# Factors influencing ammonium removal in vertical flow constructed wetland for CSO treatment: a statistical approach

Facteurs d'influence de l'élimination de l'ammonium au sein des filtres plantés de macrophytes à écoulement vertical : une approche statistique

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# ABSTRACT

The paper presents a statistical approach to the description of ammonium removal in constructed wetlands for the treatment of combined sewer overflows (CSO). Due to the nature of rainfall CSO events occur randomly and vary widely in volume and pollutant loads. Vertical flow constructed wetlands have proved to be capable of coping with such conditions and of reducing impacts on receiving water bodies effectively. Yet the actual performance during a particular event depends on numerous factors that are related to design and operation of the wetland as well as to the characteristics of the event. In order to improve the understanding of the removal processes extensive lab-scale experiments, have been carried out in several projects at different institutions in Germany. This paper presents findings related to ammonium removal and the probability of a breakthrough of ammonium. Results indicated the infiltration rate, the type of sand, the inlet ammonium concentration and the hydraulic inlet load as main parameters influencing the probability of ammonium breakthrough.

# RÉSUMÉ

L'article présente une approche statistique décrivant l'élimination de l'ammonium par les filtres plantés de macrophytes à écoulement vertical pour le traitement des surverses de déversoirs d'orage (DO). De par la nature des eaux pluviales urbaines, les surverses de DO peuvent se produire de façon aléatoire. Le volume et les charges polluantes sont extrêmement variables. Les filtres plantés de macrophytes à écoulement vertical sont considérés comme des structures fiables pour le traitement de tels influents et pour limiter fortement leurs impacts sur les milieux récepteurs. Cependant la performance de ces systèmes dépend de nombreux paramètres, qui relèvent autant de la conception que du mode opératoire et des caractéristiques de l'évènement appliqué. Afin d'améliorer la compréhension des processus d'élimination de l'ammonium, un nombre important d'alimentations a été effectué sur colonnes expérimentales au cours de plusieurs projets de différentes institutions en Allemagne. Cet article présente les résultats statistiques relatifs à l'élimination de l'ammonium et la probabilité d'observer une saturation du filtre en ammonium. Les résultats indiquent que la vitesse d'infiltration, le type de sable, la concentration en ammonium dans l'influent et la charge hydraulique dans l'influent sont les principaux paramètres influençant la saturation du filtre en ammonium.

# **KEYWORDS**

Ammonium, Combined sewer overflow treatment, Experimental columns, Logistic regression, Vertical flow constructed wetland

#### NOMENCLATURE

β <sub>0</sub>	-	value of Xi corresponding to a $DP_{\!\!\!\!\!\!\!\!(i\text{-}1)}$ reference situation	d	duration of the dry period before the feeding
$\beta_{C_{NH_4-N,in}}$	L mg⁻¹	regression coefficient related to the $\ensuremath{FR}$ inlet ammonium concentration	m s⁻¹	filtration rate
$eta_{\scriptscriptstyle DP}$	d⁻¹	regression coefficient related to the $\boldsymbol{h}_{\mathrm{in}(\mathrm{i})}$ duration of the dry period before the feeding	mm	inlet hydraulic loading
$\beta_{\text{FR}}$	-	regression coefficient related to the $L_{\rm NH_4,in(i-1)}$ filtration rate	g m⁻³	inlet ammonium load of the last event
$\beta_{h_{in}}$	mm <sup>-1</sup>	regression coefficient related to the $L_{\rm NH_4, out(i-1)}$ inlet hydraulic loading	g m <sup>-3</sup>	outlet ammonium mass of the last event
$\beta_{L_{NH_4,ret.}}$	m <sup>3</sup> g <sup>-1</sup>	regression coefficient related to the $L_{\text{NH}_4, \text{ret.}(i-1)}$ last event	g m⁻³	ammonium mass retained during the last event
$\beta_{\text{sand}}$	-	regression coefficient related to the $p\!\left(breakth./ref.\right)$ type of sand	-	probability of a breakthrough under the reference situation
$C_{_{NH_4}\text{-}N,in(i)}$	mg L <sup>-1</sup>	inlet ammonium concentration of the $p(\ensuremath{\textit{breakth.}}/X_i)$ studied event	-	probability of a breakthrough
$C_{NH_4,in(i\text{-}1)}$	mg L <sup>-1</sup>	inlet ammonium concentration of theCu last event	-	uniformity coefficient
$C_{\rm NH_4-N,out(i-1)}$	mg L <sup>-1</sup>	of the last event	m³	filter material volume
d10	mm	first percentile diameter of the grain $V_{\mbox{in(i-1)}}$ size distribution	m³	inlet volume of the last event
d60	mm	sixth percentile diameter of the grain $V_{\mbox{out(i-1)}}$ size distribution	m³	outlet volume of the last event
d90	mm	last percentile diameter of the $\mbox{grain} X_i$ size distribution	-	linear combination of explanative variables

