Modeling External Carbon Addition in Combined N-P Activated Sludge Systems with an Extension of the IWA Activated Sludge Models

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ABSTRACT

The aim of this study was to expand the IWA Activated Sludge Model No. 2d (ASM2d) to include the effect of adding a readily biodegradable exogenous substrate to anoxic zones of biological N/P removal systems, where it can be used as growth substrate by the Polyphosphate Accumulating Organisms (PAOs) but can not be used by PAOs in the anaerobic zone. The model change was to add a new biodegradable substrate component and process terms for its use by PAOs and other heterotrophic bacteria. The new model and the original ASM2d were first calibrated/validated under dynamic conditions with the results of both batch tests to observe nitrate uptake rates (NURs), phosphorus release rates (PRRs) and anoxic phosphorus uptake rates (PURs) with the settled wastewater and a 96-hour measurement campaign in the full-scale MUCT bioreactor. The results of similar batch tests with ethanol and fusel oil as the external carbon sources were used to adjust the kinetic and stoichiometric coefficients in the expanded ASM2d. The results of these two tests were used to compare predictions of the new model and the original ASM2d. For this purpose, it was assumed that the added external carbon sources were treated as the new component $S_{A,1}$ (in the expanded ASM2d) or a fraction of S_A (in the ASM2d). In the latter case, much higher COD utilization rates were predicted under anoxic conditions, whereas the anoxic PURs in the two-phase experiments were underestimated. In spite of the mechanistically inappropriate approach to treat some external sources as the ASM2d components, the original (calibrated) ASM2d predicted NO_3-N and PO_4-P concentrations in the full-scale bioreactor only slightly different from the new model.

KEYWORDS

Activated sludge, ASM, denitrification, external carbon, mathematical modeling, nutrient removal, simulation.

INTRODUCTION

External carbon sources are readily biodegradable compounds, which are added to biological nutrient removal (BNR) processes to enhance the rate and amount of denitrification within the existing capacity of the activated sludge system above that accomplished by the "ordinary" heterotrophs (those grown on the wastewater influent carbon) to improve the overall nitrogen (N) removal efficiency. Activated sludge mathematical models have been proven to be useful tools

for evaluating and optimizing the effect of external carbon sources, provided that wastewater biodegradability (COD fractions), kinetics and stoichiometric parameters were determined (Onnis-Hayden and Gu, 2008). The same authors demonstrated practical implications of differences in denitrification kinetics for two external carbon sources; methanol and a commercial compound (MicroC). Two process configurations were considered, a modified Ludzak-Ettinger (MLE) and 4-stage Bardenpho, and the manipulated parameters included external carbon dosage, pre-anoxic and post-anoxic volumes ,and temperature. Phillips et al. (2009) used a dynamic model to optimize the mixed liquor recycle rate and studied factors that affected nitrogen removal, including the influent wastewater readily biodegradable COD/N ratio and acetate addition. The strategies for dosing external carbon sources and calculations of the optimum COD/N ratios were investigated by Latimer et al. (2009) (sugar addition to a continuous flow reactor) and Filali-Meknassi et al. (2005) (acetate addition to a SBR). Using a simplified ASM2d, De Lucas et al. (2005) modeled the results of nitrate utilization experiments with various agro-food industrial wastewaters. Subsequently, the denitrification potential of each external carbon source and values of the most important kinetic and stoichiometric parameters for the denitrification process were evaluated. Furthermore, a relationship between the mean denitrification rate and the readily biodegradable substrate characteristics (the content of fermentation products) was proposed for the examined agro-food industrial wastewaters.

A few studies focused specifically on modeling with the addition of methanol as the external carbon source. Purtschert and Gujer (1999) developed a mathematical model for a specific group of bacteria degrading methanol (methylothrops). The results of that study showed that the degradation of methanol can be modeled using two types of microorganisms depending on the mode of cultivation. Takacs et al. (2007) proposed a different approach to calculate design parameters and optimize operation of denitrification systems with methanol. In order to accurately simulate methanol utilization in four full-scale WWTPs, the default BioWin model was expanded by adding aerobic growth of methylotrophs on methanol and removing the ability of "ordinary" heterotrophs to use methanol under aerobic conditions. Dold et al. (2007) investigated the denitrification kinetics with the addition of methanol and other external carbon sources, such as ethanol, acetate and sugar addition. In that study, modeling was used to design the optimal experimental batch tests procedure, and to estimate the maximum specific growth rate of heterotrophs grown on the external carbon sources.

In combined N and P removal systems, the effect of the external carbon sources on the growth of Polyphosphate Accumulating Organisms (PAOs) in enhanced biological P removal (EBPR) processes has not been considered. In the existing activated sludge models for such systems, readily biodegradable substrates are divided into two groups, fermentation products and fermentable readily biodegradable, in order to address competition for them by "ordinary" heterotrophs and PAOs. The fermentation products (S_A) are assumed to be only acetate (although covering a wide range of compounds) and directly available for PAOs, whereas fermentable readily biodegradable compounds (S_F) are not directly available for PAOs but can ultimately be transformed to S_A. The possibility that PAO may grow on these fermentation derived soluble substrates (e.g. S_A) has been ignored in these models because, as noted by Henze et al. (2000), "*it is unlikely that such substrates ever become available under aerobic or anoxic conditions in a biological nutrient removal (BNR) plant"*. However, this assumption does not apply when the external carbon source is added to anoxic zones of the BNR plants. Furthermore, there are compounds (e.g. ethanol) which are known to be fermentation products but reported not to be utilized by PAOs. For example, Satoh et al. (2000) proposed a modified conceptual model for anaerobic COD metabolisms that assumes the presence of soluble substrate, $S_{A'}$, which is not utilized by PAOs either directly or via fermentation but is available for "ordinary" heterotrophs

in the presence oxygen or nitrate.

The aim of this study was twofold. Firstly, the IWA Activated Sludge Model No. 2d (ASM2d) was expanded to consider a new readily biodegradable substrate, available to PAOs under anoxic and aerobic conditions, but not available under anaerobic conditions. The concept was derived from the observations of Swinarski et al. (2009) that some substrates (e.g. ethanol and distillery waste products) had no significant impact on PO_4-P release (in contrast to other substrates, such as acetic acid or the readily biodegradable fraction of settled wastewater), but enhanced anoxic PO_4-P uptake. Secondly, the new model was compared with the original ASM2d based on predictions of laboratory experiments and field measurements in a full-scale plant (MUCT process configuration). The study is part of the on-going EU supported project carried out in cooperation with the Water Environment Research Foundation (WERF) Nutrient Removal Challenge Program.

