

# Supporting Information: Modeling of copper sorption onto GFH and design of full scale GFH adsorbers

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## Use of GFH-calcite versus GFH layers

Long-term column experiments with running times of almost 2 years and different adsorber layers revealed that a GFH layer clogged after 400 days (1200 bed volumes). In contrast, the column with a 1:1 weight ratio GFH-calcite layer was still showing sufficient hydraulic permeability after 730 days (5900 bed volumes) (Fig. S 1). The clogging of the GFH layer is probably caused by the increased particle retention due to the lower average grain diameter in the GFH layer (0.8 mm) compared to the GFH-calcite layer (1.8 mm). With the same long-term column experiments it could be shown that calcite increases the pH in the first days of the experiment at low flow rates and therefore high copper removal from the beginning of the experiment is obtained.

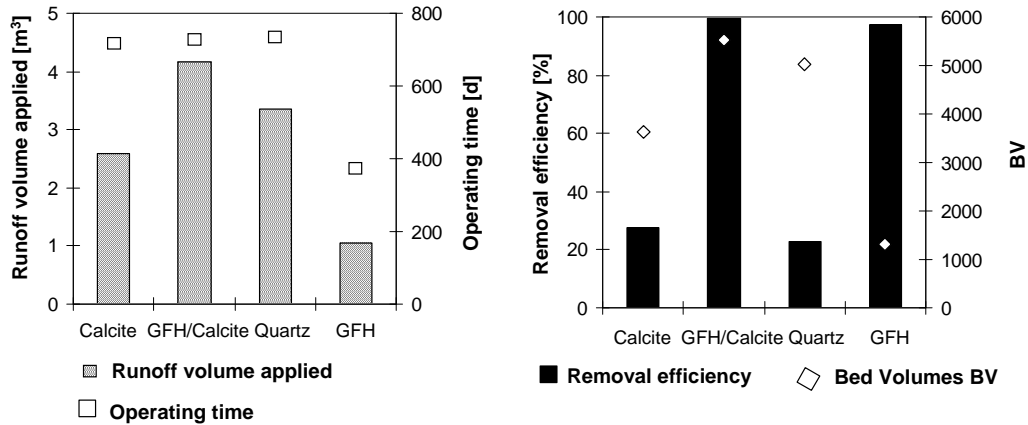


Figure S 1: Removal efficiency based on mass balances, operating time, applied runoff volume/bed volume (BV) of long term column experiments with different layers.

## Variable flow rate experiments with a GFH-calcite layer

The goal these experiments was to assess film diffusion under varying flow rates. The height of the GFH-calcite layer was 7.4 cm and the experiments were conducted with a similar flow variation scheme as used for the GFH layers. But in contrast to the GFH experiments, not only one but two flow variations were applied in series. The duration of the period in between was 16 days at a low flow rate of  $0.3 \text{ m h}^{-1}$ . This strategy allows simulation of two dynamic runoff events with a period with no runoff of 16 days in between. Additionally, possible effects of GFH preloading at the beginning of the second series can be assessed.

Generally, the effluent concentrations of both series follow the same pattern as observed with the prior GFH experiments. Interestingly, the effluent concentrations of the second run are only slightly higher than in the first series (Fig. S 2a,b). Apparently, copper diffuses into the grain during the 16 days with a low loading rate. Additionally, adsorbed copper accumulated during the first flow variation at and near the surface can diffuse into the GFH grain in the low loading period. As a consequence, the sorption capacity at or near the grain surface is available at the beginning of the second flow variation.