#### **INTRODUCTION**

Combined sewer overflows (CSOs) are known to highly impair the physical, chemical and ecological quality of water courses (Bertrand-Krajewski et al., 1998; Hall et al., 1998). The toxic impact of unionized ammonia ( $NH_3$ ) on water organisms is considered as one of the most relevant ecological effects (Borchardt and Sperling, 1997; Holzer and Krebs, 1998). At high pH values and high temperatures  $NH_3$  originates from less toxic ionized ammonium ( $NH_4$ ) that is emitted via CSO discharges.

In Germany, the standard strategy to control CSO emissions and to reduce impacts on receiving water bodies is to provide storage volume at CSO structures. After the rain event the retained volume is conveyed to the wastewater treatment plant (WWTP). If the receiving water body is particularly sensitive the remaining CSO discharge is treated in Vertical Flow Constructed Wetlands (VFCW). Such systems are by now widely used. In order to improve the understanding of the removal processes and to optimize the design of the systems intensive research has been carried out over the last 20 years (see Uhl and Dittmer, 2005; Dittmer and Schmitt, 2011, Henrichs et al., 2007; Langergraber et al., 2009, Woźniak et al., 2007).

Concerning ammonium the results consistently indicate, that removal mainly occurs as a two-step process. Ammonium is adsorbed by the filter media during the feeding and then biologically degraded during rest period before the next event begins. Ammonium is retained mainly by (i) biotic adsorption on biomass and/or (ii) abiotic cationic exchange between liquid phase and filter material (Vymazal, 2007). The sorption process can be described by isotherms, which are based on an equilibrium hypothesis between the adsorbed and dissolved phases. If the ammonium load of the inflow exceeds the sorption capacity of the filter media this leads to a breakthrough (Zhao et al., 2010; Vymazal, 2007; Woźniak et al., 2007).

In several projects lab-scale filter columns have been used with only slight differences in the experimental setup. The projects had different aims and scopes. Some aimed at the development of deterministic models and their calibration (see Dittmer et al., 2005, Meyer et al., 2008; Meyer et al., 2012). Results show that the actual performance during a particular event depends on numerous factors that are related to design and operation of the wetland as well as to the characteristics of the event. Yet the number of experiments in each project was too small to apply multivariate statistics and

to describe the influence of each factor in detail.

In the presented study data from various projects were collected and subjected to a consistent statistical analysis. The aim was to quantify the influence of the most relevant factors on the ammonium removal.

#### 1 1 MATERIALS AND METHODS

#### 1.1 1.1 Experimental setup

Experiments were designed to reproduce full-scale RSFs in one dimension. The filter consists of different layers of porous media inside Plexiglas columns (inner diameter: 195 mm, total height: 2.30 m) (figure 1).

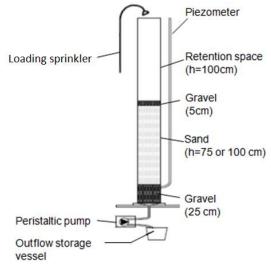


Figure 1: Experimental columns (according to Woźniak, 2008)

The columns were fed by a pump with composite combined sewage. The water passes a 1 m layer of sandy filter media. Only in one project the layer was 0.75 thick. Gravel (2/8 mm) on top of the sand was supposed to limit erosion. The filter was supported by a 0.25 m gravel layer (2/8 mm). The outflow was limited by a peristaltic pump. This corresponds to full scale plants where the filtration rate is kept constant by a flow regulator. After each loading event the columns were completely drained.

