Do wastewater pollutants impact oxygen transfer in aerated horizontal flow wetlands?

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Abstract

Aerated treatment wetlands are an increasingly recognized nature-based technology for wastewater treatment that relies heavily on mechanical aeration. Although aeration–mediated oxygen transfer into the wastewater can be impeded by wastewater pollutants, little is known about the link between the volumetric oxygen mass transfer coefficient k_{La} and the organic carbon concentration of the wastewater in aerated wetlands. In this study, oxygen transfer experiments were carried out in a lab-scale gravel column using clean water and wastewater from a pilot-scale horizontal flow (HF) aerated wetland treating domestic sewage. The α–factor, which describes the ratio of the volumetric oxygen mass transfer coefficient k_{La} in wastewater to clean water, was reduced by increasing soluble chemical oxygen demand ($\mathrm{COD_s}$). The derived regression equation $\alpha = 1.066 - 0.0014$ mg $\mathrm{COD_s}$ $\mathrm{L^{-1}}$ was incorporated into a numerical process model to simulate the impact of the reduced oxygen transfer on a hypothetical HF aerated wetland. The simulations re-

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vealed that α and treatment efficacy for nitrogen were substantially reduced by COD_s at low aeration (k_{La} of 1 h^{-1}) and high influent wastewater strength (COD_s of 300 mg L^{-1}). At the same k_{La} and influent COD_s concentration, longitudinal gradients of α and concentrations for dissolved oxygen (DO), NH_4–N and NO_x–N in the simulated wetland were shifted up to 21% of wetland length downstream. These effects decreased with increasing k_{La} and were found to be negligible at $k_{La} > 3$ h^{-1}, which corresponds to an air flow rate of approximately 400 L m^{-2} h^{-1}. Following this, higher organic carbon concentrations reduce oxygen transfer in HF aerated wetland systems, thus resulting in decreased treatment efficacy.

Keywords: domestic sewage, constructed wetland, numerical process modeling, nature-based technology, aeration, alpha factor

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Highlights:.

- Oxygen absorption experiments were conducted in a gravel column with real wastewater
- α linearly decreased with increasing COD_s concentration
- Numerical process model was extended with $\alpha = f(COD_s)$
- Reduction of treatment efficacy due to changes in oxygen transfer was simulated

1. Introduction

Nature–based technologies were recently mentioned as potential contributors to adress the worldwide challenges of the deterioration of water resources caused by inadequate wastewater treatment [1]. Treatment wetlands, a kind of nature–based technology, are usually simple in design, which translates into low operational costs, low maintenance and operation requirements and robust treatment under a wide range of climate conditions [2–4].

Aerated wetlands are intensified treatment wetlands in which air is injected into the wetland basin to serve the dissolved oxygen (DO) demand of the microbial community present. This increases treatment capacity and efficacy [5, 6]. Aerated wetlands are increasingly recognized for their capacity to remove organic carbon, nitrogen and phosphorous from industrial and domestic wastewater [7, 8], as well as organic trace contaminants [9] and associated toxicological effects [10]. However, it is still not well understood how oxygen transfer is impacted by wastewater pollutant concentrations in an aerated wetland. The oxygen mass transfer rate of aeration depends on the size of the injected air bubbles and the rheological conditions in the proximity of the bubbles, which in turn depend on the operational (e.g. plant design, aeration system, air flow rate (AFR), reactor hydraulics) and environmental conditions (influent wastewater oxygen demand and pollutant concentration) [11–13]. Aeration is a critical research topic for wastewater treatment technologies involving the injection of air or oxygen such as activated sludge and membrane bioreactor technologies [12–16], biofilters [17], anaerobic ammonia oxidation (ANNAMOX) systems [18], granular sludge reactors [19] and aerated wetlands [7, 20] as aeration is the main contributor of associated operational costs [21]. However, research on aeration in wetlands, especially oxygen transfer , has not evolved to the same extent as for activated sludge and membrane bioreactor technologies. Recently, Boog et al. [22] developed and applied a numerical process model that is able to simulate oxygen transfer for aeration in horizontal flow (HF) aerated wetlands; however, did not include the link of the volumetric oxygen mass transfer coefficient k_{La} to wastewater pollutant concentration. The ratio of k_{La} in wastewater to that in clean water is termed the α–factor. In wastewater, α is reported to be affected through surfactants, microbial activity and solid matter concentration [12, 13, 23]. Solid matter is reported to alter bubble coalescence behavior in activated sludge and membrane–bioreactor systems operated at high mixed–liquor suspended solid concentrations (0.5–30 g L^{-1}) [24–26]. The impact of microbial activity was also found to alter α in membrane–bioreactors at high mixed–liquor suspended solids concentration [25, 27]. Microbial activity in the studies by Germain et al.[25] and Henkel et al.[27] was linked to the effect of mixed–liquor suspended solids concentration (biomass was present as suspended flocs) and, in [25], also to surfactants that were contained in the liquid fraction of the biomass. Despite investigations are lacking, it is quite unlikely that similarly high suspended solids concentrations will be observed in HF aerated wetlands and that the effect of solid matter and solid–phase microbial activity on α plays such a significant role for HF aerated wetlands. In contrast, the effect of surfactants in aerated HF wetlands is, most probably, of high importance.

Surfactants attach at the gas–water interface and hinder inter-facial oxygen mass transport. Surfactants can reduce α and, therefore, the oxygen mass transfer rate down to 50% [23, 26, 28]. Additionally, in treatment systems with plug–flow, surfactants decrease along the system length [29]. In such systems, α is the lowest at the influent zone, in contrast, the oxygen demand is the highest at the influent zone. This trend could be similar for HF aerated wetlands based on observed concentration gradients and hydraulics [7, 30]. Exploring the potential change of α with influent wastewater strength and along the length in HF aerated wetlands is, thus, of fundamental interest.

Surfactants, however, are not a common wastewater quality parameter analyzed in wetland research studies [7, 8] or recommended for full–scale design and operation [31, 32]. Jiang et al. [33] recently developed a process model for activated sludge systems using influent organic carbon concentration (measured as total chemical oxygen demand ($\mathrm{COD_t}$)) as a proxy for surfactants to dynamically estimate α. It is questionable whether this estimation of α holds for aerated wetlands as well. In aerated wetlands, different aerators are used and the observed $\mathrm{COD_t}$ concentration can be lower than the $\mathrm{COD_t}$ range considered by Jiang et al. [33]. Additionally, HF aerated wetland hydraulics will induce a longitudinal gradient of surfactants that should be considered to estimate α. By using a commonly analyzed parameter such as COD or total organic carbon (TOC) to predict α, the derived knowledge can be more useful for aerated wetland researchers, designers and operators, as well as, for using computer models based on COD or TOC.

