Mass and charge conservation check in dynamic models: application to the new ADM1 model

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Abstract This paper proposes a systematic methodology for the analysis of the mass and charge balances in dynamic models expressed using the Petersen matrix notation. This methodology is based on the definition of the model components via elemental mass fractions and in the estimation of the COD as a function of the redox equations associated with these elements. This approach makes the automatic calculation of all the stoichiometric coefficients under different measuring units and the study of COD, charge or mass fluxes easier. As an example of its application this methodology was applied to the ADM1 in order to illustrate its usefulness for the analysis of organic matter characterisation, nitrogen release or biogas composition in anaerobic digestion. The application of the methodology for a rigorous integration of different IWA models is proposed for further study.

Keywords Mass balance; charge balance; continuity equations; modelling; anaerobic digestion; ADM1

Introduction

Mathematical modelling and simulation is a commonly used tool in research and the management of environmental systems. Different IWA Task Groups have carried out intensive work into developing models for WWTP and rivers: the ASM1, ASM2 and ASM3 (Henze *et al.*, 2000) to model the transformations in activated sludge processes, the ADM1 (Batstone *et al.*, 2002) to describe the anaerobic digestion transformations and the RWQM1 (Reichert *et al.*, 2001) developed for the prediction of water quality in rivers. The matrix format proposed by Petersen (1965) has been used to develop all those models. However, some differences in model structure, components and hypotheses exist: the description of the organic nitrogen, the pH dynamics (or alkalinity variations), the fractionation of the carbonaceous substrate, gas–liquid interchanges, etc.

Furthermore, many different units were used to define the model components. Engineered systems models have usually been based on chemical oxygen demand (COD) and nitrogen content per unit of COD, while water chemists and biologists are more familiar with organic carbon content or dry weight mass fractions of organic compounds (Reichert *et al.*, 2001; Marañon *et al.*, 2004). The RWQM1 established a systematic methodology for model definition and mass balance that can be used to standardise the rest of the existing IWA models. The use of elemental mass fractions creates a rigorous theoretical basis for bio-geochemical conversion processes that can bring the derivation of most of the commonly used quantification measures, ease the checking of mass and charge continuity of process transformations and simplify the connections between models.

This paper presents the systematic application of this methodology to mathematical models based on the Petersen matrix description. The new anaerobic digestion model

(ADM1) has been used as an example to illustrate the usefulness of the methodology proposed.

Methods
The fundamentals of the model formulation with elemental mass fractions are based on the hypothesis that the mass of each component in the model is made up of time constant mass fractions of the elements C, H, O, N and P (Reichert et al., 2001). Furthermore, each component may have an associated charge per unit of mass. The elemental mass fractions ($\alpha_{C,i}$, $\alpha_{H,i}$, $\alpha_{O,i}$, $\alpha_{N,i}$ or $\alpha_{P,i}$) for a generic model component X_i are defined as the mass of C, H, O, N or P per unit of mass of this component (X_i). The calculation of these mass fractions is immediate for all those model components that own a known composition formula, but a proper estimation must be carried out for the remaining elemental mass fractions. According to the hypothesis above, the sum of all elemental mass fractions of each component X_i must be unity.

$$\alpha_{C,i} + \alpha_{H,i} + \alpha_{O,i} + \alpha_{N,i} + \alpha_{P,i} = 1 \tag{1}$$

The charge density ($\alpha_{Ch,i}$) for a generic model component X_i is defined as the electric charge associated to its unit of mass. For each component X_i, it is calculated as the quotient of its molecular charge and its molecular weight. Normally, not all the components X_i can be defined by a molecular formula, their molecular weight being unknown. However, once the elemental mass fractions and the charge density have been assigned, *one unit of mass* of any model component X_i can be expressed with a general formula as follows:

$$\left[C_{(\alpha/12)}H_{(\alpha)}O_{(\alpha/16)}N_{(\alpha/14)}P_{(\alpha/31)}\right]^{\alpha_{Ch,i}} \tag{2}$$

Conservation equations
Each column of the Petersen matrix gathers the stoichiometric coefficients for each i model component, while the rows represent the mass transformation for the different j processes. Conservation equations are the mathematical equivalent to the principle that in physical, chemical or biological transformations, neither matter nor net electric charge is created or destroyed. Commonly, model components are expressed in terms of concentration (amount of component per unit of volume). The stoichiometric unit of a generic model component X_i refers to the measurement unit on which the amount of each component is expressed in the model (for example COD, mol, mass, etc.). Based on the elemental mass fractions and charge density previously defined, six conservation equations can then be written for each of the j processes included in the model:

$$\sum_i \nu_{ij} \cdot \beta_{C,i} = \sum_i \nu_{ij} \cdot \beta_{H,i} = \sum_i \nu_{ij} \cdot \beta_{O,i} = \sum_i \nu_{ij} \cdot \beta_{N,i} = \sum_i \nu_{ij} \cdot \beta_{P,i} = \sum_i \nu_{ij} \cdot \beta_{Ch,i}$$

