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Supplementary Material

for

# DOM removal from Lake Kinneret by adsorption columns and biodegradation: a pilot study and modeling

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## 1. Production of PD-MMT granules for the pilot

Pursuant to adjusting the laboratory preparation protocol[1] to an industrial scale, around 60 kg of granular PDADMAC composite were produced. Under factory conditions, the granule productions stages were as follows:

a. Composite production was done in a polypropylene tank of volume of 2 $m^3$, by adding bentonite and PDADMAC polymer at a 1:6 ratio. The mixing was carried out for two hours followed by pumping to a belt press by a diaphragm pump (Sun Pepper, USA)

b. Pressing the created solution was carried out using a 250 L belt press.

c. Drying the sludge was done in 400 L oven at 70°C for two days.

d. Performing initial granulation was then carried out.

e. An additional final drying was done at 105°C.

f. The final granulation and sifting into particles in a range of 0.6 - 2.3 mm.

## 2. Adsorbent characterization

**Table S1a. Physical properties of the granular activated carbon (GAC), regenerated GAC (rGAC), and granular pDADMAC-montmorillonite composite (PD-MMT) used in this study.**

| | **BET surface area** | **Zeta potential** | **Iodine number** |
|---|---|---|---|
| | **$m^2 \cdot g^{-1}$** | **mV** | **$mg \cdot g\ C^{-1}$** |
| **GAC** | 1000 ± 50* | -12 | 800 |
| **rGAC** | N.D. | -42 | 810 |
| **PD-MT** | 14.5** | +30 | N.D. |

* Donau Carbon[2], **Zusman *et al.*[1], N.D. – Not determined

**Table S1b. Elemental composition of GAC and rGAC (%w/w).**

| | C | O | H | N | S |
|---|---|---|---|---|---|
| **GAC** | 88.8 | 2.1 | 0.6 | 0.18 | 0.46 |
| **rGAC** | 81.1 | 12.8 | 1.5 | 0.13 | 0.15 |

# 3. Lake Kinneret water characteristics.

**Table S2: Average results from sampling water quality parameters - Inlet water to pilot in 2019**

| PARAMETER | VALUE | UNIT |
|---|---|---|
| Ammonia as NH4+ | 0.1 | mg/l |
| Alkalinity as CaCO3 | 126.0 | mg/l |
| Aluminum | 276.0 | µg/l |
| Arsenic | 0.8 | µg/l |
| Boron | 0.1 | mg/l |
| Barium | 60.8 | µg/l |
| Bicarbonate AS HCO3 | 125.1 | mg/l |
| Bromide | 2.1 | mg/l |
| Calcium | 45.6 | mg/l |
| Copper | 2.2 | µg/l |
| DOC | 2.9 | mg/l |
| EC | 1294.6 | dS/cm |
| Hardness as CaCO3 | 254.3 | mg/l |
| Iron | 40.5 | µg/l |
| Lead | 0.5 | µg/l |
| Liithium | 11.9 | µg/l |
| Magnesium | 34.1 | µg/l |
| Manganese | 0.9 | µg/l |
| Molibdene | 1.0 | µg/l |
| Nitrate as NO3- | 0.9 | mg/l |
| Potasium | 8.5 | mg/l |
| Silica as SIO2 | 10.6 | mg/l |
| Sodium | 148.0 | mg/l |
| Strontium | 680.4 | µg/l |
| Sulfate as SO4-- | 68.0 | mg/l |
| TOC | 2.8 | mg/l |
| Turbidity | 0.3 | NTU |
| UV 254 nm | 0.025 | 1/cm |
| Vanadium | 2.8 | µg/l |
| Zinc | 33.4 | µg/l |

## 4. Physical-chemical results monitored at the site.

Physical-chemical parameters were measured in parallel to measurements related to organic matter. The results are shown for inlet temperature (Fig S1-A), electrical conductivity for the inlet and outlet (Fig S1-B), pH for the inlet and outlet (Fig S1-C) and turbidity for the outlet (Fig. S1-D). Here, the results for inlet water, GAC and PD-MMT outlet water are presented. Changes in the quality of the water entering the pilot columns during the period of one year were mainly due to changes recorded in Lake Kinneret, which can affect the water treatment process in general, and affect the DOM adsorption processes in particular. There was also fluctuation in DOC values (11.4%) and in absorption at 254 nm (20.8%) from both average values of the inlet water as was shown in Fig. 2 in the article.