Thus, this paper investigates the link of α to wastewater organic carbon concentration in HF aerated wetlands and investigates the associated impact on the removal of organic carbon and nitrogen. Oxygen transfer experiments in a lab–scale gravel column with wastewater from a pilot–scale HF aerated wetland were carried out to derive an equation to estimate α based on organic carbon concentration measured as TOC and COD. This equation was then incorporated into a process model. To investigate the impact of influent organic carbon concentration on α and treatment efficacy, a simulation scenario analysis was carried out. By providing new insights on oxygen transfer in HF aerated wetlands, this study provides a significant advancement in research on aeration in HF aerated wetlands.

2. Material and methods

2.1. Pilot–Scale aerated wetland and water quality analysis

Wastewater samples for the oxygen transfer experiments were taken from the pilot–scale aerated HF wetland named *HAp* at the research facility in Langenreichenbach, Germany described by Nivala et al. [34] (Figure 1; Figure S1 in supplementary information). The wetland was loaded with primary–treated domestic sewage at a hydraulic loading rate (HLR) of 0.576 m^3 d^{-1} (equivalent load of a five person household considering the new German standard for small–scale treatment wetlands [32]). Medium gravel (8–16 mm) was used as the main media and coarse gravel (16–32 mm) for the in- and effluent zones. The wetland was planted with *Phragmites australis* and had been operating in steady state for 7.5 years prior to the start of this study. The aeration system consisted of a network of drip irrigation lines (AzudDrip, Azud, d_{line} = 16 mm, orifice diameter of 1 mm, orifice spacing of 0.3 m) at a line spacing of 0.3 m, which translates into an uniform aeration grid on the wetland bottom. Air was supplied by electric diaphragm pumps (Mistral 2000, AQUA MEDIC) operated 24 h d^{-1} [35]. Routine weekly sampling of the in- and effluent was conducted to ensure stable operation of the wetland during sampling for the oxygen transfer experiments. Water samples of 30 L were taken during December 2017 to February 2018 at locations indicated in Figure 1 according to the procedures in Nivala et al. [34]. To quantify total and soluble organic carbon content, all samples were analyzed for total organic carbon (TOC, DIN EN 1484, Shimadzu TOC-VCSN,) and dissolved organic carbon (DOC, DIN EN 1484, Shimadzu TOC-VCSN, filtration by 0.45 µm ceramic filter). Due to logistical reasons, total (COD_t) and soluble chemical oxygen demand (COD_s) concentrations were not analyzed, indeed, were estimated by regression on TOC and DOC concentrations and sampling location within the wetland. Briefly, the regression equations were calibrated and validated by measurements of TOC, DOC, COD_t and COD_s of additional samples taken during February to April 2018 at similar sample locations of two other HF aerated wetlands at the site with similar design (Supplementary information (S) Section S2). Corresponding COD_t and COD_s (filtered through a 0.45 µm glass fiber filter) were analyzed using test–kits (LCK 514 & LCK 314, Hach–Lange) and a spectrophotometer (DR3900, Hach–Lange); TOC and DOC as previously described.

2.2. Oxygen transfer experiments

A laboratory column experiment was conducted to simulate oxygen transfer of the pilot–scale aerated HF wetland. The keep the laboratory conditions as close to the conditions observed for the pilot–scale system, the cylindrical glass column ($d_{col} = 0.15$ m, $h_{col} = 1.00$ m, $h_{gravel} = 0.95$ m, $h_{water} = 0.9$ m) was filled with similar gravel than what was used in the pilot–scale wetland *HAp* ($d_{gravel} =$ 8–16 mm, porosity of 0.38) and equipped with a section of an aeration line similar to that used in *HAp* (AZUD Drip, $d_{line} = 16$ mm, $d_{orifice}$ $= 1$ mm, one orifice) (Figure 2). The column was controlled at 20 °C using a water jacket (LAUDA). Aeration was provided by an electric diaphragm

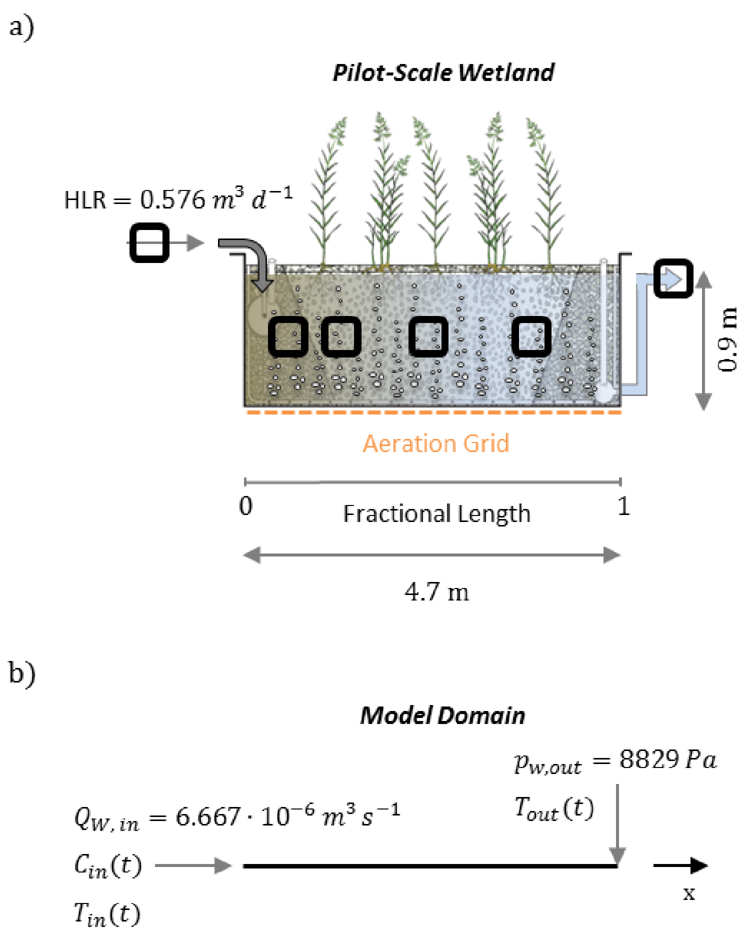

Figure 1: a) Experimental pilot–scale wetland (width of 1.2 m, sampling points indicated by black squares); b) corresponding domain of the 1D process model. HLR is the hydraulic loading rate. Modified with permission from Boog et al. [22].