$$= 0 \tag{3}$$

Where ν_{ij} is the corresponding stoichiometric coefficient of the Petersen matrix and the conversion parameters $\beta_{C,i}$ $\beta_{H,i}$ $\beta_{O,i}$ $\beta_{N,i}$ $\beta_{P,i}$ and $\beta_{Ch,i}$ are the mass of C, H, O, N and P, and the charge respectively, in one stoichiometric unit of the model component X_i. These equations contain information about the transformation and allow the prediction of one stoichiometric coefficient ν_{ij} in each process j without the need for any experiment, provided the remaining coefficients are known. The conversion parameters can be calculated if and only if a unique mathematical relationship exists between the stoichiometric unit of component X_i and its elemental mass fractions and charge density. As many model components have been traditionally expressed in terms of COD, a simple and systematic

methodology for estimating the relationship between its COD and its mass should be established in order to apply the mass conservation equations described above.

The relationship between the COD and the mass of every model component can be based on redox equations when its elemental mass fraction and charge density have been previously defined. The notion of theoretical oxygen demand (ThOD) has been introduced to characterise the corresponding concept, and in order to apply it to inorganic compounds as well (Gujer et al., 1999). The principle of ThOD assumes that each reactive electron is equivalent to 8 g of ThOD and, therefore, when an element is oxidised to its redox state of reference (CO_2, H_2O, O_2, NH_4^+, PO_4^{3-}, etc.), there is an exchange of electrons, to which an equivalent ThOD value is associated. Table 1 shows the equivalent ThOD for C, H, O, N, P and charge.

The total ThOD of *one unit of mass* of a generic model component X_i can then be calculated as the sum of the individual ThOD contributions of each element or charge multiplied by the corresponding coefficient of its general formula (2).

Mass and charge balance in the extended ADM1 model

The ADM1 model (Batstone et al., 2002) includes disintegration and hydrolysis, acidogenesis, acetogenesis and methanogenesis steps that take place in treatment systems based on the anaerobic digestion process. In addition to the biochemical processes, mechanisms included to describe physico-chemical processes are acid-base reactions and non-equilibria liquid–gas processes. The methodology presented above has been applied to the model in order to characterize the components involved in the processes, calculate the conversion parameters for identifying possible imbalances, visualizing the whole stoichiometric matrix based on different formalisms, and constructing mass fluxes through the model transformations.

Components and processes of the extended model

This study has been based on the differential equation (DE) implementation of the ADM1 model, including 30 components and 19 biological processes, 3 gas–liquid transfer kinetic processes and 6 acid-base kinetic processes. To be coherent with the objective of this study, 9 more components and 3 more processes have been added for complete definition of the processes. This approach allows the application of the continuity check not only to those formalisms for which the model is arranged (COD, carbon, nitrogen) but to all elements (hydrogen, oxygen, phosphorus and electric charge).

Closed mass balances require that some model components act as source-sink for each element. This role has been associated to inorganic carbon, water, ammonia, inorganic phosphorous and protons for C, H, N, P and charge respectively. For anaerobic conditions, the oxygen balance is accomplished without any source-sink component. Two forms of inorganic phosphorous have been included (S_{h2po4-}; $S_{hpo4=}$) acting as source-sink for the phosphorus, in the same way that it is already implemented for the inorganic

Table 1 ThOD for some elements and charge

Element or charge Z		State of reference		Equivalent ThOD
C	Carbon	CO_2	$+32$	g ThOD (mol C)$^{-1}$
H	Hydrogen	H_2O	$+8$	g ThOD (mol H)$^{-1}$
O	Oxygen	O_2	-16	g ThOD (mol O)$^{-1}$
N	Nitrogen	NH_4^+	-24	g ThOD (mol N)$^{-1}$
P	Phosphorus	PO_4^{3-}	$+40$	g ThOD (mol P)$^{-1}$
$-$	Negative charge	Zero charge	$+8$	g ThOD (mol $(-)$)$^{-1}$
$+$	Positive charge	Zero charge	-8	g ThOD (mol $(+)$)$^{-1}$

