

## Impact of Particle Property Distribution on Hydrolysis Rates in Integrated Wastewater Modelling

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### ABSTRACT

A new modelling approach for integrated urban wastewater systems had been presented. It was based on the idea that the particle settling velocity distribution is a key parameter for wastewater quality prediction along a catchment/combined sewer/primary treatment system during dry and wet weather. This distribution information was then used to feed a hydrolysis model in which the hydrolysis rates of particles depend on their settling velocities. Comparison of wastewater quality results from simulations was performed under dry and wet weather conditions. The comparison revealed that with a classic constant hydrolysis rate, the effluent nitrogen concentration was overestimated most of the time during pollutant concentration peaks. On the other hand, oxygen demand can differ by 30% in the first aerated tank of a pre-denitrifying system during a rain event.

### KEYWORDS

Settling velocity, urban wastewater system, water quality modelling, wet weather treatment

### INTRODUCTION

Particle size and particle settling velocity distributions (PSVD) are known to be important characteristics determining the dynamics of many processes along the whole wastewater line such as the settling process occurring in many wastewater subsystems: sewers, retention tanks, grit chambers, primary and secondary settlers, and the river. Studies have also suggested that particle size (and thus the related settling velocity ( $V_s$ )) could have a significant impact on biological treatment processes such as activated sludge systems, anaerobic digestion, biofilms or biofilters.

In this work we focus more specifically on the variation of hydrolysis rates due to physical properties of particles. Indeed, it is well accepted that biodegradability slows down with an increase of particle size (Levine *et al.*, 1991; Hvitved-Jacobsen *et al.*, 1999; Morgenroth *et al.*, 2002). However, this is poorly (or not) taken into account in current models. In activated sludge systems, for instance, variation of hydrolysis rates can have a non-negligible impact on the readily biodegradable organic matter that becomes available for denitrification. Indeed, low hydrolysis rates will make that the hydrolysis of particulate matter is slower, releasing readily biodegradable substrate not in the first anoxic activated sludge reactors for denitrification but later in the aerobic reactors where it will be removed aerobically, consuming additional oxygen (and energy). Moreover, the longer presence of particulate matter may lead to increased sludge mass in the system, leading to increased sludge loading of the secondary clarifiers. Sludge wastage may have to be reduced, endangering nitrification. An improved hydrolysis model that accounts for these particle properties thus appears useful.

Mechanisms of hydrolysis are fairly well understood: substrate that is too large in size and thus not directly available to biomass for assimilation and degradation first needs to be hydrolysed. Two concepts describing hydrolysis are reported in literature: 1) enzymes are

secreted by bacteria, released in the bulk and adsorbed onto the particle's surface; or 2) bacteria are directly fixed onto the particle's surface where secreted enzymes are released to produce soluble substrate (Vavilinet *et al.*, 2008). In both cases, hydrolysis is considered as a surface site limited process. Nevertheless, the question on how physical and chemical particle properties impact hydrolysis rates and kinetics still remains.

Since hydrolysis models are still hardly able to predict field observations, a number of more or less complicated models were proposed. In a review on hydrolysis modelling in aerobic wastewater treatment Morgenroth *et al.* (2002) report different hydrolysis kinetics. Reaction stoichiometry can vary by differentiating various bacteria populations that either degrade soluble or particulate substrate. Hydrolysis rates that depend on the type of organic particles (i.e. slow, medium and fast) are also found in recent models, and the hydrolysis process can be either sequential, i.e. transformation of slowly hydrolysable substrate ( $X_s$ ) into medium hydrolysis rate  $X_s$ , and then into readily hydrolysable  $X_s$  (Spérandio and Paul, 2000) or parallel, i.e. all organic particles are hydrolysed directly into soluble substrate, but at various rates (Sollfrank and Gujer, 1991; Hvitved-Jacobsen *et al.*, 1999). Dimock and Morgenroth (2006) also used two surface-based hydrolysis models for activated sludge. One assumes that the particle diameter is continuously reduced during the hydrolysis process (called shrinking particle model). The other one assumes that particle break up increases the surface area of particles (called particle breakup model). Currently these models are calibrated on the basis of data collected at the WWTP influent where different COD fractions with specific hydrolysis rates are determined. However, these data are used to obtain a fixed fractionation of COD, independent of wastewater composition changes induced by various upstream conditions (wet weather, settling/resuspension in sewers, biodegradation in sewers...).