METHODOLOGY

Conceptual and mathematical models

A conceptual model of the ASM2d expansion considering a new readily biodegradable substrate term, $S_{A,1}$ is illustrated in Figure 1. Based on this concept, a mathematical model for CNP activated sludge systems was developed as an expansion of theASM2d (Table 1). The new model incorporates one new component ($S_{A,1}$) and six new processes, i.e. aerobic and anoxic growth of heterotrophs on $S_{A,1}$, aerobic and anoxic storage of poly-P with $S_{A,1}$, and aerobic and anoxic growth of PAOs on $S_{A,1}$. The component $S_{A,1}$ is termed “other fermentation products” to differentiate from acetate (S_A) and denote that this kind of substrate is not available for PAOs under anaerobic conditions. With such a model structure, the increased nitrate utilization rates (NURs) under anoxic conditions and the increased phosphate utilization rates (PURs) under both anoxic and aerobic conditions can be accounted for.

Figure 1 - Model Concept Considering a New Readily Biodegradable Substrate, Only Available for PAOs under Anoxic and Aerobic Conditions

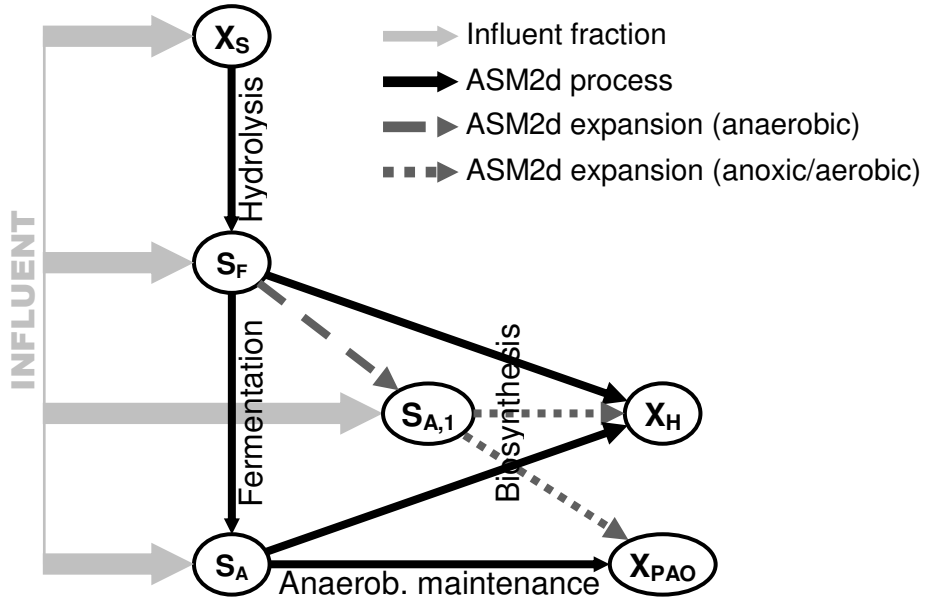


Table 1 – Stoichiometric Matrix and Process Rates for the Expanded ASM2d Including the New Process Variable ($S_{A,1}$) and Six New Processes

Process \ Component	S_{O2}	$S_{A,1}$	S_{NH4}	S_{NO3}	S_{PO4}	X_{PP}	X_H	X_{PAO}
Aerobic growth of X_H on $S_{A,1}$	$-\frac{1-Y_{H1}}{Y_{H1}}$	$-\frac{1}{Y_{H1}}$	$-i_{N,BM}$		$-i_{P,BM}$		1	
Anoxic growth of X_H on $S_{A,1}$		$-\frac{1}{Y_{H1}}$	$-i_{N,BM}$	$-\frac{1-Y_{H1}}{2.86Y_{H1}}$	$-i_{P,BM}$		1	
Aerobic storage of X_{PP} (with $S_{A,1}$)	$-Y_{SA1}$	$-Y_{SA1}$			-1	1		
Anoxic storage of X_{PP} (with $S_{A,1}$)		$-Y_{SA1}$		$-\frac{Y_{SA1}}{2.86}$	-1	1		
Aerobic growth of X_{PAO} on $S_{A,1}$	$-\frac{1-Y_{PAO1}}{Y_{PAO1}}$	$-\frac{1}{Y_{PAO1}}$	$-i_{N,BM}$		$-i_{P,BM}$			1
Anoxic growth of X_{PAO} on $S_{A,1}$		$-\frac{1}{Y_{PAO1}}$	$-i_{N,BM}$	$-\frac{1-Y_{PAO1}}{2.86Y_{PAO1}}$	$-i_{P,BM}$			1

Process	Process rate, ρ_j
Aerobic growth of X_H on $S_{A,1}$	$\mu_{H1}\frac{S_{O2}}{K_{O2,H}+S_{O2}}\frac{S_{A1}}{K_{SA1,H}+S_{A1}}\frac{S_{NH4}}{K_{NH4,H}+S_{NH4}}\frac{S_{PO4}}{K_{PO4,H}+S_{PO4}}\frac{S_{ALK}}{K_{ALK,H}+S_{ALK}}X_H$
Anoxic growth of X_H on $S_{A,1}$	$\mu_{H1}\eta_{NO3,H1}\frac{K_{O2,H}}{K_{O2,H}+S_{O2}}\frac{S_{NO3}}{K_{NO3,H}+S_{NO3}}\frac{S_{A1}}{K_{SA1,H}+S_{A1}}\frac{S_{NH4}}{K_{NH4,H}+S_{NH4}}\frac{S_{PO4}}{K_{PO4,H}+S_{PO4}}\frac{S_{ALK}}{K_{ALK,H}+S_{ALK}}X_H$
Aerobic storage of X_{PP} (with $S_{A,1}$)	$q_{PP1}\frac{S_{O2}}{K_{O2,PAO}+S_{O2}}\frac{S_{A1}}{K_{SA1,PAO}+S_{A1}}\frac{S_{PO4}}{K_{PO4,PAO}+S_{PO4}}\frac{S_{ALK}}{K_{ALK,PAO}+S_{ALK}}\frac{K_{MAX}-X_{PP}/X_{PAO}}{K_{IPP}+K_{MAX}-X_{PP}/X_{PAO}}X_{PAO}$
Anoxic storage of X_{PP} (with $S_{A,1}$)	$q_{PP1}\eta_{NO3,PAO1}\frac{K_{O2,PAO}}{K_{O2,PAO}+S_{O2}}\frac{S_{NO3}}{K_{NO3,PAO}+S_{NO3}}\frac{S_{A1}}{K_{SA1,PAO}+S_{A1}}\frac{S_{PO4}}{K_{PO4,PAO}+S_{PO4}}\frac{S_{ALK}}{K_{ALK,PAO}+S_{ALK}}\frac{K_{MAX}-X_{PP}/X_{PAO}}{K_{IPP}+K_{MAX}-X_{PP}/X_{PAO}}X_{PAO}$
Aerobic growth of X_{PAO} on $S_{A,1}$	$\mu_{PAO1}\frac{S_{O2}}{K_{O2,PAO}+S_{O2}}\frac{S_{A1}}{K_{SA1,PAO}+S_{A1}}\frac{S_{NH4}}{K_{NH4,PAO}+S_{NH4}}\frac{S_{PO4}}{K_{PO4,PAO}+S_{PO4}}\frac{S_{ALK}}{K_{ALK,PAO}+S_{ALK}}X_{PAO}$
Anoxic growth of X_{PAO} on $S_{A,1}$	$\mu_{PAO1}\eta_{NO3,PAO1}\frac{S_{NO3}}{K_{NO3,PAO}+S_{O2}}\frac{K_{O2}}{K_{O2,PAO}+S_{O2}}\frac{S_{A1}}{K_{SA1,PAO}+S_{A1}}\frac{S_{NH4}}{K_{NH4,PAO}+S_{NH4}}\frac{S_{PO4}}{K_{PO4,PAO}+S_{PO4}}\frac{S_{ALK}}{K_{ALK,PAO}+S_{ALK}}X_{PAO}$

