


# GREY-BOX DYNAMIC MODEL OF A DRINKING WATER TREATMENT PLANT

Blaž Korotaj<sup>1</sup>, Hrvoje Novak<sup>2</sup> and Mario Vašak<sup>3</sup>

<sup>1,2,3</sup>University of Zagreb, Faculty of Electrical Engineering and Computing, Laboratory for Renewable Energy Systems (url: [www.lares.fer.hr](http://www.lares.fer.hr)), Unska 3, HR-10000, Zagreb, Croatia

<sup>1</sup> [blaz.korotaj@fer.hr](mailto:blaz.korotaj@fer.hr), <sup>2</sup> [hrvoje.novak@fer.hr](mailto:hrvoje.novak@fer.hr), <sup>3</sup> [mario.vasak@fer.hr](mailto:mario.vasak@fer.hr)

## Abstract

In the paper a concept of a general reaction volume in a drinking water treatment plant (DWTP) is introduced, where several such volumes need to be stacked in series with corresponding input chemicals used in them to finally represent the entire plant. A general case in which a reaction volume is not fixed is elaborated. The overall derived plant model is of a grey-box form with a small number of tunable parameters, which is beneficial for adaptation to a particular DWTP based on its laboratory and on-line measured data.

The developed mathematical models of reaction volumes are stacked and inputs in different volumes selected such that they represent a concrete DWTP for which a decision-support system is being developed. A preliminary validation is performed against laboratory-determined plant input-output data.

## Keywords

DWTP, reaction volume, fast reactions, dynamical model.

## 1 INTRODUCTION

The extremes of raw water shortage and abundance tend to raise frequency due to climate change effects, with the corresponding chemical content considerably varying over shortening time periods. On the other hand, the drinking water produced from raw water must meet the dynamic quantity requirements of water distribution systems and at the same time the quality requirements that are getting stricter and stricter. This makes the drinking water production in drinking water treatment plants (DWTPs) a dynamically demanding process in which the operators' experience for running the plant, related often to steady-state recipes, should be additionally supported for a more resilient water service. The DWTP management task is further aggravated with non-availability of on-line sensory data for different water quality parameters in the plant. A first-hand solution to the raised situation comes in a form of a decision-support system for the DWTP operation relied on model predictive control (MPC) principles, while in a long-run it should evolve to a closed-loop optimal control system where the operators are left out of the control loop and just have a supervisory and monitoring role. In order to create a decision-support system for highly dynamical plant conditions described above and also enable soft-sensing for plant monitoring, a dynamical model of the DWTP is needed.

Different software tools exist to relate raw and treated water quality parameters for a DWTP. A very popular one is EPA WTP [1] which in the back-end uses static or quasi-dynamic empirical models, recently enriched also with stochastic modelling to represent relations between spreads of inputs and outputs. There are also attempts to build-up detailed dynamical models for specific parts of a DWTP with a high number of parameters that require complex tuning [2]. The framework of Mixed Logical Dynamical (MLD) systems [3] is also tried for modeling and control of a DWTP [4]. The main drawback here is the computation time.

Significant research focus is put on making DWTP models using artificial neural networks [5], [6]. The main disadvantage in that case is ensuring the appropriate structure of the network and of

course the need for a large amount of process data for parameters tuning. Dynamical model and system identification of coagulant dosage system for DWTPs have been presented as well [7]. In [7] the model is based only on mixing different concentrations of elements entering the tank, while neglecting a very important issue which are time-transients in concentration due to chemical reactions that take place. There exists a lack of systematic approaches to modelling the entire DWTP with a simply parametrizable dynamic model and this article stems from the intention to fill this gap and enable dynamic decision-support for DWTPs based on MPC.