pump at AFR of 510, 1359 and 2718 L m^{-2} h^{-1}. AFR was measured using a thermal mass flow meter (TSI 4043, TSI GmbH). Dissolved oxygen (DO) was measured using optical oxygen probes (DP-PSt3-YOP, PreSens GmbH) connected to a measurement converter (Oxi 4 Mini, PreSens GmbH) and a laptop for data recording (Software OXY4 v2.30, PreSens GmbH). Ambient air pressure was measured by a weather station outside the building to correct DO concentrations to a pressure of 1013 hPa.

Oxygen transfer experiments with the sampled wastewater and clean (tap) water (h_{water} = 0.9 m) were carried out using the non–steady state absorption method according to the German guideline DWA M–209 [36]. For each trial, a solution of $NaSO_4$ was added (plus 0.5 mg L^{-1} of $CoSO_4 \cdot H_2O$ as catalyst) prior to each water sample to deplete DO below 0.1 mg L^{-1} and to inhibit re–aeration while filling the column. Then total dissolved solids (TDS) were measured using a hand–held device (M350i, WTW Weilheim) prior to filling the column. Afterwards, aeration was started and DO was recorded until saturation. After each trial the column was flushed with tap water to wash out the sample solution and clean the column. Each trial was conducted in triplicate to obtain a reliable estimate of k_{La}. For each trial and sensor position, k_{La} and the apparent DO saturation concentration S_O^* were estimated using non–linear regression nls() function of the R statistical software [37]. The estimated k_{La} were averaged over the three replicated trials, the three oxygen sensors, and, corrected to a temperature of 20 °C (Equation S3, $\theta = 1.024$ as recommended by [11] and [36]) and a TDS concentrations of 1000 mg L^{-1} (Equation S4); this corrected parameter is termed $k_{La,20,1000}$. Then, the α–factor was computed as the ratio of $k_{La,20,1000}$ in

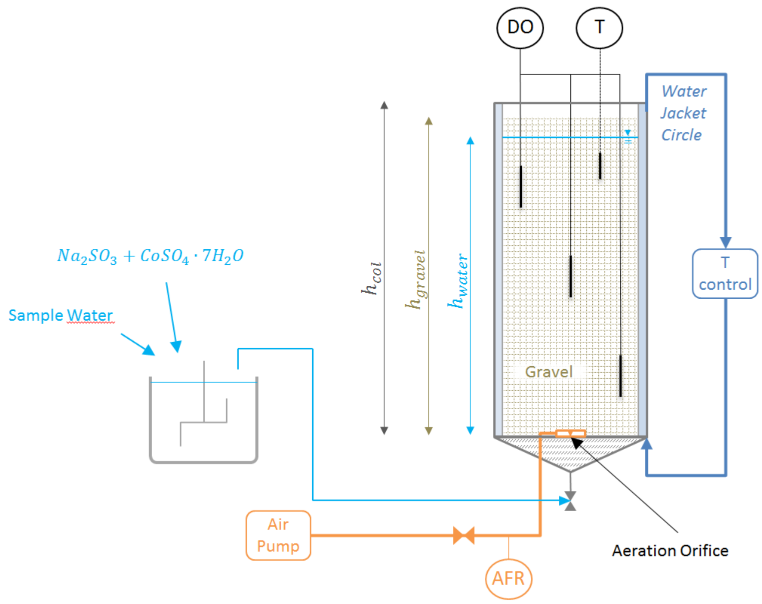

Figure 2: Set–up of the gravel column (d_{col} = 0.15 m, h_{col} = 1.00 m, h_{gravel} = 0.95 m, h_{water} = 0.9 m) used for the oxygen transfer experiments. Positions of DO sensors were 0.10, 0.45 and 0.80 m above the aeration orifice.

wastewater ($_{ww}$) to clean water ($_{cw}$) ($\alpha = {}^{k_{La,20,1000,ww}}/_{k_{La,20,1000,cw}}$). Finally, the computed α was regressed on COD_t, COD_s, TOC and DOC concentration of the corresponding water sample (lm() function of the R statistical software [37]).

2.3. Process model

A numerical process model was used to analyze the impact of organic carbon concentration on the α–factor in simulation scenarios of a hypothetical HF aerated wetland at different influent wastewater strengths and volumetric oxygen mass transfer coefficients k_{La} and to estimate the associated impact of the impacted oxygen transfer on treatment performance. The design of the hypothetical HF aerated wetland was based on the pilot–scale wetland *HAp* described in section 2.1. Therefore, the process model used was based on the 1D reactive transport model by Boog et al. [22], which was also based on a similar HF aerated wetland design. This model was implemented in the open–source finite–element code OpenGeoSys (OGS, v5.7.1 [38]) coupled to the geochemical solver IPhreeqc [39] (coupling via operator–splitting [40]). It simulates water flow using a dual–permeability approach; advective–dispersive transport of solute and particulate wastewater components, biodegradation and bacterial growth according to the Constructed Wetland Model No. 1 (CWM1)[41] and aeration as a first–order mass transport process. Additionally, the model also simulates convective–conductive heat transport; however, this feature is not of relevance here as water temperature is restricted to 20 °C during the simulations. The full set of model equations and descriptions are presented in Boog et al. [22]. Here, oxygen mass transfer from air to water (Equation 1 and 2) was extended with the equation $\alpha = f(\mathrm{COD_s})$ (Equation 3) that was derived from the oxygen transfer experiments. Considering the similarity of the pilot–scale system used in this study and by Boog et al. [22] and the fact that the gravel column was based on the pilot–scale wetland design, this modeling approach is reasonable. Due to the simple description of solid matter transport and attachment, the model lacks accuracy in simulating solid matter turnover within HF aerated wetlands. This translates into a less reliable simulation of spatial patterns for $\mathrm{COD_t}$ compared to $\mathrm{COD_s}$. Therefore, the regression equation using $\mathrm{COD_s}$ as regressor (Equation 3) was chosen to estimate α during the simulations.