Table 2 Extended stoichiometric matrix for the ADM1 model

M. de Gracia et al.

		1	2	3	4	5	6	7
		S_{su} Monosaccharides $C_6H_{12}O_6$	S_{aa} Amino acids $C_4H_{6.1}O_{1.2}N$	S_{fa} Long chain fatty acids $C_{16}O_2H_{32}$	S_{hva} Valeric acid $C_5H_{10}O_2$	S_{va-} Valerate $C_5H_9O_2$	S_{hbu} Butyric acid $C_5H_9O_2$	S_{bu-} Butyrate $C_4H_7O_2$
1	Disintegration							
2	Hydrolysis of chyd.	1						
3	Hydrolysis of prot.		1					
4	Hydrolysis of lipids	0.0500		0.9500				
5	Uptake of sugars	−1					0.1170	
6	Uptake of AA		−1		0.2116		0.2392	
7	Uptake of LCFA			−1				
8	Uptake of valerate				−1			
9	Uptake of butyrate					−1		
10	Uptake of propionate							
11	Uptake of acetate							
12	Uptake of hydrogen							
13	Decay of X_{su}							
14	Decay of X_{aa}							
15	Decay of X_{fa}							
16	Decay of X_{c^4}							
17	Decay of X_{pro}							
18	Decay of X_{ac}							
19	Decay of X_{h2}							
20	Valerate acid-base				−1	1		
21	Butyrate acid-base						−1	1
22	Propionate acid-base							
23	Acetate acid-base							
24	Inorg C acid-base							
25	Inorg N acid-base							
26	Inorg P acid-base							
27	Equilibrium H^+-OH^-							
28	H_2 dissolution							
29	CH_4 dissolution							
30	CO_2 dissolution							
31	Water condensation							
		kgCOD	kgCOD	kgCOD	kgCOD	kgCOD	kgCOD	kgCOD

		8	9	10	11	12	13	14
		S_{hpro} Propionic acid $C_3H_6O_2$	S_{pro-} Propionate $C_3H_5O_2^-$	S_{hac} Acetic acid $C_2H_4O_2$	S_{ac-} Acetate $C_2H_3O_2^-$	S_{co2} Carbon-dioxide CO_2	S_{hco3-} Bicarbonate HCO_3	S_{nh4+} Ammonium NH_4
1	Disintegration					$-1.4E\text{-}03$		$-4.4E\text{-}04$
2	Hydrolysis of chyd.					$1.1E\text{-}03$		$0.0E+00$
3	Hydrolysis of prot.					$0.0E+00$		$0.0E+00$
4	Hydrolysis of lipids					$2.2E\text{-}05$		$0.0E+00$
5	Uptake of sugars	0.2430		0.3690		$7.2E\text{-}03$		$-6.2E\text{-}04$
6	Uptake of AA	0.0460		0.3680		$-4.1E\text{-}04$		$6.6E\text{-}03$
7	Uptake of LCFA			0.6580		$-9.9E\text{-}04$		$-3.7E\text{-}04$
8	Uptake of valerate	0.5076		0.2914		$-4.9E\text{-}04$		$-3.7E\text{-}04$
9	Uptake of butyrate			0.7520		$-3.3E\text{-}04$		$-3.7E\text{-}04$
10	Uptake of propionate	-1		0.5472		$8.5E\text{-}03$		$-2.5E\text{-}04$
11	Uptake of acetate			-1		$1.5E\text{-}02$		$-3.1E\text{-}04$
12	Uptake of hydrogen					$-1.7E\text{-}02$		$-3.7E\text{-}04$
13	Decay of X_{su}					$-4.7E\text{-}03$		$3.9E\text{-}03$
14	Decay of X_{aa}					$-4.7E\text{-}03$		$3.9E\text{-}03$
15	Decay of X_{fa}					$-4.7E\text{-}03$		$3.9E\text{-}03$
16	Decay of X_{c4}					$-4.7E\text{-}03$		$3.9E\text{-}03$
17	Decay of X_{pro}					$-4.7E\text{-}03$		$3.9E\text{-}03$
18	Decay of X_{ac}					$-4.7E\text{-}03$		$3.9E\text{-}03$
19	Decay of X_{h2}					$-4.7E\text{-}03$		$3.9E\text{-}03$
20	Valerate acid-base							
21	Butyrate acid-base							
22	Propionate acid-base	-1	1					
23	Acetate acid-base			-1	1			
24	Inorg C acid-base					-1	1	
25	Inorg N acid-base							-1
26	Inorg P acid-base							
27	Equilibrium H^+-OH^-							
28	H_2 dissolution							
29	CH_4 dissolution							
30	CO_2 dissolution							
31	Water condensation							
		kgCOD	kgCOD	kgCOD	kgCOD	kmoleC	kmoleC	kmoleN

Table 2 (*cont.*)