In this paper, a major simplifying assumption is that all chemical reactions that take place in DWTP reaction volumes are performed instantaneously when all reactants are present, in the amount dictated by the scarcest reactant that is annihilated. The dynamic DWTP model consists of a series of generalized reaction volumes where the volume can be fixed or varying. While deriving a dynamic model for a single generalized reaction volume, the number of tuneable parameters is kept low by exploiting mathematical descriptions of the underlying physical and chemical processes (grey-box approach). The DWTP considered in this paper consists of 4 reaction volumes, but the modelling framework is readily adaptable to different numbers of reaction volumes. In the considered DWTP model, the pre-oxidation processes take place in the first and second reaction volumes, the third reaction volume is used for coagulation, flocculation, sedimentation and filtering processes, while the fourth reaction volume is used for final chlorination and pH correction. The model is created and tested in the Matlab/Simulink software environment. For the considered DWTP in Spain, the values of the water quality variables simulated by the model at the outlet of the final reaction volume are compared with the actual laboratory measurements for a preliminary validation.

The paper is structured as follows: Section 2 describes the modelling of a DWTP reaction volume; the dynamical model for the full plant is set in Section 3, while Section 4 reports the simulation results in Matlab/Simulink and the laboratory data comparison.

## 2 MODELLING OF A DRINKING WATER TREATMENT PLANT

Drinking water treatment plants (DWTPs) receive raw water and perform necessary chemical and mechanical treatment upon it to achieve drinking water standards. The focus of the paper is put on the chemical treatments in different reaction volumes of DWTPs. Thus, the whole model includes the models of individual reaction volumes as building elements in which different chemical reactions of the water treatment plant occur.

### 2.1 Model for fast reactions with two reactants

Before modelling the concrete chemistry of a DWTP, the extensively used modelling framework of fast chemical reactions is introduced.

Assume that the following chemical reaction is given:



where  $a$  and  $b$  are stoichiometric coefficients. Using the ratio of stoichiometric coefficients, one can write differential equations of changes in the concentrations of reactants A and B:

$$V \frac{d[A]}{dt} = (q_{A_{in}}[A]_{in} - \frac{a}{b}q_{B_{in}}[B]_{in}) - (q_{A_{in}} + q_{B_{in}})[A] - V \cdot \frac{a}{b} \cdot [B] \cdot \delta(f([B])), \quad (2)$$

$$V \frac{d[B]}{dt} = (q_{B_{in}}[B]_{in} - \frac{b}{a}q_{A_{in}}[A]_{in}) - (q_{A_{in}} + q_{B_{in}})[B] - V \cdot \frac{b}{a} \cdot [A] \cdot \delta(f([A])), \quad (3)$$

where  $[A]_{in}$  ( $\frac{\text{mol}}{\text{L}}$ ) and  $[B]_{in}$  ( $\frac{\text{mol}}{\text{L}}$ ) are the concentrations in the input carrier fluids of A and B,  $V$  (L) is the volume of the tank where the reaction takes place,  $q_{A_{in}}$  ( $\frac{\text{L}}{\text{s}}$ ) and  $q_{B_{in}}$  ( $\frac{\text{L}}{\text{s}}$ ) are the volume flows

of carrier fluids for solutes A and B,  $\delta$  is the Dirac delta function, while the function  $f(x)$  is defined as:

$$f(x) = \begin{cases} \neq 0 & \text{for } x = 0, \\ 0 & \text{for } x > 0. \end{cases} \quad (4)$$

Since the concentrations cannot be negative, the following inequalities hold:

$$[A] \geq 0, [B] \geq 0. \quad (5)$$

The corresponding time-discretized system is:

$$[A]_{k+1} = \max(0, \alpha[A]_k + (1 - \alpha)([A]_{in,k} - \frac{a}{b}[B]_{in,k}) - \frac{a}{b}[B]_k), \quad (6)$$

$$[B]_{k+1} = \max(0, \alpha[B]_k + (1 - \alpha)([B]_{in,k} - \frac{b}{a}[A]_{in,k}) - \frac{b}{a}[A]_k), \quad (7)$$

where  $\alpha = e^{-\frac{T_s}{T}}$ ,  $T_s$  is the model sampling time,  $[X]_k = [X](kT_s)$  and  $T = \frac{V}{q_{A_{in}} + q_{B_{in}}}$ .