In most experiments the filter material was river sand. Some others used lava sands. Each column contained only one type of filter material. Main characteristics of the material varied between the different projects within the ranges given in table 1.

Table 1: Soil parameters of the tested filter materials							
sand d10 Cu= d60/d10 d90 porosity carbonate							
	[mm]	[-]	[mm]	[%]	[%]		
lava sands (L)	[0.06;0.10]	[4;9]	[1.20;2.00]	[38;55]	[2;22.4]		
river sands (R)	[0.10;0.20]	[3;6]	[1.20;1.90]	[32;47]	[2;33.9]		

## 1.2 **1.2** Feeding, Operation and Sampling

Loading characteristics were chosen to represent real conditions. Realistic inlet concentrations and hydraulic loading sequences were obtained from literature values and from corresponding full-scale investigations (Woźniak, 2008, Dittmer and Schmitt, 2011). Wastewater was collected from municipal wastewater treatment plants (after primary sedimentation) and diluted with tap water to obtain concentrations within the range of CSO quality parameters.

After installation of the experimental setup the columns were fed with hydraulic batches of 500 mm (=  $0.5 \text{ m}^3/\text{m}^2_{\text{filter}}$ ) regularly once or twice per week for a minimum time span of 8 weeks (installation period). This installation period was conducted in order to establish the biocoenosis in the filter media. After sorption capacity was well developed loading characteristics like hydraulic load, pollutant load and dry periods were varied.

Four different filtration rates  $(1 \times 10^{-5}, 2 \times 10^{-5}, 3 \times 10^{-5} \text{ and } 5 \times 10^{-5} \text{ m s}^{-1})$  were tested on river sands and three on lava sands  $(1 \times 10^{-5}, 5 \times 10^{-5} \text{ and } 10 \times 10^{-5} \text{ m s}^{-1})$ . In all experiments inflow was much higher than the outflow. Thus, the filter was operated under saturated conditions most of the time. This represents typical hydraulic conditions at full scale plants.

The limits of removal capacity were tested in single high load events (> 1.500 mm). Due to the limited retention volume of the filter columns (max. 1.0 m, see fig. 1) higher hydraulic loads had to be separated into batches. The next batch was always applied the column before the previous one had been totally infiltrated – in this way a re-aeration (and instant nitrification) was prohibited.

55 high loads events were continuously monitored and investigated to estimate the breakthrough probability. Inflow samples were taken from each batch of the feeding. Outflow concentration was monitored in intervals ranging from 18 to 500 mm.

#### 1.3 1.3 Datasets and statistical analysis

Table 2 summarizes the operational conditions of the dataset. A configuration is defined by a type of material coupled with specific filtration rate. The first line gives the range of the particular parameter, the second line the mean value.

Table 2: Feeding conditions of columns								
sand	config.	number of events	FR	$C_{NH_4-N,in}(i)^*$ $h_{in}(i)$ $D$		<b>DP</b> (i - 1)	$P(i-1) L_{NH4-N,ret}(i-1)$	
		[-]	[10 <sup>-5</sup> m s <sup>-1</sup> ]	[mg L <sup>-1</sup> ]	[mm]	[d]	[g m <sup>-3</sup> sand]	
	L1x10 <sup>-5</sup>	6	1	[3.8; 8.9] 6.7	[501; 2538] 1567	[1; 12] 5	[2.32; 18.7] 8.3	
lava sand (L)	L5 x10 <sup>-5</sup>	1	5	- 15.7	- 499	- 1	6.7	
	L10 x10 <sup>-5</sup>	4	10	[6.0; 8.5] 6.3	[501; 2204] 1243	[1; 12] 6	[3.9; 12.5] 5.7	
	R2 x10 <sup>-5</sup>	20	1-2	[1.3; 22.0] 8.0	[501; 2518] 1554	[1;67] 7	[2.2; 18.0] 7.4	
river sand (R)	R3 x10 <sup>-5</sup>	12	3	[1.3; 39.0] 17.8	[501; 1109] 698	[1;40] 10	[0.1;13.7] 3.9	
	R5 x10⁻⁵	12	5	[4.0; 22.4] 9.1	[501; 1557] 1010	[1; 7] 5	[2.0; 10.1] 5.6	