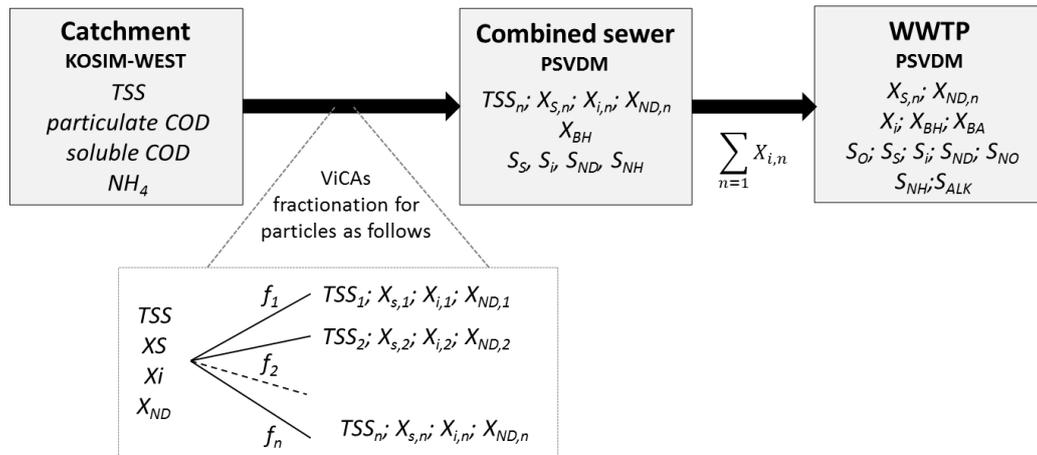
Various recent studies have demonstrated that the particle settling velocity distribution is highly varying as wastewaters move from the urban catchment to the biological treatment (Maruéjols *et al.*, 2011). Maruéjols *et al.* (2013a) demonstrated that a PSVD model allows reproducing the dynamic evolution of the PSVD of wastewaters as the suspended solids move through an integrated urban wastewater system including the following subsystems: an urban catchment, combined sewer, retention tanks, grit chamber and primary clarifier under dry (DW) and wet weather (WW) conditions. This paper aims at showing the potential of such PSVD information to obtain a better description of the hydrolysis phenomena in a pre-denitrifying activated sludge treatment system and a better prediction of WWTP effluent quality under DW and WW. The novel concept of linking the PSVD to hydrolysis rates and the impact of PSVD model parameters on effluent quality is discussed.

## MATERIAL AND METHODS

### Particle settling velocity distribution model (PSVDM)

In the context of urban wastewater management, an integrated model (Figure 3) was developed to simulate the variation of total COD, TSS and TKN based on particle settling velocity distribution (PSVD) measurements at retention tanks (RT), sewer, grit removal, and primary clarifier (PC) (see Maruéjols *et al.*, 2013a). The whole model reproduces PSVD by fractionating TSS and total COD in various classes having specific settling velocities and specific hydrolysis kinetics (see below). Figure 1 presents the state variables in each of the subsystems and the link between them.  $X_{S,n}$ ,  $X_{i,n}$  and  $X_{ND,n}$  represent hydrolysable and inert particulate COD and hydrolysable nitrogen respectively (following ASM1 nomenclature, Henze *et al.*, 1987). The catchment model used is KOSIM-WEST (Solvi, 2006) producing TSS, particulate and soluble COD and ammonium. At this stage the particulate pollutants are not yet fractionated. However, when they enter the sewer system, they are fractionated as in Figure 1. The fractionation coefficients  $f_n$  (%) are directly measured in the field with the ViCAs measurement protocol (Chebbo and Gromaire, 2009). These coefficients

are then applied for all particle fractions, leading to concentrations of TSS<sub>n</sub>, X<sub>S,n</sub>, X<sub>i,n</sub> and X<sub>ND,n</sub>.