		15	16	17	18	19	20	21
		S_{nh3}	$S_{hpo4=}$	S_{h2po4-}	S_{h+}	S_{oh-}	S_{h2}	S_{ch4}
		Ammonia NH_3	Dehydrogen-phos HPO_4^{2-}	Hydrogen-phosph H_2PO_4	Ion hydroxyl H^+	Ion hydroxyl OH^-	Dissolved hydrogen gas H_2	Dissolved methane gas CH_4
1	Disintegration		−1.8E-05		−4.1E-04			
2	Hydrolysis of chyd.		3.1E-04		6.3E-04			
3	Hydrolysis of prot.		0.0E+00		0.0E+00			
4	Hydrolysis of lipids		1.1E-04		2.2E-04			
5	Uptake of sugars		−6.9E-05		4.8E-04		0.1710	
6	Uptake of AA		−5.6E-05		−6.7E-03		0.0552	
7	Uptake of LCFA		−4.2E-05		2.9E-04		0.2820	
8	Uptake of valerate		−4.2E-05		2.9E-04		0.1410	
9	Uptake of butyrate		−4.2E-05		2.9E-04		0.1880	
10	Uptake of propionate		−2.8E-05		1.9E-04		0.4128	
11	Uptake of acetate		−3.5E-05		2.4E-04			0.95
12	Uptake of hydrogen		−4.2E-05		2.9E-04		−1.00	0.94
13	Decay of X_{su}		5.5E-04		−2.8E-03			
14	Decay of X_{aa}		5.5E-04		−2.8E-03			
15	Decay of X_{fa}		5.5E-04		−2.8E-03			
16	Decay of X_{c4}		5.5E-04		−2.8E-03			
17	Decay of X_{pro}		5.5E-04		−2.8E-03			
18	Decay of X_{ac}		5.5E-04		−2.8E-03			
19	Decay of X_{h2}		5.5E-04		−2.8E-03			
20	Valerate acid-base				4.8E-03			
21	Butyrate acid-base				6.3E-03			
22	Propionate acid-base				8.9E-03			
23	Acetate acid-base				1.6E-02			
24	Inorg C acid-base				1			
25	Inorg N acid-base	1			1			
26	Inorg P acid-base		−1	1	−1			
27	Equilibrium H^+-OH^-				1	1		
28	H_2 dissolution						1	
29	CH_4 dissolution							1
30	CO_2 dissolution							
31	Water condensation							
		kmoleN	kmoleP	kmoleP	kmoleH	kmoleH	kgCOD	kgCOD

		22	23	24	25	26	27	28
		S_I Soluble inerts	X_c Composites	X_{ch} Carbohydr $C_6H_{10}O_5$	X_{pr} Proteins $C_4H_{6.1}O_{1.2}N$	X_h Lipids $C_{51}H_{98}O_6$	X_{su} Sugar degraders	X_{aa} Amino acid degr.
1	Disintegration	0.10	-1	0.20	0.20	0.30		
2	Hydrolysis of chyd.			-1				
3	Hydrolysis of prot.				-1			
4	Hydrolysis of lipids					-1		
5	Uptake of sugars						0.10	
6	Uptake of AA							0.08
7	Uptake of LCFA							
8	Uptake of valerate							
9	Uptake of butyrate							
10	Uptake of propionate							
11	Uptake of acetate							
12	Uptake of hydrogen							
13	Decay of X_{su}		1				-1	
14	Decay of X_{aa}		1					-1
15	Decay of X_{fa}		1					
16	Decay of X_{c4}		1					
17	Decay of X_{pro}		1					
18	Decay of X_{ac}		1					
19	Decay of X_{h2}		1					
20	Valerate acid-base							
21	Butyrate acid-base							
22	Propionate acid-base							
23	Acetate acid-base							
24	Inorg C acid-base							
25	Inorg N acid-base							
26	Inorg P acid-base							
27	Equilibrium H^+-OH^-							
28	H_2 dissolution							
29	CH_4 dissolution							
30	CO_2 dissolution							
31	Water condensation							
		kgCOD	kgCOD	kgCOD	kgCOD	kgCOD	kgCOD	kgCOD

M. de Gracia et al.

231

Table 2 (*cont.*)

		29	30	31	32	33	34	35
		X_{fa} LCFA degraders	X_{c4} Val and but degr.	X_{pro} Propionate degr.	X_{ac} Acetate degraders	X_{h2} Hydrogen degr.	X_I Particulate inerts	G_{CO2} Carbon-dioxide gas CO_2
1	Disintegration						0.20	
2	Hydrolysis of chyd.							
3	Hydrolysis of prot.							
4	Hydrolysis of lipids							
5	Uptake of sugars							
6	Uptake of AA							
7	Uptake of LCFA	0.06						
8	Uptake of valerate		0.06					
9	Uptake of butyrate		0.06					
10	Uptake of propionate			0.04				
11	Uptake of acetate				0.05			
12	Uptake of hydrogen					0.06		
13	Decay of X_{su}							
14	Decay of X_{aa}							
15	Decay of X_{fa}	− 1						
16	Decay of X_{c4}		− 1					
17	Decay of X_{pro}			− 1				
18	Decay of X_{ac}				− 1			
19	Decay of X_{h2}					− 1		
20	Valerate acid-base							
21	Butyrate acid-base							
22	Propionate acid-base							
23	Acetate acid-base							
24	Inorg C acid-base							
25	Inorg N acid-base							
26	Inorg P acid-base							
27	Equilibrium H^+-OH^-							
28	H_2 dissolution							
29	CH_4 dissolution							
30	CO_2 dissolution							− 1
31	Water condensation							
		KgCOD	kgCOD	kgCOD	kgCOD	kgCOD	kgCOD	kmoleC