Study site

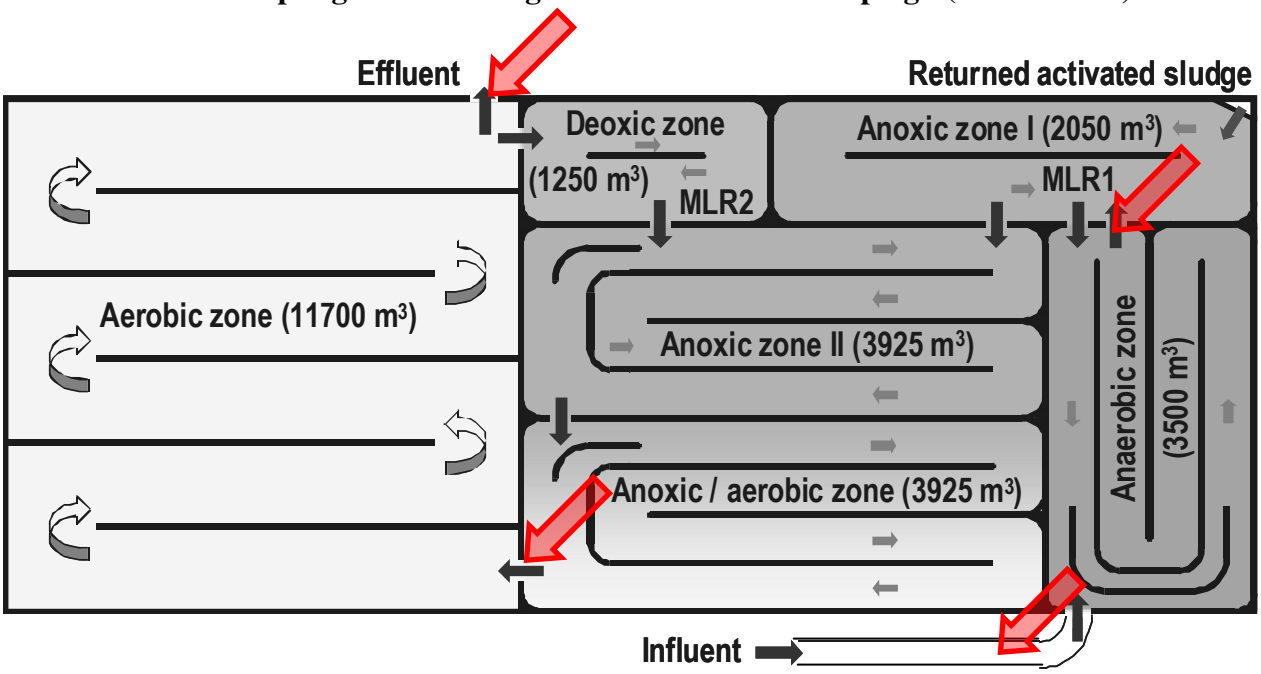
Field measurements at a full-scale bioreactor and lab-scale experiments were conducted at the Wschod WWTP (570,000 PE) in the city of Gdansk (northern Poland). The WWTP BNR system consists of six parallel bioreactors, designed according to the Modified University of Cape Town (MUTC) process configuration, and twelve circular secondary clarifiers. The treatment goal is to meet the most stringent effluent criteria in the European Union, which is an effluent total N (TN) concentration of 10 g/m^3 and total P (TP) concentration of 1 g/m^3. More details concerning the process configuration and recent N/P removal efficiencies at the plant can be found elsewhere (e.g. Swinarski et al., 2009).

Collection of a database for the modeling study

The lab-scale data were collected from various types of batch tests. In order to evaluate the impact of different carbon sources (including ethanol and fusel oil) on the denitrification capability of the full-scale process biomass (WWTP mixed liquor), two different batch test methods for NUR measurements were carried out using WWTP mixed liquor taken from the returned activated sludge (RAS) lane. The first was a conventional NUR measurement, in which the carbon source and nitrate (KNO_3) were added at the beginning of a 4-hour test. In the second batch test procedure (so-called phosphate release rate (PRR)/anoxic PUR), a mixture of WWTP mixed liquor and settled wastewater was contacted for 2.5 hours under anaerobic conditions. After that time, the external carbon source and nitrate were added and the test continued for 4.5-5 hours. In similar experiments with the settled wastewater, no external carbon source was added. More details about the procedure, scope of analyses and sampling frequency can be found elsewhere (Makinia et al., 2009). The aerobic PURs and ammonia utilization rates (AURs) were measured in two-phase experiments, in which the anoxic conditions in the second phase were replaced by aerobic conditions (no KNO_3 added, a DO concentration set point of 6 g O_2/m^3). In addition, three-phase experiments with the settled wastewater were also carried out including anaerobic conditions (2 h), anoxic conditions (4 h, after addition of KNO_3) and aerobic conditions (6 h, at a DO concentration set point of 6 g O_2/m^3). These experiments were described in detail by Makinia et al. (2010a). The NUR measurements with the external carbon sources were conducted in a glass beaker with the maximum working volume of 4.0 dm^3, whereas the other experiments were conducted under well-controlled conditions in an apparatus consisting of two parallel batch reactors (max. volume of 4.0 dm^3). The reactors were equipped with electrodes and probes for monitoring of pH, ORP, temperature, and DO concentration. The automated control system maintained DO concentration and temperature around set points in the reactors. Batch test temperatures were in the range of 13 to 22 ^oC.