**Figure 1.** Scheme of the state variables used in each subsystem. TSS and particulate COD (containing nitrogen) are the pollutants to be fractionated,  $f_n$  are the fractionation parameters (%) and TSS<sub>n</sub>, X<sub>ND,n</sub>, X<sub>S,n</sub> and X<sub>i,n</sub> are the particulate variables of the PSVDM. TSS<sub>n</sub> is not modelled in ASM1 and the X<sub>i,n</sub> are summed into a single X<sub>i</sub> fraction because they do not take part in any transformation process.

In ASM1, slowly biodegradable organic matter (X<sub>S</sub>) is hydrolysed in readily biodegradable matter (S<sub>S</sub>) slowly biodegradable organic nitrogen (X<sub>ND</sub>) is hydrolyzed at the same rate in readily biodegradable organic nitrogen (S<sub>ND</sub>). In the PSVDM, the same approach is used, except that X<sub>S</sub> and X<sub>ND</sub> are now fractionated in a number of particle classes allowing various hydrolysis rates to be set depending on the “size” of the particles as approximated by their settling velocity. In the WWTP model slowly biodegradable organic matter and organic nitrogen products that result from decay of biomass are distributed evenly over the five first classes with the highest hydrolysis rates since it is assumed that the ones with lower rates would only be relevant for particles with high settling velocities that are mostly removed in primary clarifiers.

### Relation between settling velocity and hydrolysis

As far as the authors know, only a few models linking particle size to hydrolysis rates exist (Dimock and Morgenroth, 2006). However, so far, no detailed study was performed that links the particle settling velocity to the hydrolysis rate  $k_h$ . Thus, for the time being a conceptual model is proposed based on the idea that hydrolysis is a surface limited reaction where hydrolysis rates decreases with particle radius and, according to the Stokes’ law, with particle settling velocity, as represented on Figure 2. Such kinetics leads to a hydrolysis rate that depends hyperbolically on the particle radius (Equation 1). Furthermore, Stokes’ law describes settling velocity to be function of the square of the radius (Equation 2), leading to Equation 3, which allows calculating hydrolysis rate values for different particle settling velocities. In these equations  $k_H$  is the hydrolysis rate (gCOD/(gCOD.d)),  $\omega$  the surface specific hydrolysis rate constant (gCOD.m/(gCOD.d)) and  $\alpha$  a constant coefficient.

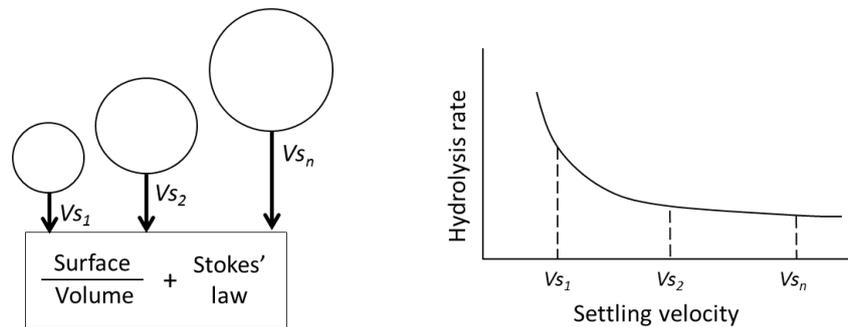
$$k_H = \omega \cdot \frac{\text{Sphere surface}}{\text{Sphere volume}} = \omega \cdot \frac{3}{\text{radius}} \quad (1)$$

From Stokes’ law:

$$\text{radius} = f(\sqrt{Vs}) \quad (2)$$

By replacing the radius by a function of  $V_s$ :