$$r_{S_o,aeration} = \alpha\, k_{La,T}\; (S_o^* - S_o) \tag{1}$$

$$k_{La,T} = k_{La,20}\, \theta^{20-T} \tag{2}$$

$$\alpha = 1.066 - 0.0014\, \mathrm{mg\ COD_s\ L^{-1}} \tag{3}$$

Here, $r_{S_o,aeration}$ is the oxygen transfer rate in g L^{-1} s^{-1}, $k_{La,T}$ and $k_{La,20}$ are the volumetric oxygen mass transfer coefficients at temperature T and at 20 °C in s^{-1}, respectively. S_O^* and S_O are the actual and saturation dissolved oxygen concentration in g L^{-1}, θ is the temperature correction factor ($\theta = 1.024$ as recommended by [11] and [36]). The model was discretized into a finite–element mesh of 94 line elements with an element size of 0.05 m each using the open–source mesh generator GMSH [42]. A regular time–stepping scheme with a step size of 1800 s was applied in all simulations. The same parameter set as in Boog et al. [22] was used, except for k_{La}. Originally, Boog et al. [22] lumped α into k_{La}. Due to the extension of the current model to explicitly consider $\alpha = f(\mathrm{COD_s})$, it was necessary to recalibrate the current model by adjusting k_{La}. Boog et al. [22] calibrated their model using data of a similar pilot–scale HF aerated wetland at the same experimental site than *HAp*. As the intention of this study is to simulate a hypothetical HF aerated wetland based on the design of the pilot–scale wetland *HAp* (section 2.1) we used the same data as Boog et al. [22] (scenario *Calibration* in [22]) to recalibrate the extended model. Recalibration started with the default values from Boog et al. [22], then k_{La} was manually increased until a fit with sufficient accuracy was achieved. After recalibration, the scenario *Cross–Validation* of Boog et al. [22] (simulation of a third HF aerated wetland at the same site) was re–run with the extended and recalibrated model to assess its validity. The goodness of fit for recalibration and validation was assessed by comparing measured pore water and effluent concentrations using the modified Nash–Sutcliff Efficiency E_1).

The validated model was then applied to analyze the performance of the pilot–scale aerated HF wetland *HAp* in different simulation scenarios. Simulation scenarios with a duration of 60 days, a constant temperature of 20 °C including three influent wastewater strengths (Table 1) and three values of $k_{La,20,cw}$ (1.0, 2.0 and 3.0 h^{-1}) were considered. Initial water depth and temperature were 0.9 m and 20 °C, respectively (Figure 1). Initial concentrations of model components were 1.0E-4 and 1.0E-3 mg L^{-1} for wastewater pollutants and bacteria, respectively. Influent loading was 0.576 m^3 d^{-1} (boundary condition of 6.666E-6 m^3 s^{-1}). In the biokinetic model CWM1, COD_t is fractionized to account for soluble and particulate as well as biodegradable and non–biodegradable fractions. To fractionize and convert influent COD_t into CWM1 model components, the recommendations for influent fractionation for the Activated Sludge Model (ASM) No.1 and No.2 [43] (Table S1) were used. Remaining initial and boundary conditions are presented in Table S2. All simulations were executed as serial runs on the high–performance computing cluster *EVE* (Dell™ PowerEdge™ R630, Intel Xeon E5-2690 v4 CPUs and/or Intel Xeon E5-2670 v2 CPUs). Post-processing and visualization using the R statistical software [37].

Table 1: Concentrations of the three influent strengths as defined by Tchobanoglous et al. [11]. COD_s was set as 0.38 COD_t.

Parameter	Influent Concentration (mg L^{-1})		
	Low Strength	*Mid Strength*	*High Strength*
COD_t	250	430	800
COD_s	95	163	304
NH_4–N	12	25	45
SO_4	20	30	50

NO_x–N is defined as zero.

H_2S is not defined by Tchobanoglous et al. [11] and was set to zero.

3. Results and discussion

3.1. Oxygen transfer experiments

In the oxygen transfer experiments using clean water and wastewater from the pilot–scale aerated HF wetland, $k_{La,20,1000}$ was estimated to be 2–15 h^{-1} answer to R1Q16](Figure 3). From 189 DO measurement curves, 32 were excluded due to distortions that impeded the derivation of reliable estimates for $k_{La,20,1000}$ (Section S3.2). $k_{La,20,1000}$ from clean water samples at AFR of 510 L m^{-2} h^{-1} were in range with values reported by Butterworth [44] for a comparable AFR and orifice size. At an AFR of 1359 and 2718 L m^{-2} h^{-1}, estimated $k_{La,20,1000}$ were up to 10 h^{-1} lower than reported by [44]. However, $k_{La,20,1000}$ varied more intense at higher AFR in this study and Butterworth [44] reported overall high standard deviations of up to 5 h^{-1}. This may be explained by the fact that Butterworth [44] performed experiments in a larger system (tank size of 1.5 m in length and width) but used only two

DO sensors. A reasonable explanation for this increase in variability with increasing AFR observed in this study cannot be given.

The mean overall $k_{La,20,1000}$ estimated from wastewater samples at an AFR of 510 L m^{-2} h^{-1} was approximately 3.5 h^{-1}, which is similar to the value at a similar AFR derived by process modeling of an HF aerated wetland by Boog et al. [22]. Considering this and the narrow difference to [44] at an AFR of 510 L m^{-2} h^{-1}, the estimated $k_{La,20,1000}$ can be interpreted as reliable. In general, $k_{La,20,1000}$ increased with increasing AFR, which was also reported from the literature [12]. In the trials using wastewater, $k_{La,20,1000}$ was reduced by increasing COD_s concentrations at a similar rate at the three AFR tested (Figure 3). This indicates that oxygen transfer was linked to the organic carbon concentration (TOC, COD) of the wastewater, however, independently of the AFR.

3.2. Link between α and organic carbon concentration

Measured COD_s concentrations of the wastewater samples describe a decreasing trend with increasing distance from the wetland influent, which was previously observed in the literature [30]. Opposed to COD_s, α increased with increasing distance from the wetland influent (Figure 4). This underlines previous findings that oxygen transfer is not uniform in treatment systems where hydraulics deviate from complete mixing [29, 45].