		36	37	38	39
		G_{H2}	G_{CH4}	S_{H2O}	G_{H2O}
		Hydrogen gas H_2	Methane gas CH_4	Water H_2O	Water steam H_2O
1	Disintegration			− 0.0073	
2	Hydrolysis of chyd.			− 0.0465	
3	Hydrolysis of prot.				
4	Hydrolysis of lipids			− 0.0380	
5	Uptake of sugars			− 0.0275	
6	Uptake of AA			− 0.1039	
7	Uptake of LCFA			− 0.2989	
8	Uptake of valerate			0.1467	
9	Uptake of butyrate			− 0.1967	
10	Uptake of propionate			− 0.2982	
11	Uptake of acetate			0.0180	
12	Uptake of hydrogen			0.5841	
13	Decay of X_{su}			− 0.1541	
14	Decay of X_{aa}			− 0.1541	
15	Decay of X_{fa}			− 0.1541	
16	Decay of X_{c4}			− 0.1541	
17	Decay of X_{pro}			− 0.1541	
18	Decay of X_{ac}			− 0.1541	
19	Decay of X_{h2}			− 0.1541	
20	Valerate acid-base				
21	Butyrate acid-base				
22	Propionate acid-base				
23	Acetate acid-base				
24	Inorg C acid-base			− 18.0	
25	Inorg N acid-base				
26	Inorg P acid-base				
27	Equilibrium H^+-OH^-			− 18.00	
28	H_2 dissolution	− 1			
29	CH_4 dissolution		− 1		
30	CO_2 dissolution				
31	Water condensation			1	− 1
		kgCOD	kCOD	kgH$_2$O	kgH$_2$O

M. de Gracia et al.

Table 3 Elemental mass fractions and charge density for the ADM1 components

	S_{su}	S_{hva}	S_{va^-}	S_{hbu}	S_{bu^-}	S_{hpro}	S_{pro^-}	S_{hac}	S_{ac^-}	S_{co2}	S_{hco3^-}	S_{nh4^+}	S_{nh3}	S_{hpo4^+}	S_{h2po4^-}	S_{h^+}	S_{oh^-}	S_{h2}	S_{ch4}
α_C	0.40	0.59	0.59	0.55	0.55	0.49	0.49	0.40	0.41	0.27	0.20	0	0	0	0	0	0	0	0.75
α_H	0.07	0.10	0.09	0.09	0.08	0.08	0.07	0.07	0.05	0	0.02	0.22	0.18	0.01	0.02	1.00	0.06	1.00	0.25
α_O	0.53	0.31	0.32	0.36	0.37	0.43	0.44	0.53	0.54	0.73	0.78	0	0	0.67	0.66	0	0.94	0	0
α_N	0	0	0	0	0	0	0	0	0	0	0	0.78	0.82	0	0	0	0	0	0
α_P	0	0	0	0	0	0	0	0	0	0	0	0	0	0.32	0.32	0	0	0	0

	S_{aa}	S_{fa}	S_i	X_c	X_{ch}	X_{pr}	X_{li}	X_{su}	X_{aa}	X_{fa}	X_{c4}	X_{pro}	X_{ac}	X_{h2}	X_i
α_C	0.47	0.75	0.56	0.57	0.40	0.47	0.76	0.51	0.51	0.51	0.51	0.51	0.51	0.51	0.56
α_H	0.10	0.13	0.06	0.08	0.06	0.10	0.12	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
α_O	0.28	0.12	0.28	0.28	0.53	0.28	0.11	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28
α_N	0.15	0.00	0.09	0.06	0.00	0.15	0.00	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.09
α_P	0.00	0.00	0.01	0.01	0.01	0.00	0.01	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.01

	S_{va}	S_{bu}	S_{pro}	S_{ac}	S_{hco3}	S_{nh4}	S_{hpo4}	S_{h2po4}	S_h	S_{oh}
α_{Ch}	−0.0099	−0.011	−0.014	−0.017	−0.016	0.0556	−0.021	−0.01	1	−0.059

Table 4 ThOD per unit of mass for the ADM1 components

	S_{su}	S_{aa}	S_{fa}	S_{hva}	S_{va-}	S_{hbu}	S_{bu-}	S_{hpro}	S_{pro-}	S_{hac}	S_{ac-}	S_{h2}	S_{ch4}
γ_i	1.067	1.516	2.920	2.039	2.059	1.818	1.839	1.513	1.534	1.067	1.085	8.0	4.0
	S_i	X_c	X_{ch}	X_{pr}	X_h	X_{su}	X_{aa}	X_{fa}	X_{c4}	X_{pro}	X_{ac}	X_{h2}	X_i
γ_i	1.552	1.842	1.0627	1.516	2.890	1.393	1.393	1.393	1.393	1.393	1.393	1.393	1.552