The effluent concentrations of both series of the GFH-calcite experiment are plotted against flow velocity in Figure S 2b. In both flow variations, the concentrations of the filtered copper remains almost constant at flow rates above  $1 \text{ m h}^{-1}$ . This is caused by increased film diffusion due to increasing

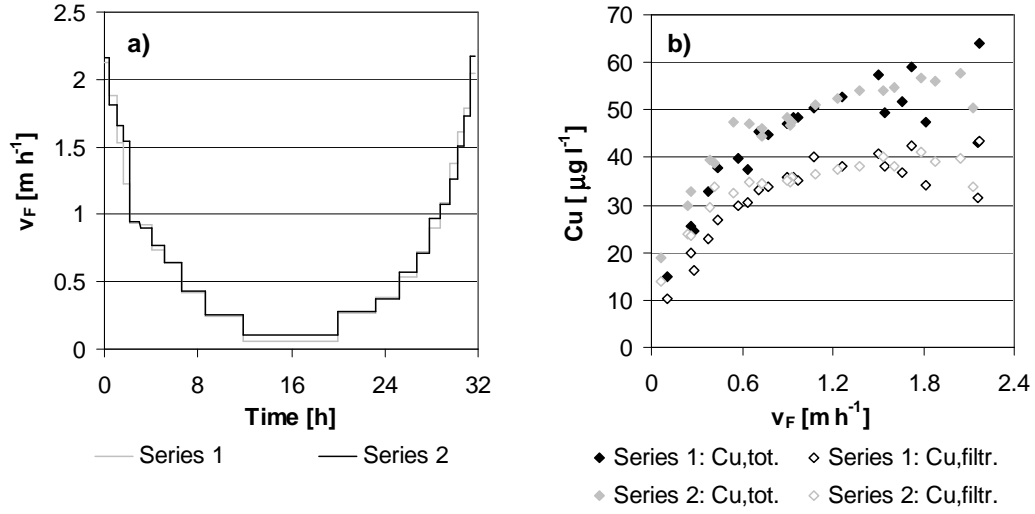


Figure S 2: GFH-calcite layer, 7.4 cm: Filter velocity (a) and effluent concentrations (b) of the first and second series of the flow rate variations. Inlet concentrations:  $\text{Cu}_{in,tot.}=300 \mu\text{g Cu l}^{-1}$ ,  $\text{Cu}_{in,filtr.}=280 \mu\text{g Cu l}^{-1}$  (see also Fig. S3).

filter velocity [1] [2].

As appears from Figure S 2b, the particulate copper ( $\text{Cu}_{tot}-\text{Cu}_{filtr.}$ ) can be measured in the effluent starting at a filter velocity of  $0.2 \text{ m h}^{-1}$ . This is in strong contrast to the GFH columns where no significant breakthrough was observed until a  $v_F$  of  $12 \text{ m h}^{-1}$  (Fig. 3). Taking into account that the point of zero charge (pzc) of GFH is 7.85 and the inlet pH is 7.1, this reduced retention can be explained by a negatively charged GFH surface due to sorption of bicarbonate or carbonate. Firm evidence of carbonate and bicarbonate adsorption was found by conducting long term GFH column experiments at relatively low  $v_F$  ( $0.2 - 0.8 \text{ m h}^{-1}$ ) [3] as well as in [4].

Except for the constant flow, all other experiments were carried out using collected roof runoff with a typical roof runoff matrix (Tab. 3). Therefore, the estimated model parameters are representative for the situation in Switzer-

land. However, if the chemistry would change significantly, e.g. due to a higher salt content or decreased pH, the model parameter would be affected, as effects of e.g. surface chemistry are not included explicitly in the transport model.

For the GFH-calcite column  $qex_{mob}$  is significantly increased compared to the GFH columns. This is mainly caused by a higher value of  $n_{mob}$  of 0.88 compared to 0.71 and 0.58 for the GFH layers. The higher value of  $qex_{mob}$  of the GFH-calcite layer can be explained mechanistically by a decreased GFH surface charge caused by sorption of bicarbonate or carbonate, as discussed. As this reaction is not included explicitly in the model, different parameter values for  $q_{mob}$  and  $n_{mob}$  describe this effect implicitly. Overall, the data of the experiment could be describe satisfactorily with the copper model.