Above a COD_t of 200 mg L^{-1} and COD_s of 80 mg L^{-1}, α decreased at a similar rate to COD_t and COD_s; however, the decrease of α with COD_t was shifted approximately +200 mg L^{-1} compared to the decrease with COD_s (Figure 5). α–COD_t and α–COD_s pairs below α of 1.0 related to the same samples from 0.0–0.25 fractional length. The shifts in COD between these

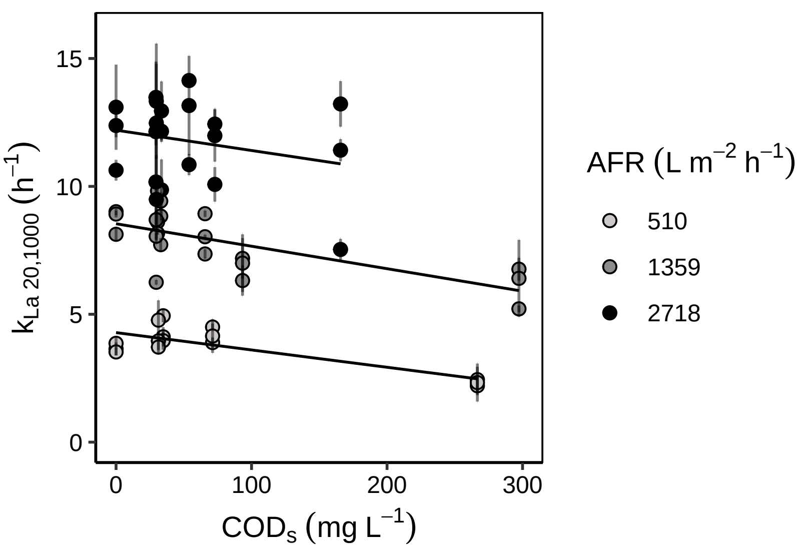

Figure 3: Estimated $k_{La,20,1000}$ as a function of COD_s concentration of the wastewater sampled from the pilot–scale system *HAp*. Dots represent mean values of replicated trials from sensor position at 0.10, 0.45 and 0.80 m. Standard deviations are shown as error bars. Solid lines represent linear regression fits for each AFR.

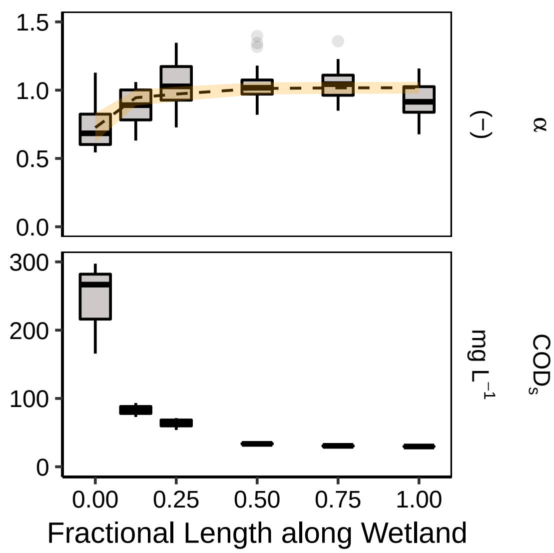

Figure 4: $\mathrm{COD_s}$ and estimated α at different fractional lengths along the experimental pilot-scale aerated HF wetland. The dashed line including orange area indicates estimation by $\alpha = f(\mathrm{COD_s})$ including the 95% confidence interval.

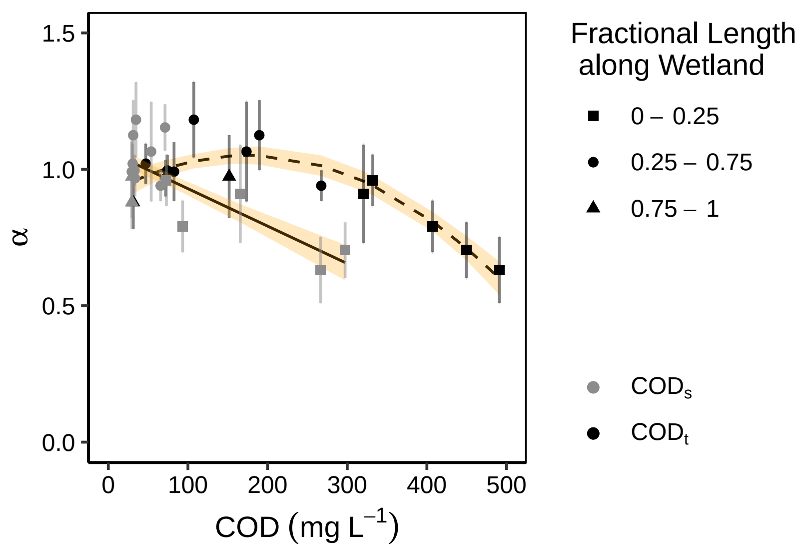

Figure 5: Estimated α vs. $\mathrm{COD_t}$ and $\mathrm{COD_s}$ concentration. Corresponding regression equations are: $\alpha = 1.066 - 1.372\text{E-}3\ \mathrm{COD_s}$, R^2=0.40 (solid line); $\alpha = 9.102\text{E-}1 + 1.602\text{E-}3\ \mathrm{COD_t} - 4.545\text{E-}6\ \mathrm{COD_t^2}$, R^2=0.52 (dashed line). Orange areas indicate the 95% confidence intervals. Regression equations for TOC and DOC can be found in Section S3.

value pairs were caused by solid matter that was accounted for in COD_t only. Additionally, α–factors scattered unregularly around 1.0 were COD consists mostly of solid matter ($COD_s \ll COD_t$ at 0.25–0.75 fractional length, Figure 5). Therefore, it is most likely that the reduction in α was caused by COD_s and that the COD of the solid matter did not substantially contribute to it. Following this, COD_s is likely a better predictor for α although R^2 of the regression equation using COD_t as regressor was higher. This is supported by the fact that COD_s, in theory, is a more reasonable proxy for surfactants compared to COD_t as surfactants are soluble. The extent of the impact of surfactants on an aeration device depends on the produced bubble size and bubble rise velocity [12]. The literature reports coarse bubble diffusors to be less affected by surfactants than fine bubble diffusors [46]. Aeration in aerated HF wetlands was reported to fall between coarse and fine bubble aeration in terms of oxygen transfer efficiency (standard oxygen transfer efficiency of 4.0–5.9% m^{-1} reported by Wallace et al. [47]). However, a median bubble diameter of 3 mm and rise velocities of 0.1–0.2 mm s^{-1} were reported from a comparable aeration system submerged in a gravel column operated at similar AFR [44]. This means that in tems of bubble characteristics, aeration in aerated HF wetland is closer to fine bubble aeration [12]. Based on visual observations of bubble movement in the oxygen absorption experiments, bubble characteristics in this study may be similar to the ones reported by Butterworth [44]; although, bubble size and rise velocity were not measured. Based on this, it is likely that the aeration device used in this study is impacted by surfactants in a similar way as fine bubble aerators.