M. de Gracia *et al.*

Table 5 Mass and charge conversion parameters of the ADM1 components

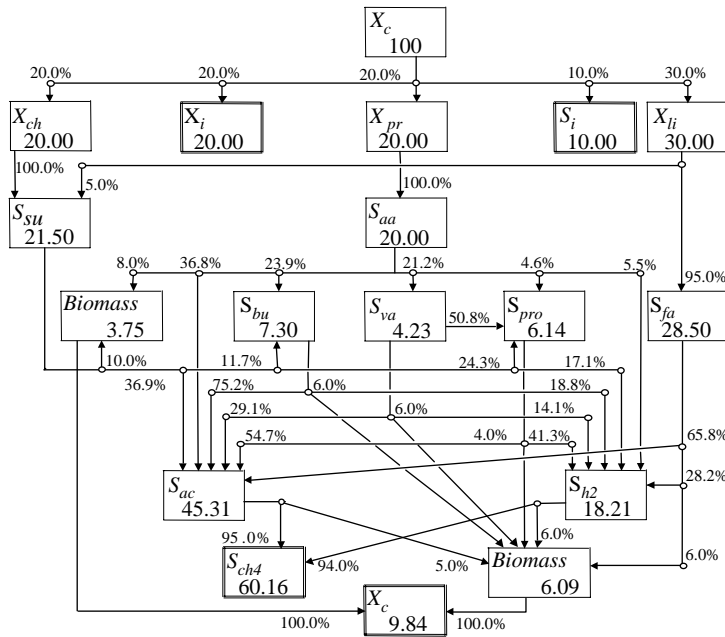| i		$\beta_{C,I}$	$\beta_{H,I}$	$\beta_{O,I}$	$\beta_{N,I}$	$\beta_{P,I}$	$\beta_{Ch,I}$
1	S_{su}	0.375	0.062	0.500	–	–	–
2	S_{aa}	0.310	0.066	0.185	0.099	–	–
3	S_{fa}	0.257	0.044	0.041	–	–	–
4	S_{hva}	0.288	0.048	0.154	–	–	–
5	S_{va-}	0.288	0.043	0.154	–	–	−0.005
6	S_{hbu}	0.300	0.050	0.200	–	–	–
7	S_{bu-}	0.300	0.044	0.200	–	–	−0.006
8	S_{hpro}	0.321	0.054	0.286	–	–	–
9	S_{pro-}	0.321	0.045	0.286	–	–	−0.009
10	S_{hac-}	0.375	0.062	0.500	–	–	–
11	S_{ac-}	0.375	0.047	0.500	–	–	−0.016
12	S_{cO2}	12	–	32	–	–	–
13	S_{hcO3-}	12	1	48	–	–	−1
14	S_{nh4}	–	4	–	14	–	1
15	S_{nh3}	–	3	–	14	–	–
16	S_{hpO4}	–	1	64	–	31	−2
17	S_{h2pO4-}	–	2	64	–	31	−1
18	S_{h-}	–	1	–	–	–	1
19	S_{oh+}	–	1	16	–	–	−1
20	S_{h2}	–	0.125	–	–	–	–
21	S_{ch4}	0.187	0.062	–	–	–	–
22	S_I	0.361	0.039	0.180	0.058	0.006	–
23	X_c	0.310	0.047	0.151	0.031	0.004	–
24	X_{ch}	0.388	0.058	0.515	–	0.010	–
25	X_{pr}	0.310	0.066	0.185	0.099	–	–
26	X_h	0.263	0.041	0.038	–	0.003	–
27	X_{su}	0.366	0.043	0.201	0.086	0.021	–
28	X_{aa}	0.366	0.043	0.201	0.086	0.021	–
29	X_{fa}	0.366	0.043	0.201	0.086	0.021	–
30	X_{c4}	0.366	0.043	0.201	0.086	0.021	–
31	X_{pro}	0.366	0.043	0.201	0.086	0.021	–
32	X_{ac}	0.366	0.043	0.201	0.086	0.021	–
33	X_{h2}	0.366	0.043	0.201	0.086	0.021	–
34	X_I	0.361	0.039	0.180	0.058	0.006	–
35	G_{co2}	12	–	32	–	–	–
36	G_{h2}	–	0.125	–	–	–	–
37	G_{ch4}	0.187	0.062	–	–	–	–
38	G_{h2o}	–	0.889	–	–	–	–
39	S_{h2o}	–	0.1111	0.889	–	–	–