In September, 2008, a 96-hour measurement campaign was carried out in the full-scale MUCT bioreactor. Grab samples were withdrawn every two hours at the following locations: reactor inlet, anaerobic zone, anoxic zone and reactor (aerobic zone) effluent (Figure 2). The samples were analyzed for several parameters including total and soluble COD (influent), TP (influent), PO_4-P (influent, anaerobic, anoxic, effluent) and nitrogen compounds: TN (influent), NH_4-N (influent, anaerobic, anoxic, effluent) and NO_3-N (anoxic, effluent). In addition, the on-line recordings of all flow rates (influent, two mixed liquor recycles, RAS and waste activated sludge (WAS)), process temperature, and DO concentrations in the aerobic compartments were also collected for the modeling study.

Figure 2 – Horizontal View of the Full-Scale MUCT Bioreactor at the Gdansk WWTP and Location of the Sampling Points during the Measurement Campaign (Red Arrows)



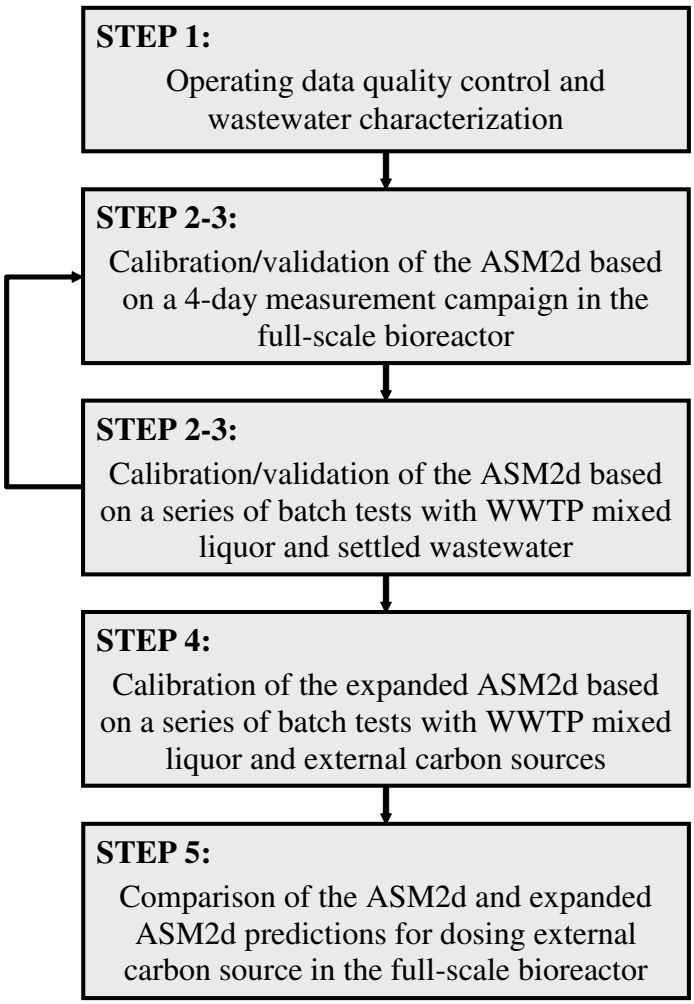
Analytical methods

Mixed liquor and mixed liquor volatile suspended solids (MLSS and MLVSS) were determined by the gravimetric method according to the Polish Standards (PN-72/C-04559). The total and soluble COD, TP, PO_4-P, NO_3-N and NH_4-N were analyzed using Xion 500 spectrophotometer (Dr Lange GmbH, Germany). The analytical procedures, which were adapted by Dr Lange GmbH, followed the Standard Methods (APHA, 1992). The TN concentrations were measured using TOC/TN analyzer (SHIMADZU Corporation, Japan). The samples for determining soluble COD was prepared according to the rapid physical-chemical method of Mamais et al. (1993).

Organization of the modeling study

The modeling study followed the steps presented in Figure 3. First (steps 1-2), the original ASM2d was calibrated/validated under dynamic conditions with the results of both batch tests with the settled wastewater (without the addition of external carbon sources) and the 96-hour measurement campaign in the full-scale MUCT bioreactor. In step 3, the results of the two types of batch tests (conventional NUR, PRR & anoxic PUR) with ethanol and fusel oil were used to adjust the kinetic and stoichiometric coefficients in the ASM2d expansion (Table 1). The results of these two tests were used in step 4 to compare predictions of the new model and the original ASM2d. For this purpose, it was assumed that the added external carbon source (ethanol or fusel oil) was treated as the new component $S_{A,1}$ (in the new model) or a fraction of S_A (in the ASM2d). Finally (step 5), the addition of external carbon source to an anoxic zone of the full-scale MUCT bioreactor was simulated with both models and the predictions were compared in terms of the NO_3-N and PO_4-P profiles and process rates for NO_3-N (S_{NO}), acetate (S_A) and "the other fermentation products" ($S_{A,1}$).

Figure 3 – Pathway in the Development and Evaluation of the Expanded ASM2d for Predicting the Effects of External Carbon sources in Combined N-P Activated Sludge Systems



Simulation tool

GPS-X ver. 5.0.2 (Hydromantis, Canada) was used as a simulator environment for implementing the developed model and running simulations.

RESULTS AND DISCUSSION

The values of parameters adjusted at each calibration level with comparison to the default ASM2d values are presented in Table 2. With these values, both process rates (PRR, anoxic/aerobic PUR, NUR and AUR) in two- and three-phase batch tests (Figure 4) and behavior of NH_4-N, NO_3-N and PO_4-P concentrations in the full-scale bioreactors (Figure 5) were matched accurately by the model predictions.