The effect of solid matter on α is still being discussed in the literature

[13]. Some authors report solid matter to increase α at mixed–liquor suspended solids concentrations of 0.5–4.0 g L^{-1} [24], others report α to decrease at mixed–liquor suspended solids concentrations of 1–30 g L^{-1} [25, 26]. Additionally, these authors studied activated sludge plants and/or membrane bioreactors. To the best of our knowledge, there are no studies available that report pore water solid matter concentrations in HF aerated wetlands. As HF aerated wetlands are operated at high retention time (order of several days) but without sludge return, it seems unlikely to observe suspended solids concentrations in the range of g L^{-1}. Therefore, it is unlikely that suspended solids concentration altered α and does so in comparable HF aerated wetlands.

The obtained value pairs of α with COD_t fit in the broader pattern obtained by Leu et al. [48] and Jiang et al. [33], however, are shifted to higher values of α (Figure 6). This shift was most probably caused by methodological differences. Leu et al. [48] and Jiang et al. [33] estimated α using off–gas tests in full-scale activated sludge plants using fine pore diffusors. Additionally, Leu et al. [48] and Jiang et al. [33] used municipal wastewater and measured influent COD_t only. In contrast, Steinmetz [49] did not find any relationship between α and organic carbon concentration measured as DOC when conducting oxygen absorption experiments using return sludge from a full-scale activated sludge plant.

Other relationships proposed to predict α are based on microbial activity [25], sludge retention time [26] or operational parameters such tank geometry [50], AFR and aeration system [23]. A link of α to microbial activity was reported by Germain et al.[25] and Henkel et al.[27] studying membrane bioreactors. Germain et al.[25] quantified microbial activity in the solid (content of extra–cellular polymeric substance) and liquid phase (soluble microbial products as COD); Henkel et al.[27] quantified the corresponding solid phase only (as mixed–liquor volatile suspended solids). Both authors attributed the impact of the solid phase to its effect on sludge viscosity and rheology. As the corresponding membrane bioreactors were operated at mixed–liquor suspended solids concentrations of one to two orders of magnitude higher than what is expected in HF aerated wetlands, the effect of solid–phase microbial activity in HF aerated wetlands is probably low. Liquid–phase microbial activity is probably acounted for in COD_s concentration. However, as it is highly likely to be linked to the magnitude of the solid–phase microbial activity, it will be of minor importance in HF aerated wetlands due to the relatively low suspended solid concentrations.

Sludge retention time was reported to be important in membrane bioreactors [26] . In aerated wetlands, sludge retention time is not actively controlled and its impact on α very difficult to determine. Further explanation on this cannot be given here. In this study, AFR did not alter the decrease in $k_{La,20,1000}$ with increasing COD (slopes in Figure 3). AFR, therefore, did not affect α. The question how other operational parameters (e.g. aeration system, tank geometry, media size) are likely to alter α across HF aerated wetlands goes beyond the scope of this study. The design of the pilot–scale system *HAp* was derived from long–term practical experience with aerated wetlands in the US [34]. This design served as the basis for the recently established German guidlines for small–scale aerated wetlands [32]. Additionally, many other HF aerated wetlands in th US and Europe are built in a similar fashion [35, 44, 51–53]. Hence, expected differences in the corresponding design and operational conditions are relatively low. It is arguable that the influence of operational conditions on α across and especially within HF aerated wetlands is much lower than the influence of COD concentration. Moreover, operational variables such as hydrodynamic conditions are not expected to substantially change across space within an HF aerated wetland due to the uniform aeration system and the presence of the gravel bed [34]. A reasonable change in the tank geometry, therefore, will be of less importance than in wastewater treatment systems without a gravel or fixed bed. Therefore, this study was limited to the influence of COD concentration. Thouroughly investigating the influence of design and operational parameters requires additional extensive experimentation, which deserves further research. Furthermore, it is arguable if the design conditions affect either α or $k_{La,20,1000}$ or both.

In summary, the current study and the studies by Leu et al. [48] and Jiang et al. [33] provide significant evidence of a link between α and $\mathrm{COD_t}$ ($\mathrm{COD_s}$). Considering that the experiments were conducted in a single gravel column under specific conditions, care should be taken when using the link to estimate α for treatment plant design and/or operation as well as process modeling.

3.3. Simulated impact of $\alpha = f(COD_s)$ on treatment efficacy

After the implementation of the regression equation $\alpha = f(\mathrm{COD_s})$ into the process model, the default values of $k_{La,20}$ were increased by approximately 0.10–0.25 $\mathrm{h^{-1}}$ during the recalibration. Measured pore water and effluent concentrations were fitted in a similar manner as in the original model