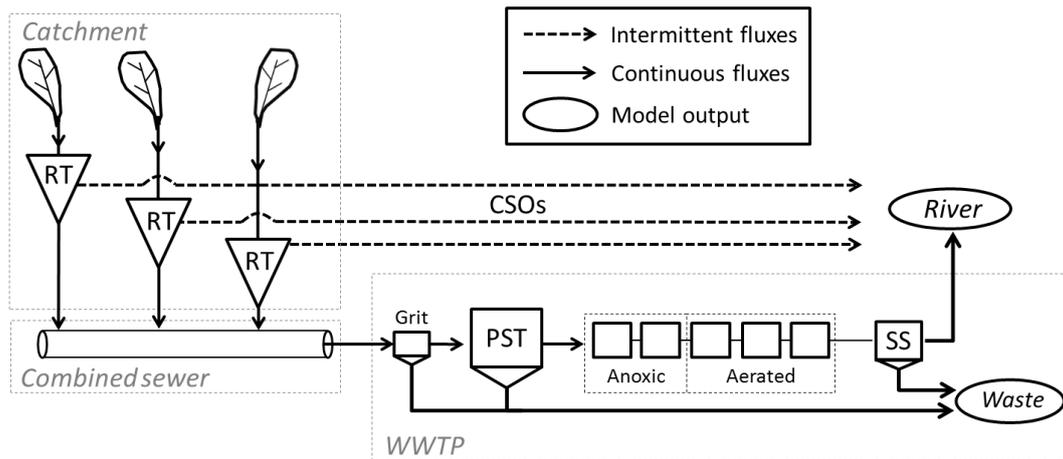
$$k_H = \alpha \cdot \frac{1}{\sqrt{V_s}} \quad (3)$$



**Figure 2.** Calculation of hydrolysis rate constants with regard to particle  $V_s$  in the proposed model.

### Description of the integrated urban wastewater system model

In order to achieve a good approximation of the measured dynamics of PSVD evolution, the number of classes was set to 10. Three identical urban catchments of 1.54 km<sup>2</sup> modelled with KOSIM-WEST (Solvi, 2006) are used to generate the combined sewer wastewater flow and quality. Processes reproduced are: dry weather flow generation, evaporation, runoff (which depends on wetting, depression filling and infiltration), accumulation and wash-off for particulates, and runoff concentration thanks to three linear reservoirs in cascade. Three identical retention tanks (RT) of 7850 m<sup>3</sup> are located at the urban catchment outlets. RT models using the PSVD concept (Maruéjols *et al.*, 2012) simulate effluent quality (TSS and COD) resulting from the settling and resuspension processes occurring during filling, storage and emptying of the RT. Results on the successful calibration and validation of the model can be found in Maruéjols *et al.* (2013b). The obtained parameter values are used in the current study. A 3.75 km combined sewer brings the wastewaters to the WWTP in about 1h20 under DW. It is modelled with a linear cascade of 10 reservoirs where pollutants are considered conservative. The WWTP includes primary treatment with a grit chamber (70 m<sup>3</sup>) and primary clarifier (2100 m<sup>3</sup>), modelled according to the PSVD model of Bachis *et al.* (2014). Biological treatment occurs in a five bioreactor system for pre-denitrification including two anoxic and three aerobic tanks, all of which have a volume of 1800 m<sup>3</sup>. Aeration is controlled to maintain dissolved oxygen concentration in the aerated tanks at 2 g/m<sup>3</sup>. Internal recycling is fixed at three times the average influent flow rate, while the return activated sludge flow rate occurs at 80% of the influent flow rate. The SRT was set at 30 days. All biokinetics parameters, except for  $k_h$  and  $K_X$ , are ASM1 default values.



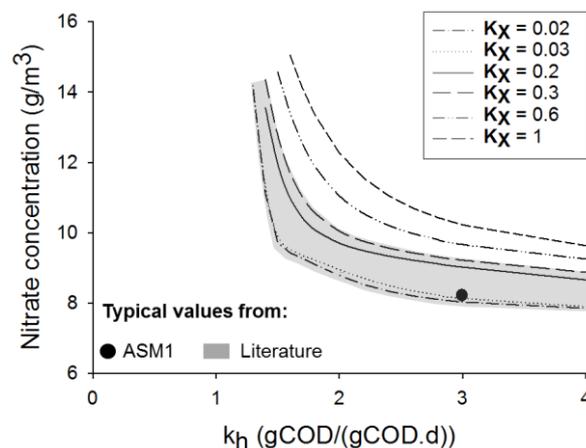
**Figure 3.** Scheme of the integrated system including three catchments equipped with off-line retention tanks (RT), a combined sewer and a WWTP composed of grit removal, primary settler (PST), pre-denitrifying activated sludge system and a secondary settler (SS).