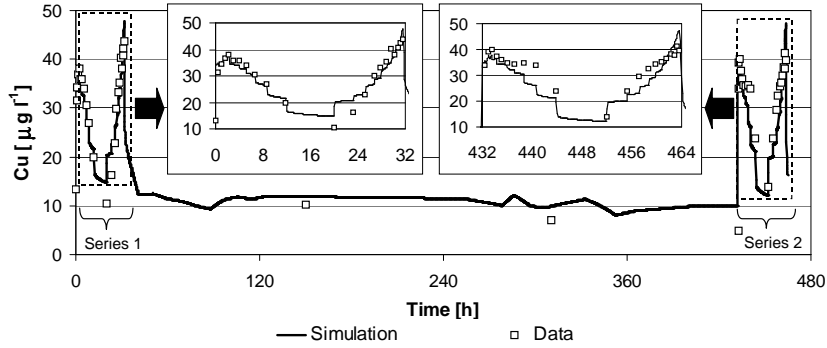


Figure S 3: Measured and simulated effluent concentration: 7.4 cm GFH-calcite layer (same data as in Figure S 2b).

# Comparison of the copper model with other mass transport approaches

## Theory

In order to compare the mass transport from the mobile zone to zone 1 with film diffusion models as in [1], the film diffusion coefficient  $\beta$  was calculated with Equations 1 and 2 [5] using data from the column experiments. The parameters are explained in Table S 1.

$$\beta = -\frac{Q}{m \cdot a_s} \cdot \ln \frac{c_{ab}}{c_{zu}} \quad (1) \qquad a_s = \frac{6(1 - \varepsilon_F)}{f_s \cdot d_K \cdot \rho_F} \quad (2)$$

Similarly, to compare pore diffusion with other data, the pore diffusion coefficient  $D_P$  was derived from the fitting parameter  $qex_{im}$  using Equations 3 and 4 (Table S 1) [6].

$$qex_{im} = \frac{a_2 D_P}{r_2} \quad (3) \qquad a_2 = \frac{A \varepsilon_{im,2}}{r_2} \quad (4)$$

While  $\varepsilon_{im,2}$  describes the porosity in zone 2,  $r_2$  refers to the length of the pore of zone 2 (in r-direction). The value of  $D_P$  is strongly dependent on the assumption for  $\varepsilon_{im,2}$  and  $r_2$ . The length of zone 2 can be assumed as 0.4 mm, which is the half of the mean GFH grain diameter. In other words,  $r_2$  is a function of the spatial discretisation in r-direction of the immobile region into zones (see Fig. 2 ). For the copper model, the calculation of  $D_P$  is critical because the immobile region consists only of 2 zones. The values of  $D_P$  calculated with this method are discussed below in the SI results section.

Table S 1: Additional parameters for calculation of  $\beta$  and  $D_P$ 

$A$	Cross sectional area of the column	$\text{m}^2$
$a_2$	Surface area of pores	$\text{m}$
$a_S$	Weight specific surface	$\text{m}^2\text{kg}^{-1}$
$\beta$	Film diffusion coefficient	$\text{ms}^{-1}$
$c_{zu}, c_{ab}$	In- and outlet concentrations	$\text{g m}^{-3}$
$d_K$	Grain diameter	$\text{m}$
$D_P$	Pore diffusion coefficient	$\text{m}^2\text{s}^{-1}$
$\varepsilon_F$	Filterbed porosity	$\text{m}^3\text{m}^{-3}$
$f_s$	Shape factor	-
$m$	Amount of GFH	$\text{kg}$
$Q$	Flow rate	$\text{m}^3\text{s}^{-1}$
$r_2$	Length of zone 2 (in r-direction)	$\text{m}$

## Results

For calculation of the film diffusion coefficient  $\beta$  with Equations 1 and 2, data from the variable flow rate experiments were used. For comparison purposes,  $\beta$  values of the sorption of organic substances onto activated carbon based on column experiments with similar  $v_F$  are considered [7]. As shown in Table S 2, the  $\beta$  values from the GFH column experiments (8.1 and 13.1 cm) are 2.5 times lower than the values of the organic substances with similar diffusion coefficient  $D_{Diff}$  in water [8]. Compared to the GFH columns, the extrapolated  $\beta$  values of the 7.4 cm GFH-calcite experiments are significantly higher. This difference is in agreement with the higher value of  $qex_{mob}$  of the GFH-calcite layer illustrated in Figure S 4 due to higher values of  $q_{mob}$  of 0.38 and  $n_{mob}$  of 0.88. It can be concluded that the calculated  $\beta$  values for copper are realistic.