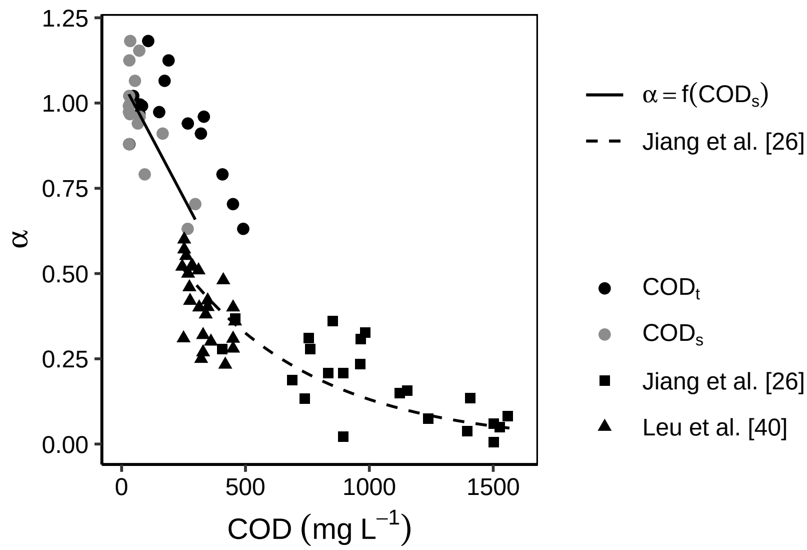

Figure 6: α vs. COD. Corresponding regression equations are: $\alpha = 1.066 - 1.372\text{E-3}\ \text{COD}_\text{s}$, R^2=0.4; $\alpha_{\text{Jiang et al. [26]}} = \exp(\text{-}1.82\text{E-3}\,\text{COD}_\text{t} - 0.213)$, R^2=0.7 [33].

by Boog et al. [22] (Figure S47–S48). The same holds for the model validation (Figure S49–S50). These results translate into a relatively low influence of wastewater COD_s on $k_{La,20}$, α and pollutant concentrations with respect to the given AFR and influent wastewater quality of the corresponding simulations.

The validated process model was then applied in a scenario analysis to simulate the impact of different influent wastewater strengths and values of $k_{La,20,cw}$ on α and the associated impact on treatment efficacy. COD_s influent concentration substantially impacted α and simulated effluent concentrations for DO, NH_4–N and NO_x–N in the scenario *High Strength* influent combined with low aeration ($k_{La,20,cw}$ of 1 h^{-1}). In the remaining scenarios, the impact of COD_s on α did not play a substantial role with respect to the effect on effluent concentrations and treatment efficacy. However, pore water patterns of day 60 at *High Strength* revealed that in the simulations considering $\alpha = f(\mathrm{COD_s})$ pore water quality gradients for DO, $\mathrm{COD_t}$, $\mathrm{COD_s}$, $\mathrm{NH_4}$–N and $\mathrm{NO_x}$–N were shifted in length even at $k_{La,20,cw} > 1$ $\mathrm{h^{-1}}$, (Figure 7). The lengths of the shifts were approximately 0.4–0.6 m (10–13% of fractional length) for $k_{La,20,cw}$ of 2–3 $\mathrm{h^{-1}}$. In contrast, the shift of pore water gradients was about 1.0–1.5 m for $k_{La,20,cw} = 1$ $\mathrm{h^{-1}}$. The impact of wastewater $\mathrm{COD_s}$ on α can, therefore, also affect redox zonation and has the potential to alter biogeochemical cycles in HF aerated wetlands.

At *Medium Strength*, $\mathrm{COD_s}$ caused a reduction in α up to 0.8 at 0–0.2 fractional length but without substantially affecting simulated $\mathrm{COD_t}$ and $\mathrm{COD_s}$ concentrations. This was caused by anaerobic bacteria X_{FB} that contributes to COD removal and grew at this fractional length. The decreased oxygen transfer limited available DO for aerobic heterotrophic COD consuming bacteria X_H. As a result the activity of X_H decreased while the activity of anaerobic bacteria X_{FB} increased. As the COD removal capacity of X_{FB} is lower than that of aerobic bacteria X_H, COD removal started to substantially deteriorate below at limited oxygen transfer (indicated by a low α). This was the case for simulations at *High Strength* influent.

In general, influent $\mathrm{COD_s}$ did not substantially impact α as well as pore and effluent water quality in the simulations scenarios *Medium Strength* and *Low Strength* and at $k_{La,20,cw} \geq 1$ $\mathrm{h^{-1}}$. Nevertheless, it must be noted that the simulations did not include temporal variations in influent wastewater strength and range of temperatures that can occur in full–scale systems. Therefore, the transfer of these results into practice is limited. However, the

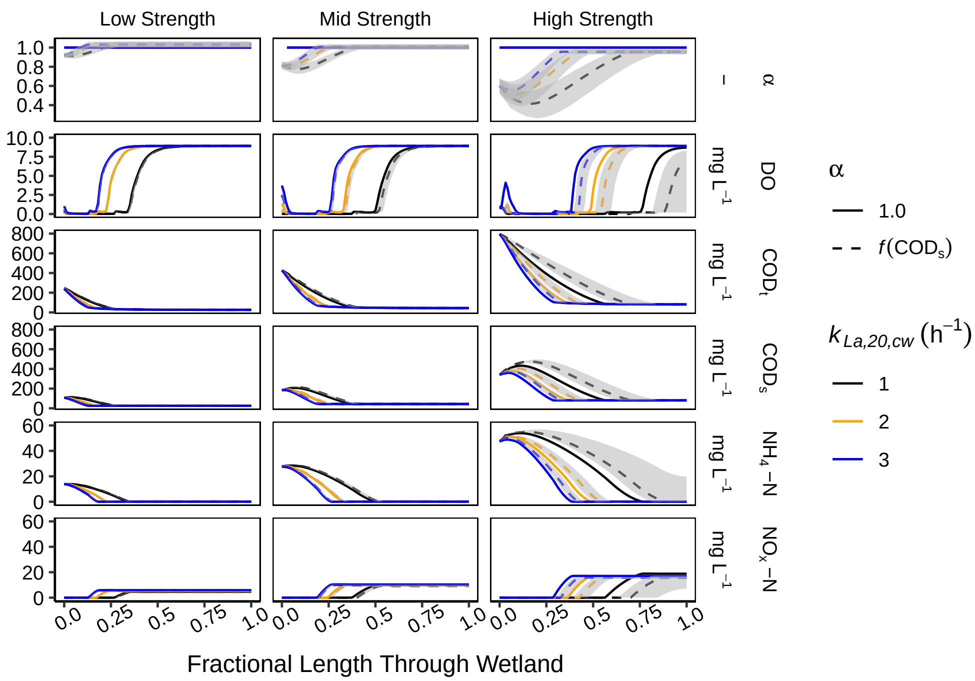

Figure 7: Simulated pore water concentration profiles of the scenario analysis at a simulated time of 60 days. Grey area indicates uncertainty introduced by the 95% confidence interval of $\alpha = f(\mathrm{COD_s})$. *Low Strength*, *Mid Strength* and *High Strength* refer to influent water qualities defined by Tchobanoglous et al. [11] listed in Table 1.

scenario analysis indicates that there can be conditions at which α should be considered. This translates into implications for further research and engineering practice.

