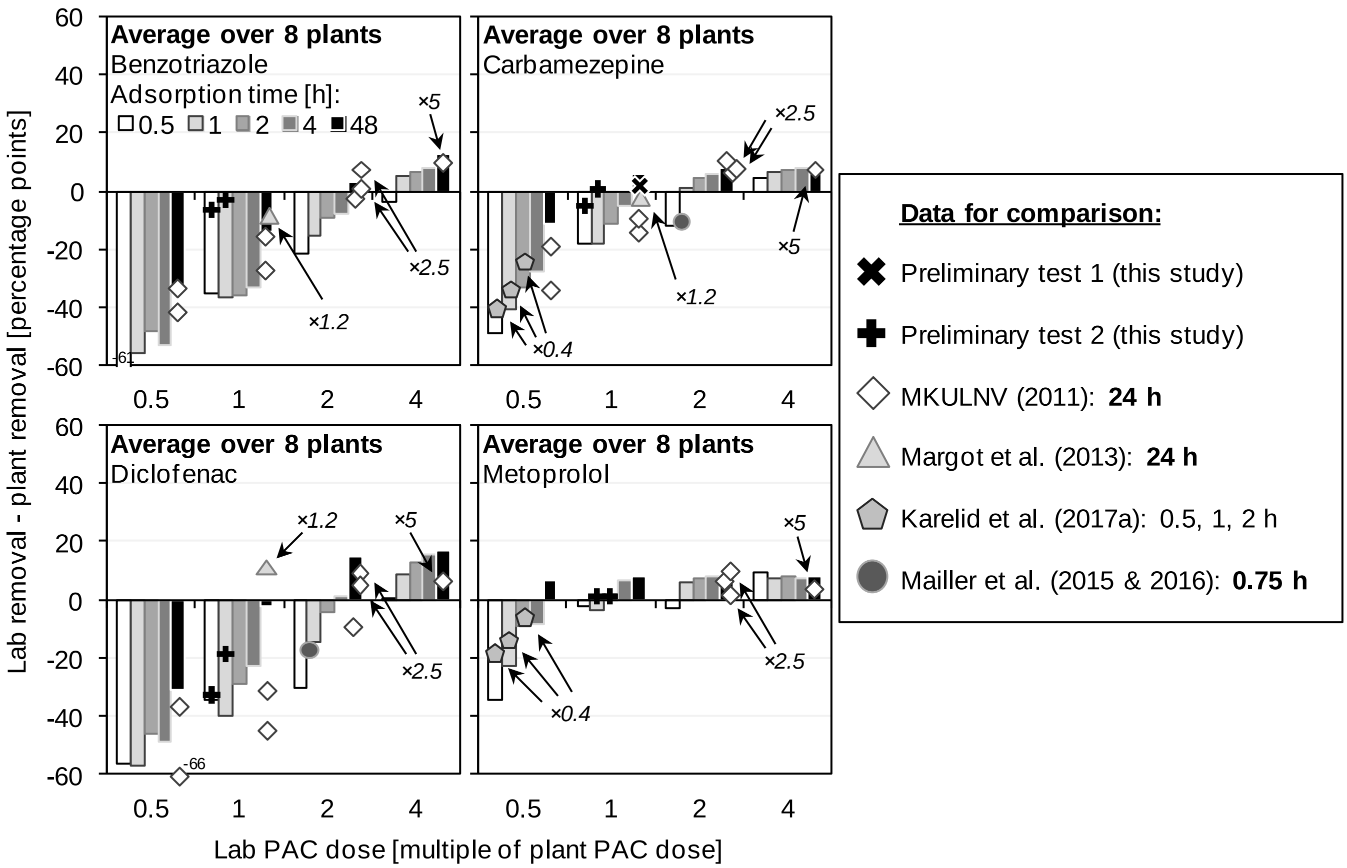


Figure 5: Average benzotriazole, carbamazepine, diclofenac, and metoprolol lab minus plant removal differences on the 8 tested PAC re-circulation plants (columns, current study, legend in benzotriazole plot), with data from preliminary tests and other studies at corresponding lab doses (as multiples of respective plant doses) and lab adsorption times, as symbols (legend box at right side); indicators point to data with slight variations of dose multiples in cited studies; differing lab contact times marked bold in legend.

4 Conclusions

- Eight different PAC re-circulation plants treating WWTP effluents performed largely differently in removing OMPs.
- Some variability between the BOM compositions of the treated waters could be revealed by LC-OCD and might impact PAC plant performance. Additional impacts are likely to arise from differing PAC products, plant operation, and biodegradation.

- DOC-, UV_{254}, and LWM-DOC-proportional PAC doses are not suitable to project OMP removals at different locations. This observation is also likely related to PAC products, plant operation, and biodegradation.
- An empirical lab procedure is proposed to estimate the removals of OMPs in PAC plants at different WWTP sites, by using multiples of the respective plant PAC doses, and fixed adsorption times. The novel approach provides a quick and useful method for scientists, practitioners, and authorities when assessing PAC performance on the large-scale.
- For single OMPs, specific lab dose-time combinations can be identified to project individual and average plant performances. Analogously, such lab combinations can be identified for projecting plant removals on average over several OMPs.
- Average OMP removals of well adsorbable, poorly biodegradable OMPs can be roughly estimated in the lab by using twice the respective plant PAC dose, combined with an adsorption time of 4 h (for all plants). The associated standard deviation is 13 percentage points, meaning 68% of plants would fall in a range of ±13% over-/underprediction.
- For projections of the average removals of all OMPs (10 OMPs found at all locations), four times the respective plant PAC dose should be combined with an adsorption time of 0.5 h. The associated standard deviation is 18 percentage points.
- The observed scattering results mostly from over-/under-predictions at two out of eight sites. However, comparisons with other studies show that the proposed procedure is relatively reliable. We encourage testing additional locations for further precision and reliability checks; however, the substantial effort of obtaining (i) corresponding PAC plant influent & effluent composite samples and (ii) samples of the PAC applied on plants should not go unnoticed.

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