## RESULTS

### Steady state sensitivity analysis of hydrolysis rate

The first step of the current study consisted in showing the impact of hydrolysis rates on activated sludge effluent quality, and more specifically on the nitrate concentration, in order to assess the relevance of having a variable hydrolysis rate depending on PSVD. As denitrification performance often depends on the release of readily biodegradable substrate from hydrolysable substrate, the hydrolysis rate becomes an important factor for treatment performance. A sensitivity analysis of the biokinetic parameters of the hydrolysis process, i.e. the maximum specific hydrolysis rate ( $k_h$ ) and the half-saturation coefficient for hydrolysis of slowly biodegradable substrate ( $K_x$ ), was thus carried out to assess the order of magnitude of its impact on effluent nitrate. Steady state simulations were performed in a typical pre-denitrification system (see above).

As shown in Figure 4, hydrolysis parameters were varied within the literature ranges of 0.3 to 4 gCOD/(gCOD.d) for  $k_h$  and from 0.02 to 1 gCOD/gCOD for  $K_x$ , while the correction factor for anoxic hydrolysis ( $\eta_h$ ) was set to 0.4. Effluent nitrate concentration values from 240 steady state simulations with different  $k_h$  and  $K_x$  values are plotted on Figure 4. Within the range of parameter values found in the literature (grey zone),  $k_h$  has a big impact on the effluent nitrate concentration, ranging from 8 to 15 g/m<sup>3</sup>. Furthermore, when  $k_h$  decreases below 1.2 gCOD/(gCOD.d), particulates accumulate that much in the system that the secondary clarifier becomes overloaded leading to an increase in effluent suspended solids. The SRT then drops so low that nitrification fails. Values are thus not reported for  $k_h < 1.2$  gCOD/(gCOD.d).



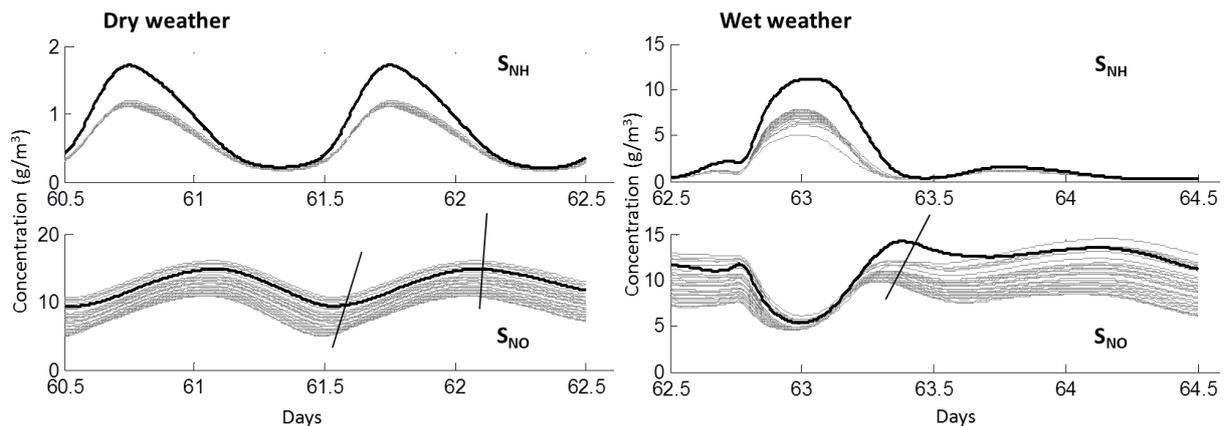
**Figure 4.** Steady state sensitivity analysis results showing effluent nitrate concentrations as function of  $k_h$  and  $K_X$ . The grey zone represents combinations of  $k_h$  and  $K_X$  values found for ASM1.

#### Dynamic simulation under dry and wet weather

Four sets of values for  $k_h$  (for a range of 10 Vs classes) were calculated following Equation 3 for  $\alpha$  values of 5.5, 3, 1 and 0.5. These were crossed with seven  $K_X$  values leading to  $4 \times 7 = 28$  simulations. Under DW conditions the particles remaining after primary treatment belong most of the time to the first five classes. This point explains why we selected  $\alpha$  values that result in an “average” or default  $k_h$  ASM1 value (around  $3 \text{ d}^{-1}$ ) for classes with medium settling velocities (classes 2, 3, 4). The  $k_h$ -values of the different classes are centered around a medium hydrolysis rate surrounded by fractions with much higher and lower hydrolysis rates. According to Equation 3 the rates for class 1 ( $25 \text{ gCOD}/(\text{gCOD}\cdot\text{d})$ ) should be even higher, but beyond this maximum value of 25 d, the results are no longer sensitive to  $k_h$  as shown on Figure 4.