Based on the  $qex_{im}$  value of 0.64 (Tab. 5) and Equations 3 and 4, the

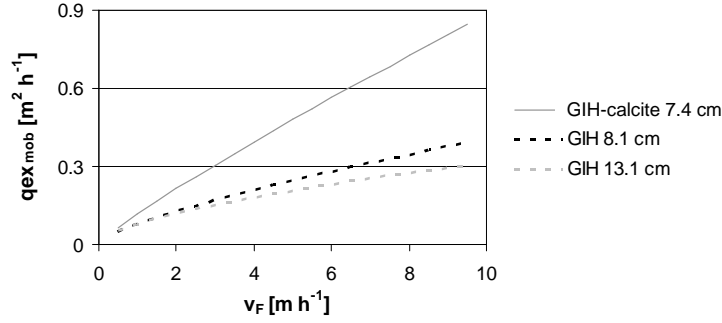


Figure S 4: Calculated  $qex_{mob}$  as a function of the filter velocity  $v_F$ .

calculated value of  $D_P$  is  $4.5 \cdot 10^{-8} \text{m}^2 \text{s}^{-1}$ . This is higher than the diffusion coefficients in water (Tab. S 2). As mentioned in the section before, the pores within the grain are described with only 1 zone in the copper model. As a result, the high value of  $D_P$  is caused by a large pore length  $r_2$  (see Fig. 2). For instance, a higher spatial resolution of the immobile region into 10 zones would result in a smaller  $D_P$  of  $4.5 \cdot 10^{-9} \text{m}^2 \text{s}^{-1}$ , as the  $r_i$  would be 10 times smaller ( $r_i = 4 \cdot 10^{-5} \text{m}$ ,  $\varepsilon_{imm,i} = 0.016$ ). Therefore, a direct comparison with pore diffusion coefficients of other experiments as well as the calculation of the Biot number to compare film and pore diffusion resistance was not performed.

Table S 2: Comparison of film diffusion coefficients of copper sorption onto GFH with the sorption of organic substances on activated carbon.

\* Extrapolated to  $v_F$  of  $10 \text{mh}^{-1}$ .  $D_{Diff}$  diffusion coefficient in water.

	$D_{Diff}$ $\text{m}^2 \text{s}^{-1}$	$v_F$ $\text{mh}^{-1}$	$\beta$ $\text{ms}^{-1}$
Benzoic acid	$8 \cdot 10^{-10}$	10.5	$3.6 \cdot 10^{-5}$
p-Nitrophenol	$7.8 \cdot 10^{-10}$	9.9	$3.7 \cdot 10^{-5}$
Acetophenone	$7.6 \cdot 10^{-10}$	9.8	$3.4 \cdot 10^{-5}$
Copper (8.1 and 13.1 cm GFH)	$7.1 \cdot 10^{-10}$	10	$1 \cdot 10^{-5}$
Copper (7.4 cm GFH-calcite)		10*	$2.5 \cdot 10^{-5}$

Due to the presence of two zones in the immobile region, the copper



model is able to describe mass transfer in the pores explicitly. This is in contrast to the Two Region Model (TRM) which would include only zone 1 [9]. As a consequence, the TRM was unable to describe the measured data satisfactorily, especially for the constant flow experiment, where mass transport within the grain occurs. For a more detailed description of the mass transport in the grain, an additional diffusion zone was added in the immobile region 1 of the copper model.

Model structures with more immobile regions and zone to cope e.g. with pore size variability were evaluated. Although they could describe the experimental data somewhat better, the parameters were correlated among each other or could only be estimated with large standard deviations.

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