\*method: DIN 38 406 T5; absolute uncertainty (AU): 0.0015  $mg_{NH4-N}L^{-1}$ ; quantitative limit (QL): 0.01  $mg_{NH4-N}L^{-1}$  or cuvette quick tests; AU: 0.05  $mg_{NH4-N}L^{-1}$ , QL: 0.015  $mg_{NH4-N}L^{-1}$ 

Ammonium mass retained during the last event  $(L_{NH4-N,ret.}(i-1))$  was calculated by subtracting outlet ammonium fluxes  $(L_{NH4-N,out}(i-1))$  from applied ammonium load  $(L_{NH4-N,in}(i-1))$ .

$$L_{NH4-N,ret}(i-1) = L_{NH4-N,in}(i-1) - L_{NH4-N,out}(i-1)$$
 where:

$$L_{NH_{4}-N,in}(i-1) = \frac{c_{NH_{4}-N,in}(i-1) \times V_{in}(i-1)}{V_{filter}} \text{ and } L_{NH_{4}-N,out}(i-1) = \frac{c_{NH_{4}-N,out}(i-1) \times V_{out}(i-1)}{V_{filter}}$$

#### 1.3.1 1.3.1 Description of the dataset and restrictions

In order to ensure the reliability of the statistical model, the differences between grain size distributions of sands were neglected. Based on previous studies (Woźniak et al., 2007) the type of sand (river sand or lava sands) was considered to be much more important than grain size distribution.

The results of columns with filtration rates of  $1 \times 10^{-5}$  (43 feedings) and  $2 \times 10^{-5}$  m s<sup>-1</sup> (1 feeding) on river sand were put together for statistical analysis, because this differing filtration rate did not indicate differing treatment performances. Likewise the influence of the thickness of the porous media was neglected.

A first analysis (principal component analysis) of the dataset showed that configurations with river sand were much more investigated than configurations with lava sands. The hydraulic and ammonium

loads on  $R3x10^{-5}$  and  $R5x10^{-5}$  were generally lower than on  $R2x10^{-5}$ . These heterogeneities are likely to impact directly the statistical results.

#### 1.3.2 1.3.2 Description of the model

The aim of the statistical analysis was to quantify the probability of a breakthrough. Based on theoretical considerations six variables were considered to be relevant: (i) quantitative variables: inlet ammonium concentration, applied hydraulic load, duration of previous dry period, mass of ammonium retained in the column during the last event and (ii) qualitative variables: type of filter material and filtration rate.

To estimate the breakthrough probability logistic regression was applied. The method allows expressing the modality of a binary variable as a linear function of quantitative and qualitative explanative variables (Dreiseiti and Ohno-Machado, 2002). The global model is:

$$p(1|X_i) = \frac{e^{X_i}}{1 + e^{X_i}}$$

 $X_i = \beta_0 + \beta_{sand} + \beta_{FR} + \beta_{C_{NH_4-Nin}}C_{NH_4-Nin}(i) + \beta_{h_{in}}h_{in}(i) + \beta_{L_{NH_4-Niret}}L_{NH_4-N,ret}(i-1) + \beta_{DP}DP(i-1)$ 

 $p(1|X_i)$  is the probability of ammonium breakthrough given the values of the variable Xi.  $p(0|X_i)$  is the probability of an absence of ammonium breakthrough and is equal to  $1 - p(0|X_i)$ .