The default values were assumed for stoichiometric coefficients except for the heterotrophic yield coefficient, Y_H, and the polyphosphate requirement for PHA storage, Y_{PO4}, which were experimentally determined based on respirometric measurements for Y_H (Makinia et al., 2009) and anaerobic phosphate release measurements for Y_{PO4}. In the latter case, the value of Y_{PO4} = 0.34 g P/g COD was different from the ASM2d default of 0.4 g P/g COD, but remained within a

typical range for simulation (0.3-0.43 g P/g COD) as reviewed by Makinia (2006). In the study of Brdjanovic et al. (2000), the authors used for simulation a higher value of Y_{PO4} (0.36 g P/g COD) compared to the values experimentally determined in batch tests with the WWTP mixed liquor and acetate (0.27-0.29 g P/g COD). The authors attributed lower values of Y_{PO4} to the presence of glycogen accumulating organisms (GAOs) based on the results of anaerobic phosphate release tests, in which acetate was still utilized even after depletion of polyphosphate in the PAO biomass. In the case of the Wschod WWTP, the results of similar experiments with surplus acetate (Makinia, 2006) revealed that the acetate utilization hardly continued after polyphosphate depletion in the biomass. This suggests that GAOs did not play a significant role at the plant and there was no need to model their metabolism in this study.

The nitrification process was calibrated with two parameters including the maximum growth of autotrophs, μ_A, and half-saturation coefficient for NH_4-N, $K_{NH4,A}$. The estimated values of both parameters were higher compared to the ASM2d defaults. Higher values of $K_{NH4,A}$ has been noted for some full-scale plants due to a higher diffusion limitation resulting from low turbulence and large floc sizes (Henze et al., 2000). In addition, the PO_4-P (nutrient) saturation coefficient for autotrophic organisms ($K_{PO4,A}$) was reduced from 0.01 to 0.001 g P/m^3. This modification, proposed in the literature by Meijer et al. (2001), was necessary to simulate high rates of the nitrification process without a limitation caused by extremely low PO_4-P concentrations that were temporarily observed in the aerobic zone of the full-scale bioreactor.

The calibration of denitrification was carried out based on the results of two batch tests which were denoted as the conventional NUR and PRR & anoxic PUR. In the conventional NUR test, model predictions were fitted to the measured NURs by adjusting two parameters: the maximum growth rate of heterotrophs (μ_H) and hydrolysis rate constant (k_{hyd}) and anoxic reduction factor for hydrolysis ($\eta_{NO3,hyd}$). In the PRR & anoxic PUR test, the k_{hyd} coefficient and anoxic reduction factor for PAO growth ($\eta_{NO3,PAO}$) were modified to calibrate the NUR in the anoxic phase of the test. The modified values of all the coefficients were reduced in comparison with the ASM2d defaults (Table 2).

In addition to the modification of Y_{PO4}, several kinetic parameters were adjusted to calibrate the EBPR process. The PRR was calibrated with three parameters: the rate constant for storage of PHA, q_{PHA}, and saturation coefficients for PAOs with respect to fermentation product (S_A), $K_{SA,PAO}$, and polyphosphate (X_{PP}), K_{PP}.The PUR was calibrated with three parameters: the rate constant for storage of polyphosphate, q_{PP}, polyphosphate storage inhibition coefficient, K_{IPP}, and PHA saturation coefficient, K_{PHA}. It should be noted that the modified values of q_{PHA} and q_{PP} were considerably higher than the ASM2d defaults. The q_{PHA} value of 6 d^{-1} is in the range of 6-8 d^{-1} reported in several studies (Makinia, 2006). In the case of phosphate uptake, the increased process rate resulting from the higher value of q_{PP} was compensated by the higher values of the inhibition coefficient for X_{PP} storage, K_{IPP}, and the saturation coefficient for PHA, K_{PHA}. This relationship is apparent from the rate expression for polyphosphate storage which is part of the ASM2d:

$$q_{PP}\frac{S_O}{K_{O,PAO}+S_O}\frac{S_{PO4}}{K_{PS}+S_{PO4}}\frac{S_{ALK}}{K_{ALK,PAO}+S_{ALK}}\frac{X_{PHA}/X_{PAO}}{K_{PHA}+X_{PHA}/X_{PAO}}\frac{K_{MAX}-X_{PP}/X_{PAO}}{K_{IPP}+K_{MAX}-X_{PP}/X_{PAO}}X_{PAO}$$

Similar to nitrification, a limitation caused by very low concentrations PO_4-P and NH_4-N was avoided by setting the saturation coefficients for NH_4-N ($K_{NH4,PAO}$) and PO_4-P ($K_{PO4,PAO}$) to 0.01 g N/m^3 and 0.001 g P/m^3, respectively.

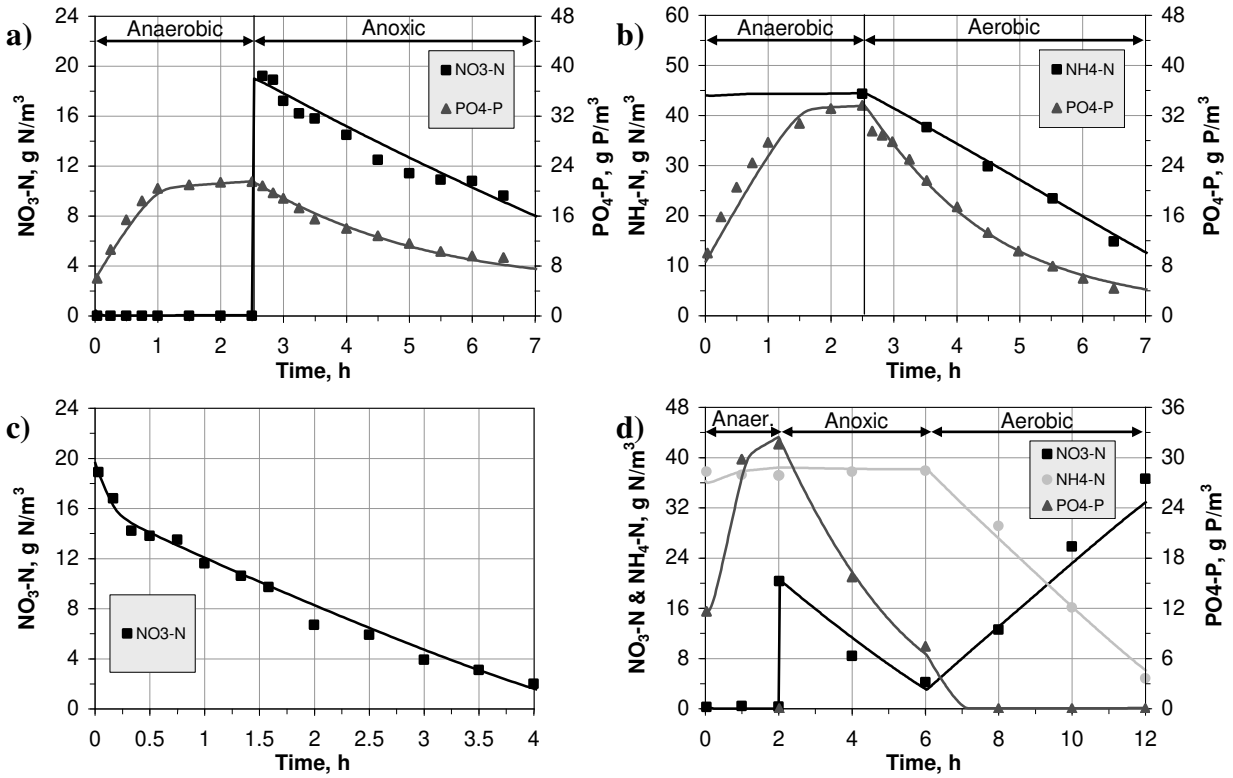
Table 2 - Kinetic Parameters Adjusted in the ASM2d and New Kinetic Parameters in the Expanded ASM2d (shadowed)