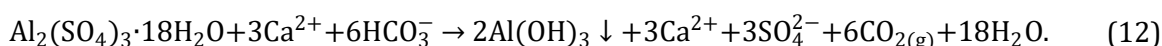
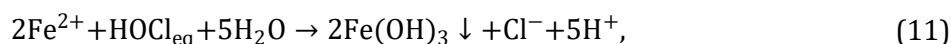
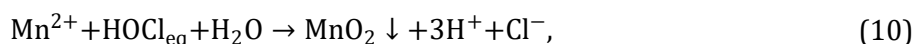
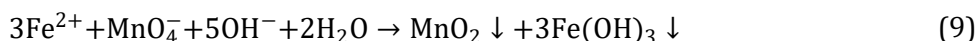
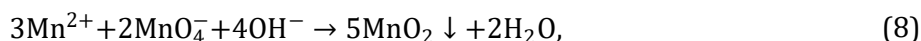
## 2.2 Chemical reactions in a DWTP

The considered chemical reactants in the reaction volumes of a DWTP are presented in Table 1. First two columns represent raw water chemical impurities, and the third and fourth columns represent reactants appearing in the reaction volumes due to the chemical treatments, with the exception of  $[Ca^{2+}]$  that can come both from the raw water and from the applied chemicals.

Table 1. The list of considered concentrations of chemical elements with their corresponding units. The variables are expressed in (mol/L).

Description	Variable	Description	Variable
Manganese	$[Mn^{2+}]$	Sulfate	$[SO_4^{2-}]$
Iron	$[Fe^{2+}]$	Total free chlorine	$[HOCl]_{eq}$
Bicarbonate	$[HCO_3^-]$	Permanganate	$[MnO_4^-]$
Magnesium	$[Mg^{2+}]$	Potassium	$[K^+]$
Calcium	$[Ca^{2+}]$	Chloride ion	$[Cl^-]$
Total organic carbon	[TOC]	Aluminium	$[Al^{3+}]$

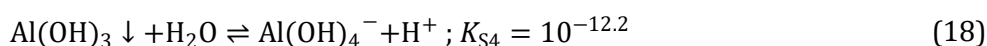
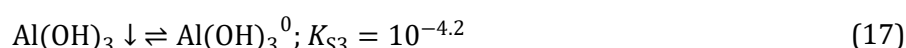
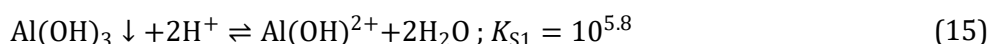
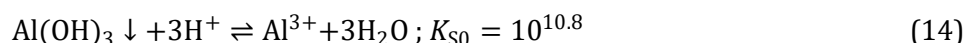
The chemical reactions considered for the DWTP are as follows [7], [8], [9], [10]:



Notation  $[HOCl]_{eq}$  represents the equivalent amount of total free chlorine and it is given as [11]:

$$[HOCl]_{eq} = [HOCl] + [ClO^-]. \quad (13)$$

Reactions (10) and (11) occur as long as one of the compounds in equation (13) exists, that is, as long as  $[\text{HOCl}]_{\text{eq}}$  is larger than zero. Further, all of the concentrations in the index marked by the letters 'eq' represent the total concentration of all species of that element, which are in a certain balance, and cause a reaction as long as the total concentration is larger than zero since due to the balance established this implies that also the reacting species is present. In case free ions appear on the right-hand side of the reaction, then this should be considered as in the case of (10) because they affect the pH value. In general, also other reactions can be modelled as far as the stoichiometry and reaction rates are known (the latter is needed only for slow reactions). The following bidirectional chemical reactions are also considered [8]:



where the constants  $K_{S0} - K_{S4}$  represent the solubility constants for each of the hydroxide species listed in reactions (14) – (18).

Chemical reaction (8) is an oxidation-reduction (redox) reaction [12] where ( $\text{Mn}^{2+}$ ) is a reducing agent and ( $\text{MnO}_4^-$ ) is an oxidizing agent. The product is manganese dioxide ( $\text{MnO}_2$ ) which precipitates. The next chemical reaction (9) is analogous to the previous one except that in it now ( $\text{Fe}^{2+}$ ) is the reducing agent. Here the products are manganese dioxide ( $\text{MnO}_2$ ) and iron hydroxide ( $\text{Fe(OH)}_3$ ) which precipitates. Chemical reactions (10) and (11) show how manganese ( $\text{Mn}^{2+}$ ) and iron ( $\text{Fe}^{2+}$ ) react with the hypochlorous acid ( $\text{HOCl}$ ). The products are manganese dioxide ( $\text{MnO}_2$ ) and iron hydroxide ( $\text{Fe(OH)}_3$ ) along with the chloride ion ( $\text{Cl}^-$ ). Chemical reaction (12) is a gas evolution reaction because ( $\text{CO}_2$ ) gas is formed. It is a precipitation reaction as well because aluminium hydroxide ( $\text{Al(OH)}_3$ ) precipitates in the amount that cannot be dissolved. Aluminium hydroxide ( $\text{Al(OH)}_3$ ) is formed when aluminium sulfate is injected to water for coagulation and particles destabilization. Calcium and sulfate in (12) react and form calcium sulfate only if the following condition according to [13] is met:

$$[\text{Ca}^{2+}][\text{SO}_4^{2-}] > K_{\text{so,CaSO}_4}, \quad (19)$$

where  $K_{\text{so,CaSO}_4}$  is the solubility constant for gypsum. If the above condition is not met, calcium and sulfate remain dissolved in water. A similar condition applies to the precipitation of calcite ( $\text{CaCO}_3$ ). That is, if ( $\text{Ca}^{2+}$ ) and ( $\text{HCO}_3^-$ ) are present, ( $\text{CaCO}_3$ ) will precipitate if the following condition is met:

$$[\text{Ca}^{2+}][\text{HCO}_3^-]^2 > K_{\text{so,CaCO}_3}, \quad (20)$$

where  $K_{\text{so,CaCO}_3}$  is the solubility constant for calcium carbonate. If condition (20) is not met, ( $\text{Ca}^{2+}$ ) and ( $\text{HCO}_3^-$ ) remain dissolved in water.

The total amount of dissolved aluminium that enters the reaction volume is calculated as follows:

$$[\text{Al}^{3+}]_{\text{eq, in}} = \min([\text{Al}^{3+}]_{\text{in}}, K_{S0}[\text{H}^+]_{\text{prv}}^3 + K_{S1}[\text{H}^+]_{\text{prv}}^2 + K_{S2}[\text{H}^+]_{\text{prv}} + K_{S3} + \frac{K_{S4}}{[\text{H}^+]}) \quad (21)$$

where  $[\text{Al}^{3+}]_{\text{in}}$  is the input concentration of aluminium and  $[\text{H}^+]_{\text{prv}}$  is the hydrogen-ion concentration from the previous reaction volume. In (12) only a part of aluminium that enters the reaction volume reacts with bicarbonate, i.e. the aluminium that enters the reaction volume reduced by dissolved aluminium which is represented as aluminium ion and various aluminium hydroxides. The non-dissolved aluminium hydroxide ( $\text{Al(OH)}_3$ ) forms aluminium hydroxide flocs

used to adsorb a part of total organic carbon (TOC) present in the treated water. Its concentration is included in the DOSE variable explained in the next subsection that deals with TOC removal by coagulation (and consequent flocculation).

### 2.3 Edwards model

Besides the chemical equations provided, another mechanism considered is the removal of total organic carbon by coagulation, for which the Edward's model [14] is used. It is a Langmuir-based semiempirical model for quantification of TOC removal by coagulation, flocculation and subsequent sedimentation and filtering. The model is a nonlinear function derived from physical relationships, primarily from the process of Langmuir sorptive removal. It conceptually divides the initial TOC ( $TOC_{initial}$ ) into sorbable and non-sorbable fractions, whose proportion is modelled as a function of the specific UV absorbance (SUVA). The final sorbable TOC concentration  $TOC_{final,sorb}$  ( $\frac{mol}{L}$ ) satisfies the quadratic equation [8]:

$$[TOC]_{final,sorb}^2 - [TOC_{final,sorb}] \left( [TOC_{initial,sorb}] - \frac{1}{bM_{TOC}} - \frac{a \cdot DOSE}{M_{TOC}} \right) - \frac{[TOC_{initial,sorb}]}{bM_{TOC}^2} = 0, \quad (22)$$