### 4.1 Temperature

The temperature (Fig S1-A) increased from 17.3 $^{0}$C at the beginning of the run in January to 29 $^{0}$C at the end of the summer in August. These temperature changes can have a positive outcome especially on the GAC adsorption process, due to improving DOM removal by adsorption and by biodegradation by bacteria[3] but might also have a negative effect on reducing adsorption by PD-MMT[1].

### 4.2 pH and electrical conductivity

The water's pH at the entry to the pilot (Fig S1 B) is affected by the water treatment upstream of the pilot and is also affected by water quality changes in the lake. Until June (~ 55,000 PV), the pH at the entrance of the pilot was always below 6.9, but after that the value rose steadily up to 7.2. The increase in pH in incoming water around June is more or less consistent with the increase in electrical conductivity (Fig. S1 C) that starts around

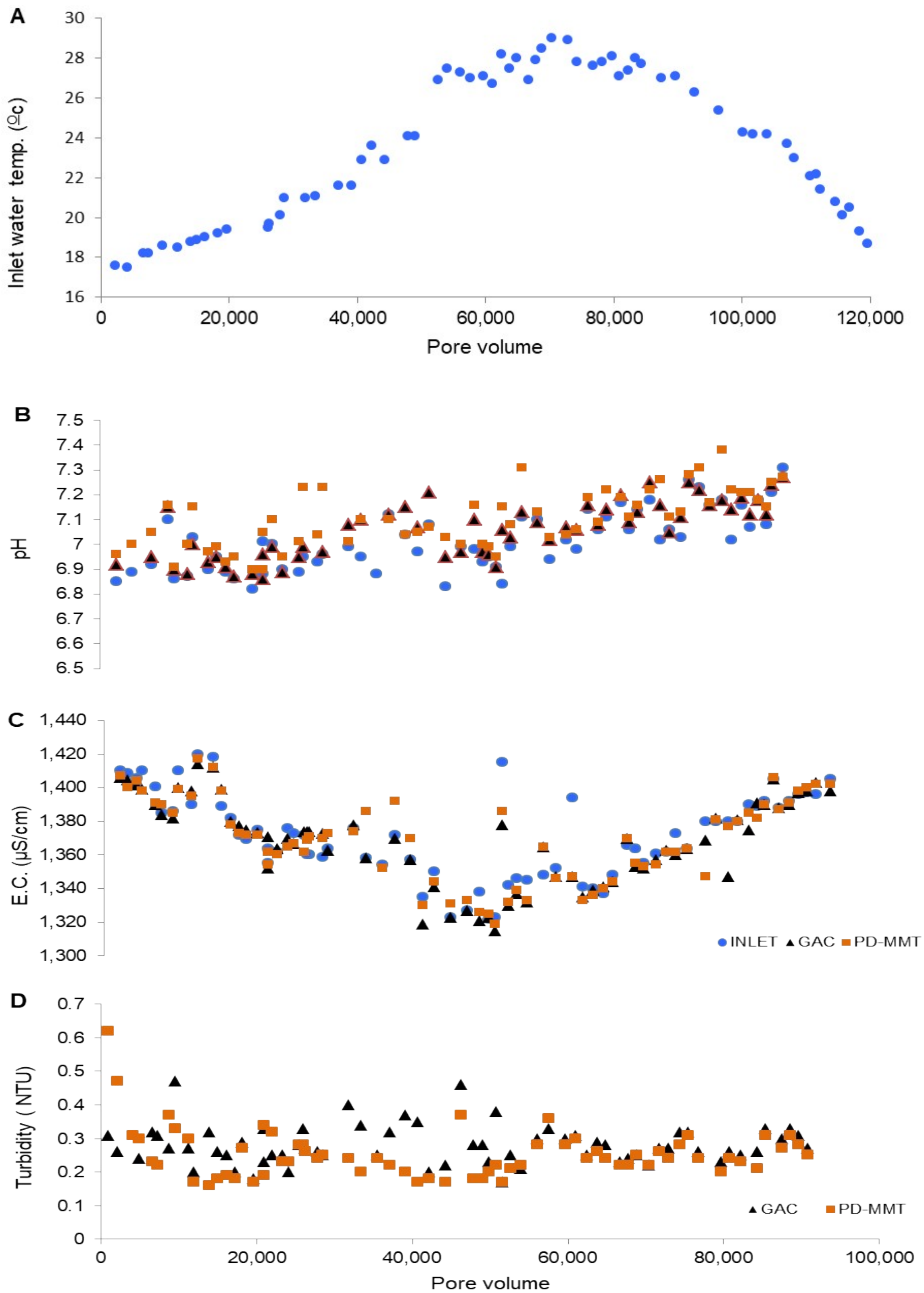


**Fig. S1: Physical chemical parameters of the water during the pilot running for GAC and PD-MMT: A- inlet temperature, B - inlet and outlet pH, C- inlet and outlet electrical conductivity, D - turbidity outlet**

1,340 µS/cm and reaches 1,400 µS/cm at the end of summer (~ 75,000 PV) and at the end of the pilot run.

The salinity of Lake Kinneret is significantly higher than the salinity of the water from surface streams (20–40 mg $L^{-1}$ chlorides)[4] that flow to the lake, due to the salinity of water springs located on the western shore of Lake Kinneret.[4]

It was suggested that the reduction in the amount of water which enters by streams into Lake Kinneret in the middle of spring (May~45,000 PV) may contribute to a moderate increase of salinity in the lake.[4,5] The changes in conductivity due to the treatment were minor. The pH increased after treatment by about 0.1-0.2 pH units on average for media.

**4.3 Turbidity**

The turbidity of the water (Fig S1-D) treated by adsorption through columns has to be the same or less than water turbidity (0.3 NTU) after sand filtration prior to adsorption columns. After ~~a~~ running for two weeks, the PD-MMT composite improved the turbidity in 93% of the cases to levels below 0.3 NTU, whereas the GAC results yielded some fluctuation over 0.3 NTU since the middle of the run.