Definition	Symbol	Unit	ASM2d default	Calibrated value
Heterotrophic organisms (X_H):				
Maximum growth rate of X_H on S_A and S_F	μ_H	d^{-1}	6.0	3.0
Maximum growth rate of X_H on $S_{A,1}$	μ_{H1}	d^{-1}		3.0
Reduction factor for anoxic activity of X_H with $S_{A,1}$	$\eta_{NO3,H1}$	-		0.8
Saturation coefficient for growth on $S_{A,1}$	$K_{SA1,H}$	g COD/m^3		4.0
Autotrophic organisms (X_A):				
Maximum growth rate of X_A	μ_A	d^{-1}	1.0	1.35
Saturation coefficient for NH_4-N	$K_{NH4,A}$	g N/m^3	1.0	1.3
Saturation coefficient for PO_4-P (nutrient)	$K_{PO4,A}$	g P/m^3	0.01	0.001
Phosphorus Accumulating Organisms (X_{PAO}):				
Rate constant for storage of X_{PHA}	q_{PHA}	d^{-1}	3.0	6.0
Rate constant for storage of X_{PP}	q_{PP}	d^{-1}	1.5	4.5
Rate constant for storage of X_{PP} on $S_{A,1}$	q_{PP1}	d^{-1}		4.5
Maximum growth rate of X_{PAO} on $S_{A,1}$	μ_{PAO1}	d^{-1}		1.0
Reduction factor for anoxic activity of X_{PAO}	$\eta_{NO3,PAO}$	-	0.6	0.5
Reduction factor for anoxic activity of X_{PAO} with $S_{A,1}$	$\eta_{NO3,PAO1}$	-		0.5
Saturation coefficient for S_A	$K_{SA,PAO}$	g COD/m^3	4.0	1.0
Saturation coefficient for $S_{A,1}$	$K_{SA1,PAO}$	g COD/m^3		4.0
Saturation coefficient for NH_4-N (nutrient)	$K_{NH4,PAO}$	g N/m^3	0.05	0.01
Saturation coefficient for PO_4-P (nutrient)	$K_{PO4,PAO}$	g P/m^3	0.01	0.001
Saturation coefficient for X_{PP}	K_{PP}	g P/g COD	0.01	0.02
Inhibition coefficient for X_{PP} storage	K_{IPP}	g P/g COD	0.02	0.05
Saturation coefficient for X_{PHA}	K_{PHA}	g COD/g COD	0.01	0.1
Hydrolysis of particulate substrate (X_S):				
Hydrolysis rate constant	k_{hyd}	d^{-1}	3.0	2.5

Table 3 - Stoichiometric Parameters Adjusted in the ASM2d and New Kinetic Parameters in the Expanded ASM2d (shadowed)

Definition	Symbol	Unit	ASM2d default	Calibrated value
Heterotrophic organisms (X_H):				
Yield coefficient	Y_H	g COD/g COD	0.625	0.67
Yield coefficient for S_{A1}	Y_{H1}	g COD/g COD		0.7
Phosphorus Accumulating Organisms (X_{PAO}):				
Yield coefficient for S_{A1}	Y_{PAO1}	g COD/g COD		0.7
PP requirement (PO_4-P release) for S_{A1}	Y_{PO4}	g P/g COD	0.4	0.34
S_{A1} requirement for X_{PP} storage	Y_{SA1}	g COD/g P		0.2

Figure 4 - Measured data vs. ASM2d Predictions for Batch Experiments with WWTP Mixed Liquor and Settled Wastewater: (a) NO_3-N and PO_4-P during the Anaerobic P release and Anoxic P Uptake (MLSS = 1.88 kg/m^3, T = 19.8 ^{o}C), (b) NH_4-N and PO_4-P during the Anaerobic P Release and Aerobic P Uptake (MLSS = 2.17 kg/m^3, T = 18.9 ^{o}C), (c) NO_3-N during the "Conventional" Denitrification (MLSS = 3.17 kg/m^3, T = 20.5 ^{o}C), (d) NO_3-N, NH_4-N and PO_4-P during a 3-Phase (Anaerobic/Anoxic/Aerobic) Experiment (MLSS = 3.54 kg/m^3, T = 13.2 ^{o}C)



The expanded ASM2d was calibrated using the results of a series of batch tests with the WWTP mixed liquor, and external carbon sources (Figure 6). In the NUR measurements with either ethanol or fusel oil, added in the amount of 350-500 g COD/^{3}, there was no significant PO_4-P released to indicate anaerobic consumption of these substrates by PAOs (Figure 6a and Figure 6c). For comparison, PO_4-P was released during similar experiments with the settled wastewater until the readily biodegradable substrate was present in the batch reactor (Makinia et al., 2010b). In the two-phase experiments (Figure 6b and Figure 6d), the addition of ethanol or fusel oil in the anoxic phase (in the amount of 30-90 g COD/m^3) increased the anoxic PURs compared to the reference experiments without addition of the external carbon sources at the beginning of the anoxic phase (Swinarski et al., 2009).

When the external carbon source (ethanol or fusel oil) was treated as $S_{A,1}$ in the new model, model predictions matched the experimental data by adjusting two kinetic parameters, (i.e. reduction factor for anoxic activity of X_H with $S_{A,1}$, $\eta_{NO3,H1}$, and saturation coefficient for growth on $S_{A,1}$, $K_{SA1,H}$) in the growth process of "ordinary" heterotrophs on the new substrate ($S_{A,1}$) (Table 2). The stoichiometric yield coefficients, Y_{H1} and Y_{PAO}, were directly determined based on the respirometric measurements (Swinarski et al., 2009). For the remaining six kinetic and stoichiometric coefficients in the new model, the same values were assumed as the corresponding parameters in ASM2d (default or calibrated). For comparison, when the external carbon source

was assumed to be a fraction of S_A in the calibrated ASM2d, much higher COD utilization rates were predicted under anoxic conditions (Figures 6a-d) and the anoxic PURs in the two-phase experiments were underestimated (Figure 6b and Figure 6d).