Since ammonium retention is a sorption process, the probability of a breakthrough must increase with the inlet ammonium load. However, the inlet ammonium concentration ( $C_{NH_4-N,in}(i)$ ) and applied hydraulic load ( $h_{in}(i)$ ) were considered separately in order to take the hydraulic characteristics of the event into account. The variables  $L_{NH_4-N,ret.}(i-1)$  and DP(i-1) describe the part of the sorption capacity that is already used be ammonia from the previous event. The higher  $L_{NH_4-N,ret.}(i-1)$  is, the more sorption sites already taken are. But with progressing dry period (DP(i-1)) the capacity is regenerated by nitrification of the retained ammonium.  $\beta_0$  is the value of  $X_i$  corresponding to a reference situation for which no feeding is applied on a lava sands column with a filtration rate of 1 x 10<sup>-5</sup> m s<sup>-1</sup> which results in a probability of breakthrough close to 0.

A breakthrough is assumed to occur when the calculated probability is higher than 50%. The best model was obtained by eliminating one-by-one the parameters (backward stepwise method) to minimize the Akaike Information Criterion (AIC) (Dreiseiti and Ohno-Machado, 2002). This criterion is based on the maximum likelihood estimation.

The parameters  $\beta_j$  were estimated by the maximizing the likelihood. The significance of these parameters was tested by the maximum likelihood ratio test with a level of 5%. Their confidence

intervals were estimated through a normal law  $\mathcal{N}(\beta_i; \sigma^2)$  with at a level of 95%.

The quality of the model was first assessed by a classification table so as to count up relevant and irrelevant predictions. The "true positive" (TP) correspond to the feedings classified as leading to a breakthrough whereas they led to a breakthrough. The "true negative" (TN) correspond to the feeding classified as "no breakthrough" whereas they did not lead to a breakthrough". The "false positive" (FP) correspond to those for which the model predicted a breakthrough while they didn't lead to one (table 3).

	Table 3: Table of classification						
Observed\Predicted	no breakthrough	breakthrough	total				
no breakthrough	TN	FP	Ν				
breakthrough	FN	TP	Р				
total	Ñ	ô	n=TP+FN+FP+TN				

Four indicators were calculated. The error rate was obtained by dividing the number of irrelevant

predictions by the total number of studied cases  $\left(\frac{FN+FP}{n}\right)$ . The sensibility indicates the ability of the model to predict the breakthrough apparition. It corresponds to the proportion of "true breakthroughs" among the total predicted breakthroughs  $\left(\frac{TP}{TP+FP}\right)$ . Inversely, the specificity informs about the ability of the model to identify the absence of breakthrough. It is calculated by dividing the number of the "true negative" by the total number of predicted "negative"  $\left(\frac{TN}{TN+FN}\right)$ .

### 2 2 RESULTS

#### 2.1 2.1 Selection of the most relevant model

The probability of a breakthrough is best represented by the logistic model:

$$p(1) = \frac{e^{x_i}}{1+e^{x_i}}$$
, where:

$$X_i = \beta_0 + \beta_{sand} + \beta_{FR} + \beta_{C_{NH_4}-N,in} C_{NH_4-N,in} (i) + \beta_{h_{in}} h_{in} (i)$$

The logistic regression showed that only four out of the tested six parameters significantly influence the appearance of a breakthrough: the type of sand, the ammonium inlet concentration, filtration rate and the applied hydraulic load. For other parameters, regression coefficients were not significantly different from 0, meaning that they have negligible influence on the probability of a breakthrough.

Unexpectedly, the initial state of the column (expressed through the duration of dry period and the retained ammonium load during the previous feeding) does not appear as an influence factor. Regression coefficients of influence parameters are given in table 4.

sand		river sand			lava sands		
<b>FR</b> [10 <sup>-5</sup> m s <sup>-1</sup> ]	1 or 2	3	5	1	5	10	
βο		-22.6 ± 0.1					
$\beta_{h_{in}}$		$4.8 \times 10^{-3} \pm 0.3 \times 10^{-3}$					
$\beta_{C_{NH_4}-N,in}$		0.13 ± 0.01					
Bsand		14.9 ± 0.5			0		
$\beta_{FR}$	0	0.0 ± 1.1	3.5 ± 0.7	0	3.5 ± 0.7	10.7 ± 0.7	

Table 4: Regression coefficients of the breakthrough probability predictive model (reference situation in bold)

In comparison with the reference situation, an increase of the filtration rate leads to an increase in the probability of a breakthrough, both for river sand or lava sands (positive regression coefficients). This highlights the influence of retention time for values higher than  $3 \times 10^{-5}$  m s<sup>-1</sup>.