## 5. Spatial distribution of DOM throughout the columns

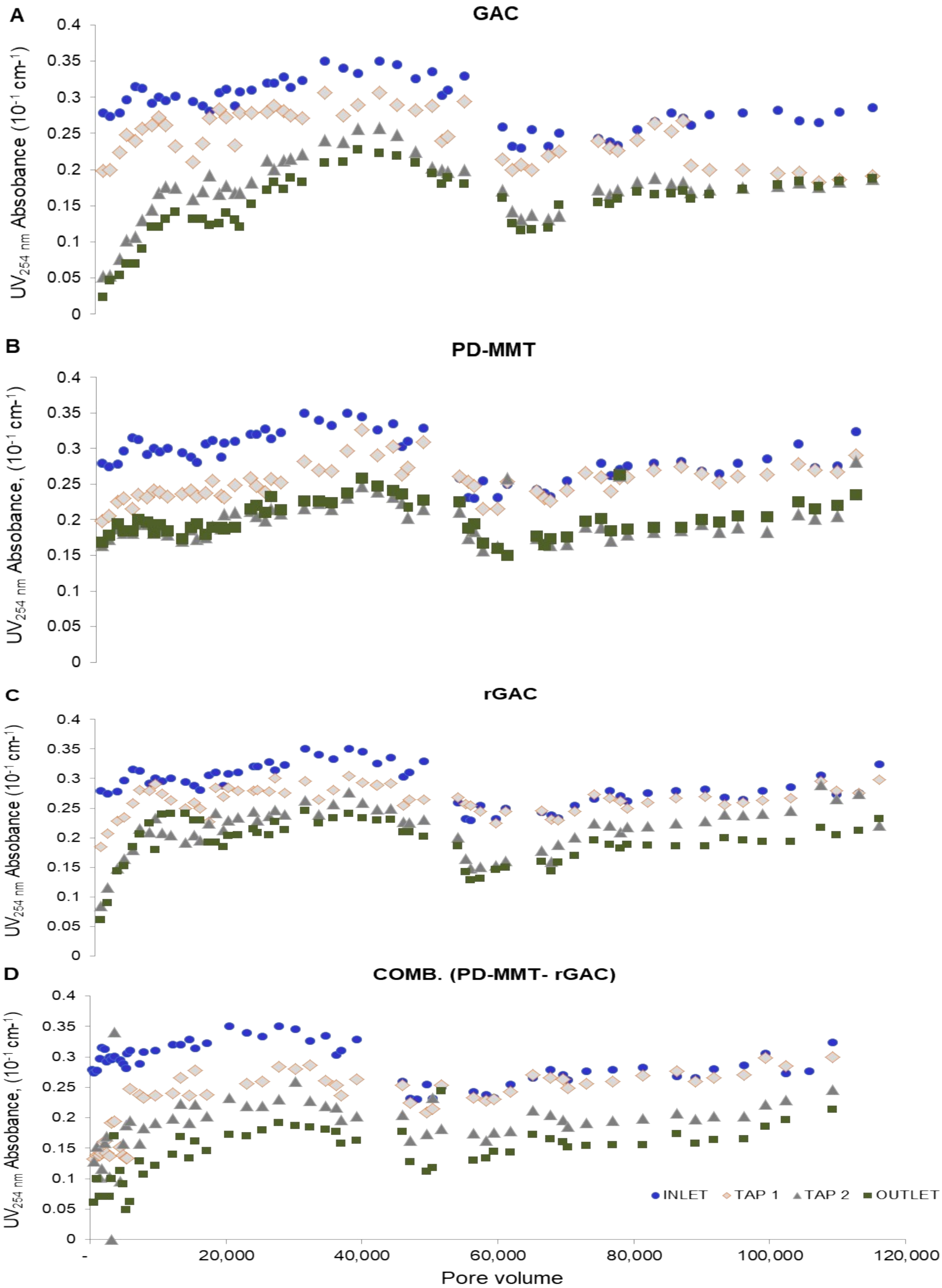


**Fig S2 A-D: Removal of DOM by the four different adsorbents expressed as $UV_{254}$ absorption monitored through three different taps in the column. The distances between the taps were 30 cm, excluding the distance between the top of the media (tap 1) that was 15 cm.**