Figure 5 - Measured data vs. ASM2d Predictions for a 4-Day Measurement Campaign in the Full-Scale MUCT Bioreactor at the Gdansk WWTP: (a) NH_4-N Concentrations in the Anoxic and Aerobic Zone Effluents, (b) NO_3-N Concentrations in the Anoxic and Aerobic Zone Effluents, (c) PO_4-P Concentrations in the Anaerobic and Anoxic Zone Effluents (partially adopted from Makinia et al., 2010a)

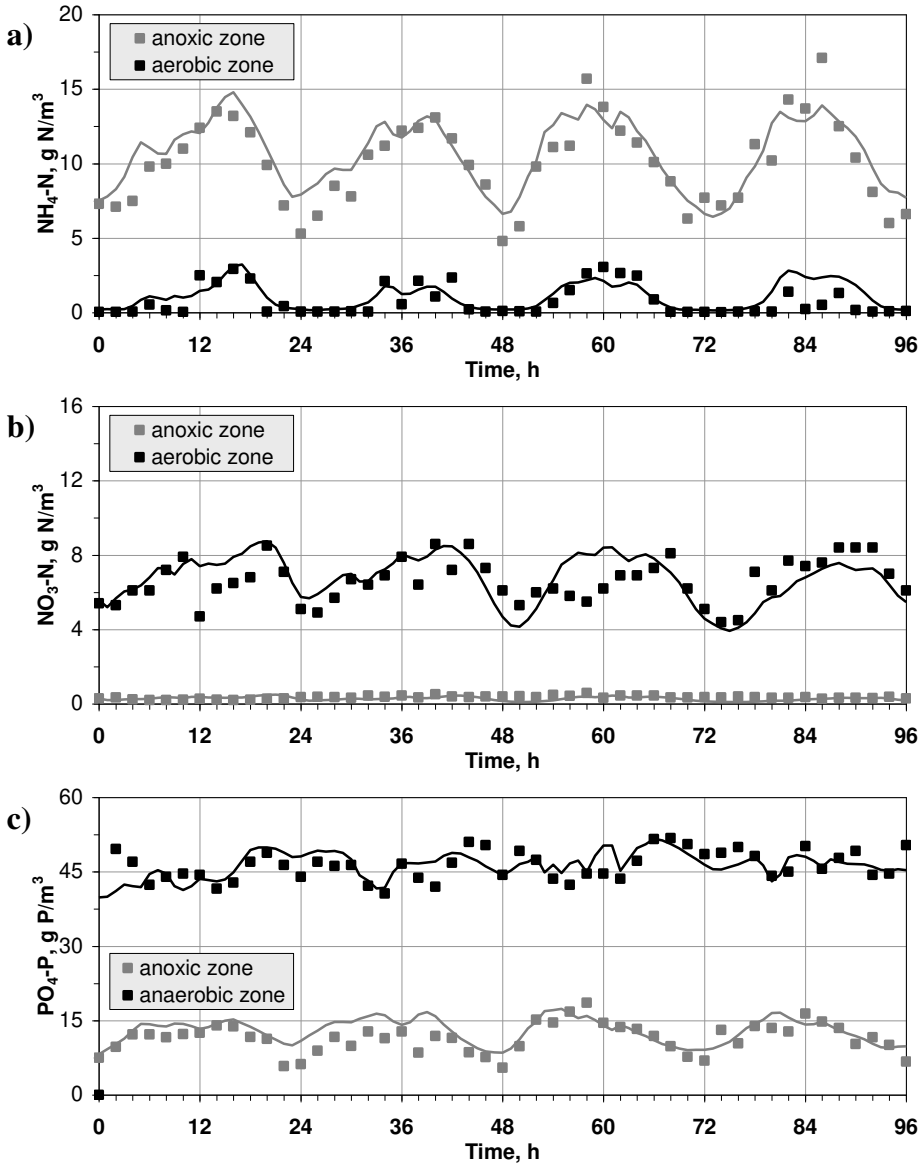
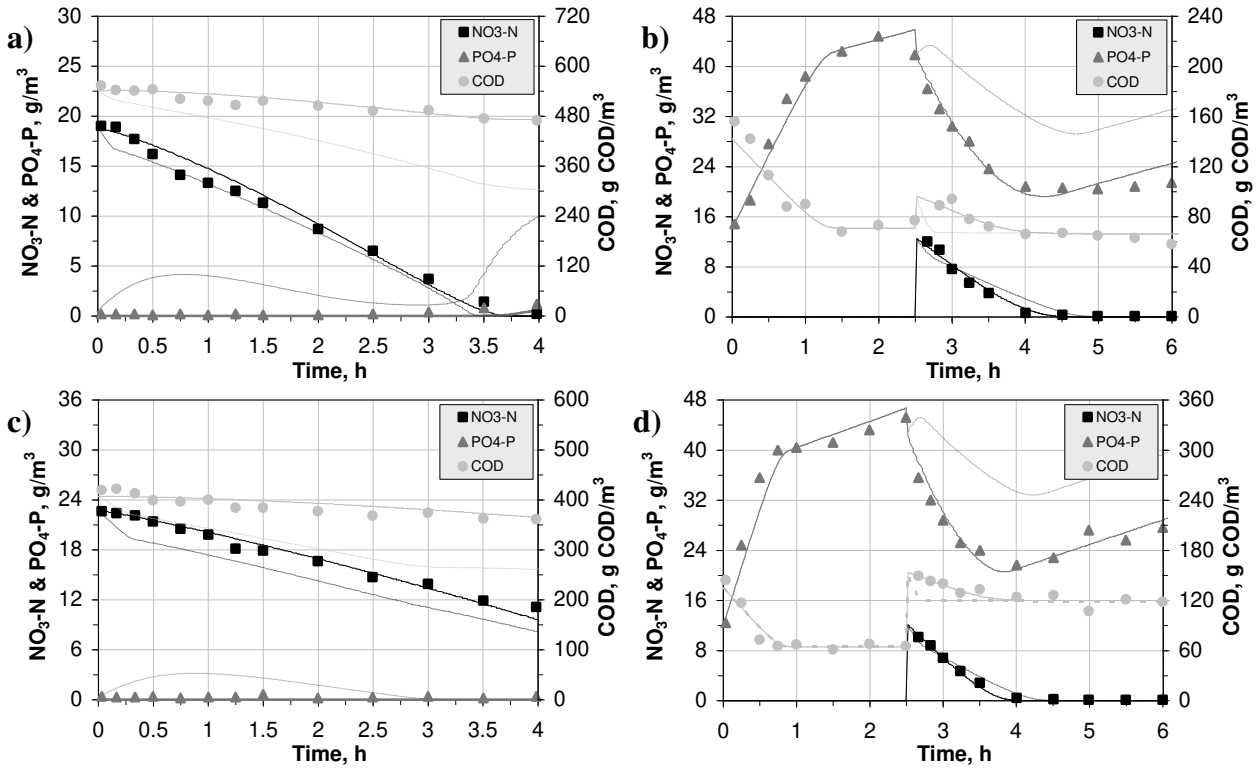
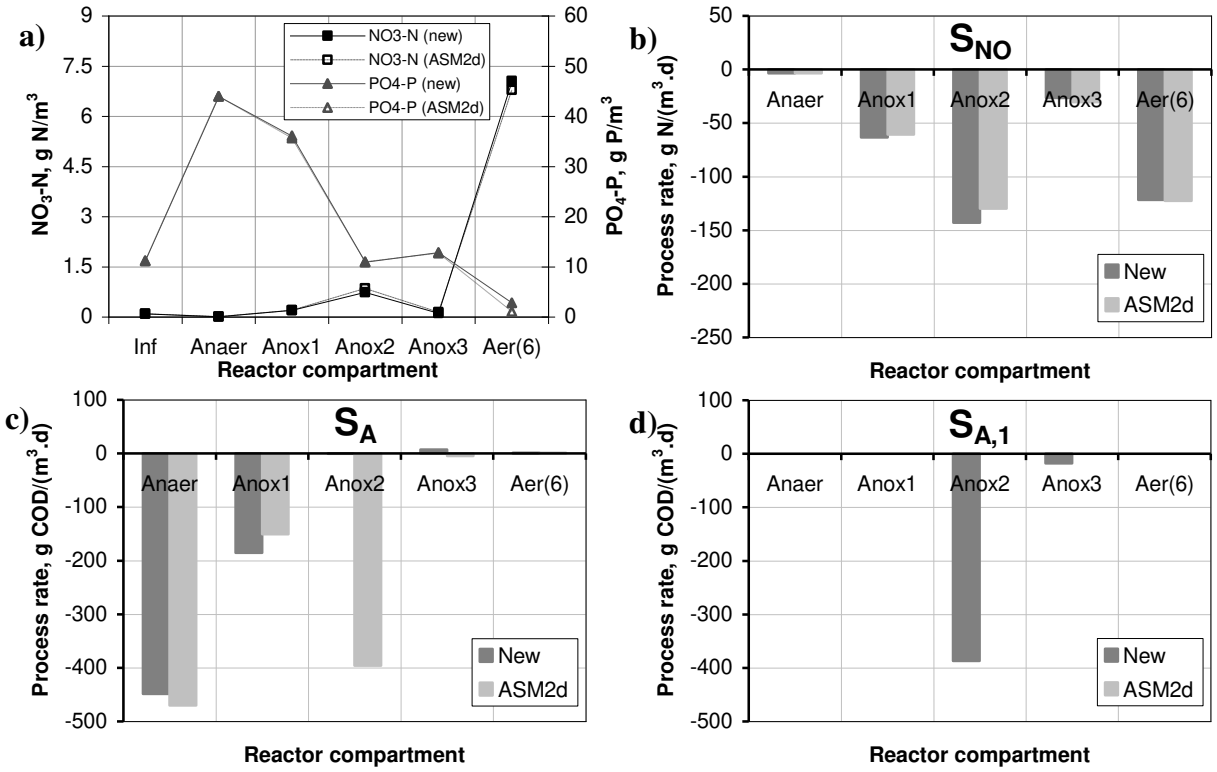