Figure 1 COD flow chart for the anaerobic digestion of 100 gCOD of X_c

carbon (S_{co2}; S_{hco3-}) or nitrogen (S_{nh4+}; S_{nh3}). The pH calculation has been incorporated by means of cations (S_{h+}) (Siegrist *et al.*, 2002), hydroxyls (S_{oh+}) and water (S_{h2o}). Two more acid-base processes and one gas–liquid transfer process have also been added, to represent the phosphate and water equilibrium and the water evaporation respectively. Finally, to complete the ADM1 gas: liquid transfer kinetics four additional components associated to the gaseous state of CH_4 (G_{ch4}), H_2 (G_{h2}), CO_2 (G_{co2}) and H_2O (G_{h2o}) have been considered for mass balancing. Table 2 shows the extended stoichiometric matrix and the components considered.
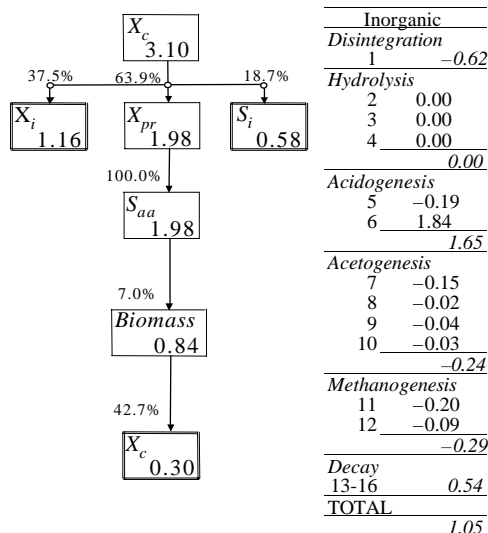
Figure 2 N mass flow chart of a mass of nitrogen equivalent to 100 g of COD of X_c. Mass of N formed or consumed (table)

	S_{co2}	S_{nh4+}	$S_{hpo4=}$	S_{h+}	S_{H2O}
Disintegration					
1	−6.36	−0.80	−0.18	4.1E–02	−0.73
Hydrolysis					
2	0.99	0.00	0.60	1.3E–02	−0.93
3	0.00	0.00	0.00	0.0E+00	0.00
4	0.03	0.00	0.32	6.7E–03	−1.14
	1.02	*0.00*	*0.92*	*19.7E–03*	*−2.07*
Acidogenesis					
5	6.84	−0.24	−0.14	1.0E–02	−0.59
6	−0.36	2.37	−0.11	−1.3E–01	−2.08
	6.48	*2.13*	*−0.25*	*−1.2E–01*	*−2.67*
Acetogenesis					
7	−1.24	−0.19	−0.11	8.1E–03	−8.52
8	−0.09	−0.03	−0.02	1.2E–03	−0.62
9	−0.11	−0.05	−0.03	2.1E–03	−1.44
10	3.09	−0.04	−0.02	1.6E–03	−2.47
	1.65	*−0.31*	*−0.18*	*1.3E–02*	*−13.05*
Methanogenesis					
11	29.66	−0.25	−0.15	1.1E–02	0.81
12	−13.23	−0.12	−0.07	5.2E–03	10.63
	16.43	*−0.37*	*−0.22*	*1.6E–02*	*11.44*
Decay					
13-16	*2.04*	*0.70*	*0.52*	*−2.8E–02*	*−1.52*
TOTAL					
	21.27	*1.35*	*0.61*	*−6.2E–02*	*−8.60*

Figure 3 Mass flow chart for the anaerobic digestion of the equivalent in mass of 100 gCOD of X_c (chart). Mass of inorganic components formed or consumed in each process (table)

Conversion parameters for the ADM1 components

Elemental mass fractions and charge density. All model components must have their associated elemental mass fractions in C, H, O, N and P and their charge density. The mass fractions assigned to components without a fixed molecular formula should agree with the literature (Eastman and Ferguson, 1981; Miron *et al.*, 2000) satisfying the following assumptions: A 28% mass of *oxygen* is estimated for the inorganic compounds and biomass (Reichert *et al.*, 2001). In the same way, a 3% in mass of *phosphorous* has been considered for the biomass, 1% for the generic organic compound (X_c), inerts (S_i, X_i), carbohydrates (X_{ch}) and lipids (X_{li}) and 0% for amino acids (S_{aa}), long chain fatty acids (S_{fa}) and protein (X_{pr}). Mass fractions in the elements *carbon*, *nitrogen* and *hydrogen* have been estimated so that they are equivalent to the parameters suggested by the ADM1 report and to satisfy equation (1). In order to avoid nitrogen release in the hydrolysis processes, it is suggested to consider similar C and N mass fractions for the proteins and amino acids. The elemental mass fractions of the generic organic compound (X_c) have been estimated in coherence with the corresponding mass fractions of the particulate inerts, proteins, carbohydrates and lipids. The resulting elemental mass fractions and charge density are shown in Table 3.