where  $M_{TOC}$  ( $\frac{mg}{mol}$ ) is the molar mass of TOC, DOSE ( $\frac{mmol}{L}$ ) is the coagulant dose, i.e. the concentration of aluminium hydroxide ( $Al(OH)_3$ ) formed by the addition of aluminium sulfate,  $b$  ( $\frac{L}{mg}$ ) is the Langmuir equilibrium constant,  $a$  ( $\frac{mg\ TOC}{mmol\ coagulant}$ ) is the total adsorbent capacity at monolayer coverage, approximated as a cubic polynomial function of pH:

$$a = x_3 \cdot pH^3 + x_2 \cdot pH^2 + x_1 \cdot pH, \quad (23)$$

and  $x_1$ ,  $x_2$  and  $x_3$  are empirical coefficients. Additionally,  $TOC_{initial,sorb}$  ( $\frac{mol}{L}$ ) is the input water concentration of sorbable total organic carbon approximated as a function of the input water SUVA:

$$TOC_{initial,sorb} = TOC_{initial}(1 - SUVA \cdot K_1 - K_2), \quad (24)$$

where  $K_1$  and  $K_2$  are empirical coefficients and  $TOC_{initial}$  ( $\frac{mol}{L}$ ) is the initial concentration of TOC. SUVA can be expressed as:

$$SUVA = \frac{UV_{254}}{TOC_{initial}}, \quad (25)$$

where  $UV_{254}$  ( $\frac{1}{cm}$ ) is the UV absorbance at a wavelength of 254 nm. According to [15],  $UV_{254}$  is linearly dependent on TOC and the expression for  $TOC_{initial,sorb}$  becomes:

$$TOC_{initial,sorb} = TOC_{initial}(1 - K_2) - K_1 \cdot \frac{M_{TOC} TOC_{initial} - l}{kM_{TOC}}, \quad (26)$$

where  $k$  and  $l$  are coefficients of equation of a line which connects TOC and  $UV_{254}$ .

Finally, the concentration of TOC in the corresponding reaction volume  $TOC_{final}$  ( $\frac{mol}{L}$ ) can be calculated as:

$$TOC_{final} = TOC_{final,sorb} + K_1 \cdot \frac{M_{TOC} TOC_{initial} - l}{kM_{TOC}} + K_2 \cdot TOC_{initial}, \quad (27)$$

where  $\text{TOC}_{\text{final,sorb}}$  can be determined by combining the quadratic equation (22) and the expression for  $\text{TOC}_{\text{initial,sorb}}$  (24). If DOSE is equal to zero, the combination of all the previous expressions easily gives that:

$$\text{TOC}_{\text{final}} = \text{TOC}_{\text{initial}}. \quad (28)$$

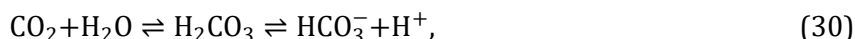
To write a differential equation for TOC, the following function is used:

$$h(K_1, K_2, x_1, x_2, x_3, \text{DOSE}, \text{pH}, \text{TOC}_{\text{initial}}) = \begin{cases} \text{TOC}_{\text{final}} & \text{if DOSE} > 0 \\ \text{TOC}_{\text{initial}} & \text{if DOSE} = 0 \end{cases} \quad (29)$$

which summarizes the Edwards model explained above.

## 2.4 Bicarbonate buffer system

Dissolved carbon dioxide ( $\text{CO}_2$ ) reacts with water ( $\text{H}_2\text{O}$ ) to form carbonic acid ( $\text{H}_2\text{CO}_3$ ), which in turn quickly dissociates to form a bicarbonate ion ( $\text{HCO}_3^-$ ) and a hydrogen ion ( $\text{H}^+$ ) as shown in the following reactions:



The presence of both a weak acid (for example,  $\text{H}_2\text{CO}_3$ ) and its conjugate base (for example,  $\text{HCO}_3^-$ ) balances the pH as a buffer system, neutralizing any excess acid or base given to the system. To relate the pH of water to bicarbonate buffer system elements, a modified version of the Henderson–Hasselbalch equation can be used [16]:

$$[\text{H}_2\text{CO}_3] = \frac{[\text{H}^+][\text{HCO}_3^-]}{K_{\text{H}_2\text{CO}_3}}, \quad (32)$$

$$[\text{HCO}_3^-] = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{K_{\text{HCO}_3^-}}, \quad (33)$$

where  $K_{\text{H}_2\text{CO}_3}$  ( $10^{-6.35} \frac{\text{mol}}{\text{L}}$ ) and  $K_{\text{HCO}_3^-}$  ( $10^{-10.22} \frac{\text{mol}}{\text{L}}$ ) are the acidity constants for carbonic acid and bicarbonate ion, respectively.