Figure 6 – Measured Data vs. Model Predictions of NO_3-N, PO_4-P and COD in Batch Experiments with WWTP Mixed Liquor and External Carbon Sources Including Ethanol (a-b) and Fusel Oil (c-d) (the New Model – Solid Lines, ASM2d – Dashed Lines)



For simulations of the full-scale bioreactor performance, it was assumed that 1 m^3/d of the external carbon source (at the concentration of 1,600,000 g COD/m^3) was added to the second anoxic zone (Anox 2) of the bioreactor. In spite of the mechanistically inappropriate approach to treat some external sources as the ASM2d components, the original (calibrated) ASM2d predicted NO_3-N and PO_4-P concentrations in the full-scale bioreactor only slightly differently from the new model. Apart from PO_4-P in the reactor effluent, the relative deviations between both model predictions for NO_3-N and PO_4-P did not exceed 10% in all the sampling points (Figure 7a). For example, the predicted effluent NO_3-N concentrations were 7.1 and 6.8 g N/m^3, respectively, for the new model and ASM2d. This similarity was explained by analyzing in detail the modeled process rates for S_{NO}, S_A and $S_{A,1}$ (Figure 7b-d) and finding comparable utilization rates of S_A (ASM2d) and $S_{A,1}$ (new model) in the second anoxic zone (Anox 2), which were 396 vs. 387 g COD/(m^3·d), respectively.

Figure 7 - Model (ASM2d and Expanded ASM2d) Predictions of the NO_3-N and PO_4-P Concentration Profiles in the Full-Scale MUCT Reactor at the Gdansk WWTP (a), and Predicted Process Rates of NO_3-N (S_{NO}), Acetate (S_A) and Other Fermentation Products ($S_{A,1}$) (b-d)



CONCLUSIONS

From this study, the following conclusions may be derived:

- A new model has been developed for combined N-P activated sludge systems with external carbon addition. The model is an expansion of ASM2d and incorporates a readily biodegradable substrate which is not available for the PAOs under anaerobic conditions but can support growth and denitrification by the PAOs under anoxic conditions.
- In comparison with the ASM2d, the new model better predicts the COD, NO_3-N and PO_4-P behaviors in batch experiments with such compounds as ethanol and fusel oil. However, in typical combined N-P activated sludge system both model predictions appear to be comparable in terms of NO_3-N and PO_4-P concentration profiles (provided that the external carbon source is added to the anoxic zone of the bioreactor). This results from a similar predicted anoxic utilization of the added external carbon by the two models regardless of the substrate concept (S_A in the ASM2d vs. $S_{A,1}$ in the new model).

ACKNOWLEDGMENTS

This study has been financially supported by European Regional Development Fund within the framework of the Innovative Economy Operational Programme 2007-2013 under the project no. UDA-POIG.01.03.01-22-140/09-01.

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