ThOD by unit of mass. Once the procedure for the ThOD calculation has been established (Table 1) and the elemental mass fractions have been estimated (Table 3), the value of ThOD per unit of mass γ_i can be calculated. Table 4 is included to present the value of ThOD per unit of mass of the ADM1 components that are expressed in terms of COD.

Conversion parameters. Table 5 shows the mass and charge conversion factors obtained for each of the model components, considering their stoichiometric unit.

Mass and charge balances of the ADM1 model

Once the elemental mass fractions and charge density for each model component have been established and the numerical values of the stoichiometric matrix have been evaluated (Table 2), all conversion parameters (Table 5) can be calculated and the six balance

equations (3) can be directly checked, detecting any possible imbalance in mass or charge. Additional stoichiometric matrices can be built in terms of C, H, O, N, P and charge, and thus the flux of mass in the model transformations can be analysed in depth.

If all the matrices are properly introduced in linked worksheets, any change in the elemental mass fractions will be automatically reflected to the stoichiometric matrices without any imbalance in mass or charge. Figure 1 and Figure 2 show the flow chart of the organic matter and nitrogen mass for the elemental mass fractions previously selected (Table 3). The table in this figure shows the inorganic nitrogen produced (positive) and consumed (negative) in each step of the process. A similar analysis can be made for the remaining elements and the electric charge. Figure 3 shows the flow chart of the mass of 100 gCOD of X_c. The table inside the figure contains the mass of inorganic components formed and consumed in each step. Any other flow chart could be easily constructed from the mass fractions, the stoichiometric matrix and the conversion parameters.

Mass flow diagrams can be used to study the influence of elemental mass fractions. For example, the stoichiometric coefficients for X_c disintegration should be coherent with the elemental mass fractions of composites, lipids, proteins, carbohydrates and inert components, in order to reduce mass compensation by the source-sink components (like carbon dioxide, ammonia, etc.). Note in Figure 3 that for the selected mass fractions and model parameters, a noticeable amount of CO_2 is being consumed when disintegration occurs in order to maintain the carbon balance. This suggests that the selected elemental mass fractions or the fractionation of X_c should be tuned. Mathematical tools (e.g. MS Excel's solver) can be used to minimize the errors in the assumptions.

The nitrogen mass flow chart can be easily used to predict the nitrogen recycled from the anaerobic digestion to the water line (Zaher *et al.*, 2002). For example, according to Figure 2, 3.10 g of influent TKN will release 1.05 g of ammonium/ammonia (34%) that would be partially recycled to the water treatment line in a WWTP. Finally, the composition of the biogas produced can be also analysed using these figures. For instance, Figures 1 and 3 show that, for the model coefficients used in the paper, 100 gCOD of X_c will produce 60.16 gCOD of CH_4 (equivalent to 0.94 moles of CH_4) and 21.27 g of CO_2 (equivalent to 0.48 moles of CO_2), in total coherence with the gas composition reported in the literature (66% of CH_4 and 34% of CO_2) (Gujer and Zehnder, 1983). For different mass fractions, the estimation of biogas production will change. For example, an X_c fractionation of 30% inerts and 70% lipids will result in a biogas composition of 77% of CH_4 and 23% of CO_2.

Conclusions

The aim of this paper was to introduce a systematic way of applying the methodology proposed in the RWQM1 for the definition and analysis of dynamic models represented in the Peterson matrix structure. This methodological application is based on the selection of the model components, including "source-sink" components of mass and charge, the definition of their elemental mass composition and charge, and the estimation of the relationship between mass and COD.

The potential of models based on elemental mass fraction has been proven. It makes a rigorous mass balance and the detection of possible imbalances easier, whether they are in the definition of the model or in the estimation of the elemental compositions. The stoichiometric matrix can be completely filled as a function of the elemental composition of the model components. Furthermore, its application makes the prediction of the COD/VSS ratio in different unit-processes, the analysis of mass fluxes in the processes and a possible standardisation of model definition easier. It also can simplify modelling

due to its versatility, as any measurement unit can be easily used (COD, total carbon, mole, mass) for the description of the model components.

The ADM1 model was easily adapted to this methodology with the incorporation of some model components and some transformations. This adaptation has turned out to be useful for selecting the elemental composition of the substrates (X_c) and by analysing, via the mass fluxes obtained, the effect of the type of waste on the resulting products (methane, carbon dioxide, etc.). The proposed methodology may be a new step forward in the standardisation of the mathematical modelling methodology of biological WWTPs. It also can facilitate the rigorous development of new interfaces for connecting the different plant's processing units, integrating the existing models for the sludge and water lines (the "plant-wide modelling" objective).

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