The 28 scenarios were simulated to compare effluent nitrogen and nitrate concentrations for a fixed hydrolysis rate (current modelling practice) and the PSVD-depending hydrolysis kinetics. Other variables such as the aeration demand for dissolved oxygen control were also evaluated. For each scenario, a period of 60 days is first run to set the initial conditions. A rain event occurs at day 62.5. Figure 5 reports  $S_{\text{NH}}$  and  $S_{\text{NO}}$  concentrations over 2 days under DW and WW conditions. The thick black curve corresponds to the simulation results obtained with ASM1 with default parameter values. When  $S_{\text{NH}}$  is low, all simulations (ASM1 and any of the PSVDM parameter sets) produce very similar concentrations. However, in periods with high  $S_{\text{NH}}$  concentrations, ASM1 leads to higher values than PSVDM. Indeed, peaks of particulate organic nitrogen ( $X_{\text{ND}}$ ) combined with lower hydrolysis rates (due to the fact that particles with higher settling velocity are entering the plant during concentration peaks), leads to less  $S_{\text{NH}}$  produced by hydrolysis/ammonification in the PSVDM model compared to ASM1 that all the time uses a relatively high hydrolysis rate.

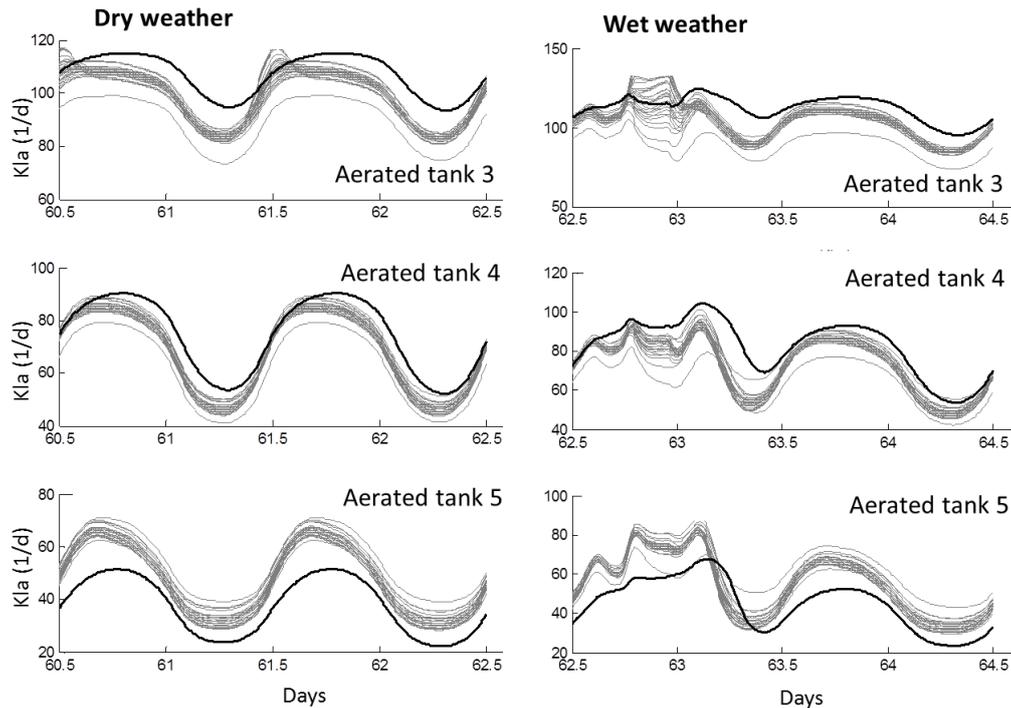
During DW, the mean effluent  $S_{\text{NO}}$  concentration changes depending on the chosen  $\alpha$  and  $K_X$  values, but the observed dynamics remain approximately the same as for ASM1. However, one can note a significant difference under WW. This difference is mainly occurring after the rain event has passed: the  $S_{\text{NO}}$  concentrations obtained with PSVDM are lower than those of ASM1. This can be explained as follows: particles with high settling velocities (and thus with lower hydrolysis rates) entering the WWTP during the rain event are retained in the sludge until they are completely hydrolysed. This longer retention thus leads to a continuous release of readily biodegradable organic matter, even after the event, that stimulates denitrification. The  $S_{\text{NO}}$  dynamics seem quite similar for the different simulations but a slight delay can be observed (see the orientation of the black lines in Figure 5). During DW,  $S_{\text{NO}}$  is low when COD (source of  $S_S$ ) is high and denitrification is occurring at high rates. Under these conditions, modification of the hydrolysis rates leads to a delay in denitrification.