## 6. Trihalomethanes Formation

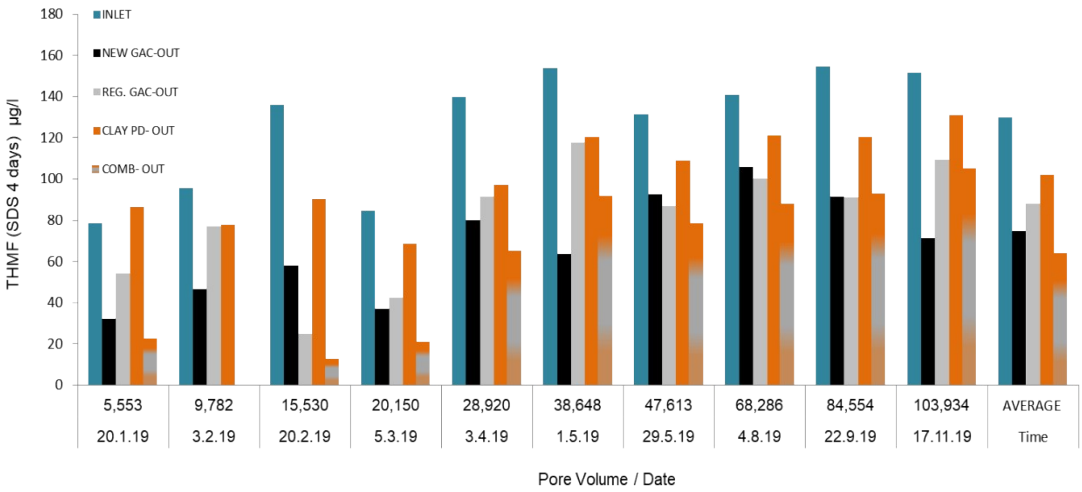


**Fig. S3: THMF (SDS-96 hrs.) (µg/l) prior and after treatment by different adsorbents during running**

**Table S3: Example of fraction of different THMFs derived from SDS testing (96 hrs.)**

| | THMF | INLET | | GAC | | PD-MMT | | rGAC | | COMB. | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | THMF (µg/L) | Fraction | THMF (µg/L) | Fraction | THMF (µg/L) | Fraction | THMF (µg/L) | Fraction | THMF (µg/L) | Fraction |
| | $CHBr_3$ | 153.55 | 0.97 | 60.84 | 0.954 | 106.04 | 0.967 | 112.2 | 0.95 | 87.61 | 0.955 |
| | $CHClBr_2$ | 4.41 | 0.028 | 2.32 | 0.036 | 3.08 | 0.028 | 4.71 | 0.040 | 3.19 | 0.035 |
| 01/05/2019 | $CHCl_2Br$ | 0.26 | 0.002 | 0.38 | 0.006 | 0.29 | 0.003 | 0.46 | 0.004 | 0.55 | 0.006 |
| | $CHCl_3$ | 0.25 | 0.002 | 0.21 | 0.003 | 0.23 | 0.002 | 0.28 | 0.002 | 0.35 | 0.004 |
| | THM TOTAL | 158.47 | 1 | 63.75 | 1 | 109.64 | 1 | 117.65 | 1 | 91.7 | 1 |
| | $CHBr_3$ | 125.46 | 0.954 | 88.9 | 0.960 | 95.73 | 0.947 | 83.8 | 0.963 | 74.2 | 0.946 |
| | $CHClBr_2$ | 5.39 | 0.041 | 3.01 | 0.033 | 4.4 | 0.044 | 2.7 | 0.031 | 3.13 | 0.040 |
| 27/05/2019 | $CHCl_2Br$ | 0.4 | 0.003 | 0.35 | 0.004 | 0.67 | 0.007 | 0.25 | 0.003 | 0.59 | 0.008 |
| | $CHCl_3$ | 0.28 | 0.002 | 0.34 | 0.004 | 0.31 | 0.003 | 0.26 | 0.003 | 0.5 | 0.006 |
| | THM TOTAL | 131.53 | 1 | 92.6 | 1 | 101.11 | 1 | 87.01 | 1 | 78.42 | 1 |

## 7. Modeling

### 7.1. Determination of the parameters ($F_1$ and $D_1$) needed for calculating the removal of FA and $NABS_{254}$ from Lake Kinneret water by a GAC filter.

The first stage was to determine the parameters that characterize the removal of FA due to adsorption/desorption by GAC, at similar dissolved salt concentration as in Lake Kinneret water (see Table S4 below). The results of Kummel *et al.