3.4. Implications

The impact of influent COD_s on oxygen transfer can be important for designing and/or operating HF aerated wetlands treating domestic or municipal wastewater if high COD_s influent concentrations are expected, and if in combination, it is intended to zone aeration and/or intended to keep the AFR at a very low level. In the computer simulations, α was substantially reduced at influent COD_s of 300 mg L^{-1}. This may transfer to the pilot–scale wetland *HAp* if operated at such high influent COD_s. However, further experimental evidence is necessary. In constrast, in other HF aerated wetlands α will probably differ due to different wastewater compositions—even though the wetlands are designed similarly.

HF aerated wetlands with zoned aeration (e.g. non–aerated portions along the length) could be helpful for experiments investigating the removal of pollutants, where the degradation process requires specific redox conditions such as for NH_4–N and NO_x–N, or specific organic trace contaminants [54]. The simulation scenario analysis showed that pore water gradients were shifted as COD_s limited oxygen transfer at a COD_s influent concentration of approximately 300 mg L^{-1} (scenario *High Strength* in Figure 7). Therefore, it could be difficult to control specific redox conditions or zonation at high influent COD_s concentrations.

A similar problem arises when it is intended to keep aeration at minimum. Keeping aeration at minimum is a commom means for designers and operators of aerobic wastewater treatment systems [16, 33, 48] to save operational costs. For instance, in the *High Strength* simulation scenarios, COD_s substantially reduced oxygen transfer and treatment efficacy for NH_4–N when $k_{La,20,cw}$ was at lowest. In contrast, treatment performance was not altered at the same $k_{La,20,cw}$ in the *Low Strength* scenario. The impact of highly variable wastewater strengths and loads will, therefore, change α dynamically. Keeping aeration at minimum requires to dynamically adjust the AFR with respect to α. This will be challenging and implies active aeration control. Such control will be of special concern for on–site or event–driven treatment plants (e.g. temporary residences, camping grounds, stormwater) as highly variable influent strength are expected in such cases. Moreover, the dynamic nature of α has to be accounted for when designing small–scale plants that are commonly not equipped with active aeration control devices.

Considering opposed gradients of pollutant concentrations and DO as well as α in the pilot–scale system *HAp* (Figure 4 and the computer simulations 7), uniform aeration provided oxygen in excess, especially from 0.5–1.0 fractional length. This translates into an unnecessarily high energy requirement and ecological footprint as well as operational costs. With respect to the experimental pilot–scale system used, aeration could be reduced from 0.5–1.0 fractional length by a factor of two. This may also apply to other studies or applications of HF aerated wetlands where uniform aeration is used and water quality gradients are similar (see [30]).

The oxygen absorption experiments and computer simulations were based on the design (media, AFR, aeration line) of the pilot–scale wetland *HAp*. Therefore, it is arguable to extrapolate from the laboratory experiments and computer simulations to HAp and to similarly designed HF aerated wetlands at the similar operational and environmental conditions. Boog et al. [22] recommended an AFR of 150–200 L m^{-2} h^{-1} for a HF aerated wetlands designed according to the German guidelines for small–scale wetlands, however, without considering the α–factor explicitly [22]. Using the their relationship $k_{La,20} = 0.511 \log(\text{AFR})$, an AFR of 150–200 L m^{-2} h^{-1} corresponds to a $k_{La,20}$ of 2.4–2.8 h^{-1}. In the simulation scenarios at a $k_{La,20,cw}$ above 2 h^{-1} treatment efficacy was high (Figure 7). Similarly, in the pilot–scale system in Boog et al. [22] treatment performance was also high at $k_{La,20}$ above 2.0 h^{-1}. Moreover, Boog et al. [22] observed similar spatial water quality gradients at this $k_{La,20}$ than generated by the simulations in this study. At an AFR of 150–200 L m^{-2} h^{-1}, therefore, a deterioration in treatment performance through the impact of COD on oxygen transfer may not be that important for the pilot–scale wetlands used in this study (HAp) and by Boog et al. [22] as well as for small–scale HF aerated wetlands under similar conditions. Although this hypothesis needs to be tested empirically. The current German design guideline for small–scale HF aerated wetlands [32], in contrast, recommends an AFR of 600 L m^{-2} h^{-1}. This AFR can be interpreted as conservative considering the results of this study and the recommendation of 150–200 L m^{-2} h^{-1} by Boog et al. [22]. Indeed, an AFR of 600 L m^{-2} h^{-1} is intended to ensure robust treatment. This AFR may also prevent fouling or clogging of aeration orifices over the long–term operation of the wetland.

4. Conclusions

This study has shown that influent COD_s concentration can impede oxygen transfer and can create a descending gradient of α along the length of HF aerated wetlands. Computer simulations revealed that the impeded oxygen transfer was linked to a loss in treatment efficacy at low $k_{La,20,cw}$. This could be relevant for designing HF aerated wetlands to treat wastewater of high–strength and high variability in strength. Considering that design recommendations for small–scale HF aerated wetlands still rely on volumetric–based and areal–based heuristics, this study describes a significant advancement for HF aerated wetland design and research. Future research should examine the validity of the equation $\alpha = 1.066 - 1.372\text{E-3 mg COD}_s\ \text{L}^{-1}$ and the process model by comparing these with additional column experiments and/or in–situ oxygen transfer measurements in pilot or full–scale HF aerated wetlands. Additionally, future research should investigate if oxygen transfer in aerated wetlands is impeded by other wasewater pollutants with respect to grey water, where the ratio of surfactants concentration to COD_s may be higher, or industrial wastewater that contains high amounts of substances potentially affecting oxygen transfer (surfactants, oils, alcohols or petroleum–based pollutants).

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6. Supplementary information

Additional information on the methodology and results of the oxygen transfer experiments and process model calibration, validation and simulation scenario analysis are supplied in the file `si.pdf`. All process model input files are supplied in the file `model_input.zip`. The OpenGeoSys source code (incl. the coupling to IPhreeqc) is available at https://github.com/ufz/ogs5.

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