The sum of the concentration of the total inorganic carbon species in the water, including carbonic acid ( $\text{H}_2\text{CO}_3$ ), bicarbonate ( $\text{HCO}_3^-$ ) and carbonate ( $\text{CO}_3^{2-}$ ) is called dissolved inorganic carbon. Concentration of carbonic acid  $[\text{H}_2\text{CO}_3]$  is the sum of  $[\text{CO}_2]$  and  $[\text{H}_2\text{CO}_3]$  because the dissolved fraction of total ( $\text{CO}_2$ ) in water is small and hydrolyses to ( $\text{H}_2\text{CO}_3$ ). So, the total concentration of dissolved inorganic carbon  $[\text{H}_2\text{CO}_3]_{\text{eq}}$  is defined as:

$$[\text{H}_2\text{CO}_3]_{\text{eq}} = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]. \quad (34)$$

Combining expressions (32), (33) and (34) yields expressions for bicarbonate ion and carbonate ion depending only on dissolved inorganic carbon:

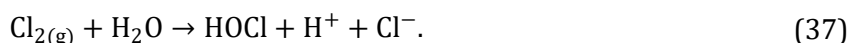
$$[\text{HCO}_3^-] = \frac{[\text{H}_2\text{CO}_3]_{\text{eq}}[\text{H}^+]K_{\text{H}_2\text{CO}_3}}{[\text{H}^+]^2 + K_{\text{H}_2\text{CO}_3}[\text{H}^+] + K_{\text{H}_2\text{CO}_3}K_{\text{HCO}_3^-}}, \quad (35)$$

$$[\text{CO}_3^{2-}] = \frac{[\text{H}_2\text{CO}_3]_{\text{eq}}K_{\text{H}_2\text{CO}_3}K_{\text{HCO}_3^-}}{[\text{H}^+]^2 + K_{\text{H}_2\text{CO}_3}[\text{H}^+] + K_{\text{H}_2\text{CO}_3}K_{\text{HCO}_3^-}}. \quad (36)$$



## 2.5 Dissolved free chlorine

The reaction of gaseous chlorine with water is instantaneous and is defined with the following reaction [11]:



The concentrations in equilibrium of the hypochlorous acid (HOCl) and the hypochlorite ion ( $\text{ClO}^-$ ) with dissolved chlorine are connected in the following way:

$$[\text{ClO}^-] = \frac{[\text{HOCl}]_{\text{eq}}}{1 + \frac{[\text{H}^+]}{A}} \quad (38)$$

where  $A$  ( $10^{-7.53} \frac{\text{mol}}{\text{L}}$ ) is the acidity constant for the hypochlorite ion. From (38) it can be seen that for the current pH of water, i.e. for the current  $[\text{H}^+]$ ,  $[\text{HOCl}]$  and  $[\text{ClO}^-]$  are analytically tied together. It is important to model disinfectant decay ( $[\text{HOCl}]_{\text{eq}}$ ) after a fast chemical reaction in this scenario, according to [8]. Disinfectant decay can be modeled as first order, that is:

$$r_d = -k_d [\text{HOCl}]_{\text{eq}} \quad (39)$$

where  $r_d$  ( $\frac{\text{mol}}{\text{L}\cdot\text{s}}$ ) is the reaction rate for the decline in disinfectant concentration with time,  $k_d$  ( $\frac{1}{\text{s}}$ ) is the first-order decay rate.