*[6] indicate that the removal of FA by GAC filtration is enhanced in water whose electrical conductivity is larger. The electrical conductivity of the water in the lake is about fourfold larger than in the stream water filtered in Kummel *et al.*[6]

The first parameter to be determined was $R_0$. The procedure was to pass through a small GAC filter a large volume of concentrated FA solution (45 mg $L^{-1}$) at a relatively slow flow rate, and to determine the cumulative adsorbed FA (as in Kummel *et al.*)[6] This procedure yielded the value $R_0$ = 0.0065 ±0.003 M, which is somewhat larger than the value of 0.0049 M[6].

In the next stage a solution of 9.9 mg $L^{-1}$ of FA was passed through two GAC columns in series at a flow rate of 6 mL $min^{-1}$ (Table S4 below).

The parameter $F_1$ was first determined from the initial stages of the adsorption, *i.e.*, under low occupation of the surface sites by FA, and then the parameter $D_1$ was determined by using $F_1$ values in fitting all the experimental data. A few rounds of calculations that introduced small variations in both $F_1$ and $D_1$ values were followed to optimize the fit of calculated values to the experimental ones. We chose to set the value of $D_1$ as in Kummel *et al.*[6]. The statistical tests yielded an $R^2$ = 0.944 (Table S4). The affinity parameter $K = F_1/D_1$ equals 14,000 L $M^{-1}$. The value of the dimensionless quantity, $Y = K*R_0$, which can be used for evaluating adsorption efficiency of FA, is 91, whereas in the case of filtration of stream water by GAC[6], a value of 71 was obtained. Hence, in terms of adsorption, the use of a GAC filter in FA removal from Lake Kinneret water is expected to be more efficient than from stream water.