**Figure 5.** Outlet  $S_{NH}$  (top) and  $S_{NO}$  concentrations (bottom) for the 28 scenarios tested, for two dry weather (left) and two wet weather days (right). The black line shows results obtained with ASM1 using default parameter values:  $k_h = 3 \text{ d}^{-1}$  and  $K_X = 0.03 \text{ gCOD/gCOD}$ .

Concerning the oxygen demand in the aeration tanks (expressed here by the simulated  $K_{1a}$ -values on Figure 6), one can see clear differences between PSVDM and ASM1 runs. As for the difference between DW and WW conditions, the same comment can be made as above. Oxygen demand predicted with ASM1 is always higher than that predicted with PSVDM for the first two aerated tanks (n° 3 and 4) while it is the opposite for the last tank (n° 5). In fact, particles with low  $V_s$  are rapidly hydrolysed in the first tanks without demanding too much oxygen while particles with high  $V_s$  and low hydrolysis rates move down to the last tank, leading to increased oxygen demand there. The oxygen consumption is thus differently distributed in the aerated tanks when comparing ASM1 and PSVDM.

During DW, it appears that the choice of the  $\alpha$  and  $K_X$  parameter values has a non-negligible impact on the oxygen demand during rain events. The demand can vary by 30% of the ASM1 oxygen demand in tank n°3 during 5-6 hours. This impact is less pronounced for tanks n°4 and 5. In the latter tank considerably more oxygen needs to be supplied according to the PSVDM. Indeed, during WW conditions, a larger range of particle classes enters the WWTP as a result of the complex settling and resuspension phenomena in the system. These conditions lead to a higher sensitivity of the overall behaviour on hydrolysis rates.



**Figure 6.** Oxygen demand during DW (left) and WW (right) in the three aerated tanks of the studied WWTP. The black curve corresponds to the reference ASM1 simulation.

## CONCLUSION

A new integrated urban wastewater modelling approach able to describe wastewater quality under dry and wet weather conditions is presented. The model is able to reproduce the evolution of the particle settling velocity distribution along the catchment/combined sewer/primary treatment system and to use this physical property information to feed a modified ASM1 hydrolysis model. A sensitivity analysis performed under steady state conditions has clearly indicated that hydrolysis kinetics significantly affects effluent quality.

Dynamic simulations revealed that dividing hydrolysis rates in various classes according to the settling velocity distribution is a powerful tool for effluent quality prediction under dry weather conditions, but particularly also under wet weather situations. The results show that:

- 1) during concentration peaks (dry and wet weather), the particle settling velocity distribution is “heavier”, leading to slower hydrolysis rates. In these conditions, simulated effluent ammonia nitrogen is higher with ASM1 than with PSVDM because of the lower hydrolysis of organic nitrogen ( $X_{ND}$ );
- 2) a delay in nitrate dynamics is observed that is more pronounced for certain PSVDM parameters: the delay is longer when the PSVD is “heavier”. The reason is that the retention of big particles in sludge leads to a longer release of readily biodegradable organic matter, that is thus more available for denitrification purposes;
- 3) oxygen demand is delayed in time in each tank depending on current conditions (day, night, dry, wet weather) for the same reason as for point 2;
- 4) The oxygen consumption is differently distributed in the aerated tanks when PSVDM is used under dry and even more so under wet weather conditions. The first two aerated tanks consume less energy and the last tank consumes more energy with PSVDM than with ASM1.

These results highlight the interest in considering the particle settling velocity distribution and its impact on hydrolysis rates for WWTP effluent quality prediction. The model will be further calibrated and validated with experimental data from respirometric experiments with fractionated wastewater samples.

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