For a given filtration rate, the probability of breakthrough is higher for river sand than for lava sands. In particular, for a given applied ammonium load, this probability is higher for river sand with a filtration rate of 1 or 2 x  $10^{-5}$  m s<sup>-1</sup> than for lava sands with a filtration rate of 10 x  $10^{-5}$  m s<sup>-1</sup>

 $(\beta_{sand}(L) + \beta_{FR}(10x \, 10^{-5}) = 10.7; \beta_{sand}(R) + \beta_{FR}(2x \, 10^{-5}) = 14.9$ , see figure 3).

It can be seen as well that an increase in the hydraulic load and the inlet ammonium concentration causes an increase in the breakthrough probability. However, respective values of  $\beta_h$  and  $\beta_{[NH4]}$  cannot directly be compared, since they do not have the same units and are involved in the regression equation in the shape of continuous explanative variables products (oppositely to the type of material and the filtration rate value). Finally, figure 3 summarizes the model results by describing the breakthrough probability against the inlet ammonium concentration for different configurations and feeding conditions.

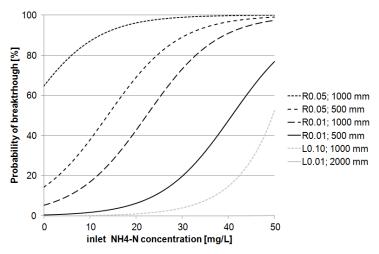


Figure 2: Probability of getting a breakthrough as a function of inlet ammonium concentration for several feeding conditions

The probability of a breakthrough is comparatively low for lava sands over the entire range of ammonium concentrations, hydraulic loads or filtration rate tested. This confirms the much higher sorption capacity of this material.

Inversely, the breakthrough probability is constantly higher than 65% for river sand with filtration rate of  $5 \times 10^{-5} \text{ m s}^{-1}$ , even at very low ammonium concentrations, for an applied hydraulic load of 1000 mm. However, when this hydraulic load reaches only 500 mm, the breakthrough probability decreases significantly (below 50% for an ammonium concentration of 11 mg<sub>NH4-N</sub>/L).

In typical ranges of CSOs concentrations (between 3-30 mg<sub>NH4-N</sub>/L, Welker, 2004), the breakthrough probability is lower than 50% for all lava sands configurations independently from the applied hydraulic load. For river sand, a probability of 50% is reached for a hydraulic load of 500 mm with a filtration rate of 1 or 2 x  $10^{-5}$  m s<sup>-1</sup> at the concentrations of 40 mg<sub>NH4-N</sub>/L. When the hydraulic load reaches 500 mm on the same column, this probability increases from 20 to 45% over the range of tested concentrations.

#### 2.2 2.3 Evaluation of the model

Table 5 represents the classification table of the selected model. Results show a satisfying match between the observed and the predicted behavior of the filter. 9 events were improperly predicted, which corresponds to an error rate to 16%. The sensibility of the model is equal to 80%, whereas the specificity (well predicted behavior frequency) is equal to 84%.

Table 5: Classification table of the logistic regression							
observed \ predicted	observed \ predicted no breakthrough breakthrough total						
no breakthrough	21	7	28				
breakthrough	2	25	27				
total	23	32	55				

## 3 3 DISCUSSION

The model does not allow testing interactions between the different influence parameters. In particular, this study highlighted the influence of the filtration rate and the type of sand. It can be assumed that the combinations of river sand and high filtration rate ( $5 \times 10^{-5} \text{ m s}^{-1}$ ) increase the risk of a breakthrough. However, not all possible combination between the media and the filtration rate were tested, which limits further interpretations. Moreover, lower hydraulic and ammonium loads were applied for the experiments on river sand with a filtration rate of 3 and 5 x  $10^{-5} \text{ m s}^{-1}$ , which underestimate the impact of the high filtration rate on the probability of getting a breakthrough. Another logistic regression could be implemented with new regression coefficients taking into account these interactions. However, the global tested model has to remain simple to preserve its reliability.