**Table S4. Removal of FA dissolved in water, which included a similar composition of salts as in Lake Kinneret, by two GAC filters in series (each 1.6 cm diameter, 20 cm length) at a flow rate of 6 mL min$^{-1}$. Experimental and calculated values of $C/C_0$.**

| Time (h) | Experiment $C/C_0$ (20 cm) | Model $C/C_0$ (20 cm) | Experiment $C/C_0$ at Exit (40 cm) | Model $C/C_0$ at Exit (40 cm) |
|---|---|---|---|---|
| 1 | n.d. | 0.112 | 0.024 | 0.008 |
| 2 | n.d. | 0.218 | 0.025 | 0.025 |
| 3 | 0.45 | 0.34 | 0.058 | 0.054 |
| 4 | 0.5 | 0.46 | 0.07 | 0.095 |
| 5 | 0.56 | 0.56 | 0.19 | 0.15 |

[a] Initial concentration of FA at entry to the filter was 0.011 mM (9.9 mg L$^{-1}$). The fraction of the pore volume in the filters was 0.57. The parameters used in the calculations were:
$R_0$ =0.0065 M; $F_1$= 140 M$^{-1}$min$^{-1}$; $D_1$ = 0.01$^{-1}$.
The statistical criteria were $R^2$= 0.944; RMSE=0.055.
n.d.: not determined

## 7.2 Increasing the capacity of the GAC column to improve THMF removal performance

**Table S5. Effect of GAC filter length on removal of FA and $NABS_{254}$ from Lake Kinneret water: Calculated values of $C/C_0$ and percent of degradation at different times[a]**

| Time | Filter length (cm) | $C/C_0$ FA | Percent Degradation of FA (%) | $C/C_0$ $NABS_{254}$ | Percent Degradation of $NABS_{254}$ (%) |
|---|---|---|---|---|---|
| 15 h | 75 | 0.502 | 39.9 | 0.731 | 23.4 |
| | 100 | 0.399 | 46.5 | 0.657 | 29.2 |
| | 150 | 0.234 | 54.1 | 0.531 | 39.6 |
| 24 h | 75 | 0.504 | 43.5 | 0.731 | 24.7 |
| | 100 | 0.399 | 51.1 | 0.658 | 31.1 |
| | 150 | 0.249 | 61.8 | 0.531 | 41.7 |
| 48 h | **75** | 0.504 | 46.6 | 0.731 | 25.8 |
| | **100** | 0.400 | 55.8 | 0.658 | 32.7 |
| | **150** | 0.250 | 68.4 | 0.531 | 44.3 |
| 5 d | 75 | 0.505 | 48.4 | 0.731 | 26.4 |
| | 100 | 0.401 | 58.2 | 0.658 | 33.5 |
| | 150 | 0.251 | 72.2 | 0.531 | 45.8 |
| 7 d | 75 | 0.505 | 48.6 | 0.731 | 26.5 |
| | 100 | 0.401 | 58.7 | 0.658 | 33.7 |
| | 150 | 0.251 | 73.0 | 0.531 | 46.1 |

[a] The radius of the cylindrical pilot column was 13 cm; the flow rate was 330 L $h^{-1}$. The initial concentrations of FA and $NABS_{254}$ in the water were $1.2 \cdot 10^{-6}$ and $2.01 \cdot 10^{-5}$ M, the kinetic adsorption rates ($F_1$, $F_2$) were 140 and 60 $M^{-1}min^{-1}$, the dissociation rate constants ($D_1$, $D_2$) were 0.01 $min^{-1}$ and the degradation rate constants ($Kd_1$, $Kd_2$) were 0.0025 and 0.0027 $min^{-1}$, respectively.

## 7. Supplementary references


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