The present study investigated the influence of the initial state of the column by a linear combination of the previous dry period and the retained ammonium load during the previous event  $(\beta_{L_{NH_4-N,ret.}}L_{NH_4-N,ret.}(i-1) + \beta_{DP} DP(i-1))$ . However, the model results did not indicate an influence of the initial ammonium being in the filter. This influence has been demonstrated on full-scale and on experimental pilots (Fournel et al., 2012; Dittmer, 2006). This can be explained by the fact, that this influence is not linear. In the next projects, it could be interesting to determinate the best way to take the initial state into account. Besides the dry period duration was generally sufficient to nitrify the major part of retained ammonium. Field experiments showed that nitrification of retained ammonia is almost completed after 2 or 3 days (Dittmer, 2006). In this study, 75% of the events were simulated after a dry period of 4 days or more.

The sewage was obtained by diluting domestic wastewater with tap water. It is possible that this method does not reproduce the proportion of nitrogen compounds. In particular, the ratio between organic nitrogen and ammonium is not respected. While (Henze et al., 2002) estimated the quantity of organic nitrogen in a domestic wastewater between 35 and 40% of total ammonium, this proportion reaches 50 to 70% in CSO or stormwater (Taylor et al., 2005; Gervin and Brix, 2001). Under unsaturated conditions, organic ammonium is transformed into ammonium through ammonification (Lee et al., 2009). The use of an influent closer to a CSO would certainly involded more uncertainties on the statistical results.

In order to simplify the model and to ensure the reliability, several influence parameters were neglected. In particular, the filter thickness varied between 0.75 and 1 m, which can influence the sorption capacity. However, several authors demonstrated that most of ammonium was retained in the upper zone of the column (von Felde and Kunst, 1997; Woźniak, 2008). Thus, this influence should be slight, which was confirmed by the graphical analysis.

Likewise several sands with different characteristics (grains size distribution, porosity, percentage of carbonates) were grouped together in two types of sand (river sands and lava sands). There again, slight differences of behavior were observed between the different sands. However, the sands were associated to a given thickness (0.75 or 1 m). Thus the distinction between the effects of the material characteristics and the filter thickness is not possible. Moreover, some sands were fed only once, which do not allow highlighting the influence of their physical characteristics.

The reliability of such a statistical model is based on the homogeneity of the dataset used. Indeed, in our case, the datasets presented some heterogeneity in terms of feeding conditions on the different configurations (number of feedings, dispersion of influent concentrations per configuration, etc.). Then, such heterogeneities create uncertainties during the data treatment and the calculation of regression coefficients. The implementation of a feeding program and protocol should be useful for further researches.

Further research is needed to determine the inlet ammonium loading corresponding to the beginning of the breakthrough. In particular, a covariance analysis would allow predicting the value of a quantitative variable as a linear function of quantitative and qualitative variables. A first trial of such a study was implemented but results are not reliable enough to be presented so far.

## 4 CONCLUSION AND OUTLOOK

The graphical and statistical analysis highlighted the influence of the type of sand and the filtration rate on ammonium removal. The performance of the system is highly improved by the use of lava sands and low filtration rates (1 or  $2 \times 10^{-5} \text{ m s}^{-1}$ ). The aim of implementing a statistical analysis was to identify the importance of influencing parameters on the probability for a breakthrough. This analysis could only be conducted due to the large number of single events and especially high load data. Feeding conditions (hydraulic loads and ammonium concentration) as well as design have to be considered. The influence of initial state could not be taken into account, which certainly needs to be expressed otherwise.

The statistical analysis included only high load events where time series of the outflow concentrations were measured. There is still a database of several hundred events with only composite samples that could be included. This would allow realizing a validation of the results. In particular, the presence and the relative impact of the tested variables can be verified.

As the column experiments represented real design and operational conditions the model should be transferable to full scale plants. However, the results need to be validated and completed on full-scale

plants.

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