## 2.6 Total dissolved calcium and magnesium

In the treatment of drinking water, lime is also used to enhance alkalinity and pH. Lime dissociates when it is added to water as follows:



The total dissolved calcium concentration is considered to be:

$$[\text{Ca}^{2+}]_{\text{eq}} = [\text{Ca}^{2+}] + [\text{CaOH}^+] + [\text{Ca}(\text{OH})_2], \quad (41)$$

where  $[\text{CaOH}^+]$  and  $[\text{Ca}(\text{OH})_2]$  are:

$$[\text{CaOH}^+] = \frac{[\text{Ca}^{2+}]K_{\text{CaOH}}}{[\text{H}^+]}, \quad (42)$$

$$[\text{Ca}(\text{OH})_2] = \frac{[\text{Ca}^{2+}]K_{\text{Ca}(\text{OH})_2}}{[\text{H}^+]^2}. \quad (43)$$

The coefficients  $K_{\text{CaOH}}$  and  $K_{\text{Ca}(\text{OH})_2}$  are the base dissociation constants for the calcium hydroxides.

The total dissolved magnesium concentration is expressed in a similar way:

$$[\text{Mg}^{2+}]_{\text{eq}} = [\text{Mg}^{2+}] + [\text{MgOH}^+] + [\text{Mg}(\text{OH})_2], \quad (44)$$

where  $[\text{MgOH}^+]$  and  $[\text{Mg}(\text{OH})_2]$  are:

$$[\text{MgOH}^+] = \frac{[\text{Mg}^{2+}]K_{\text{MgOH}}}{[\text{H}^+]}, \quad (45)$$

$$[\text{Mg}(\text{OH})_2] = \frac{[\text{Mg}^{2+}]K_{\text{Mg}(\text{OH})_2}}{[\text{H}^+]^2}, \quad (46)$$

and  $K_{\text{MgOH}}$  and  $K_{\text{Mg}(\text{OH})_2}$  are the base dissociation constants for the magnesium hydroxides as well.

### 3 MATHEMATICAL MODEL OF A DWTP

The drinking water treatment plant considered in this paper consists of four reaction volumes and is shown in Fig. 1.

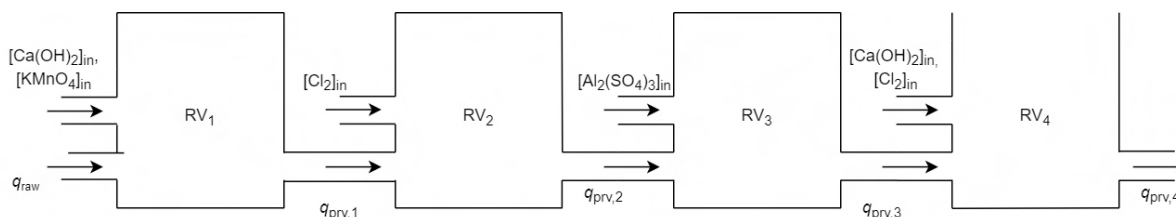


Figure 1 Scheme of the considered drinking water treatment plant

In the first reaction volume (RV<sub>1</sub>), pre-oxidation processes take place by adding the reagent potassium permanganate (KMnO<sub>4</sub>). Additionally, calcium hydroxide (lime – Ca(OH)<sub>2</sub>) is added to keep the pH stable. In the second reaction volume (RV<sub>2</sub>), chlorine gas (Cl<sub>2</sub>) is added to reduce the concentration of manganese (Mn<sup>2+</sup>) and iron (Fe<sup>2+</sup>). In the third reaction volume (RV<sub>3</sub>), coagulation, flocculation, sedimentation and filtering processes take place. In it aluminium sulfate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) is added to reduce the total organic carbon concentration. The fourth reaction volume (RV<sub>4</sub>) is used for the free chlorine establishment and pH correction. The optional addition of chlorine gas (Cl<sub>2</sub>) keeps the free chlorine on the desired level before entering the water distribution system while the optional addition of lime raises the pH to the desired value.

#### 3.1 Chemical reactions modelling

A general case in which a reaction volume  $V$  is not fixed is elaborated. One water stream from the previous reaction volume  $q_{in,1}$  is assumed, with the concentration  $[X]_{in,1}$  and also one input stream of the chemical dissolved in water carrier of flow  $q_{in,2}$  with the chemical concentration equal  $[X]_{in,2}$ . Now one can write the following differential equations for the substance  $X$  and the volume:

$$\frac{d}{dt}(V \cdot [X]) = [X] \frac{dV}{dt} + V \frac{d[X]}{dt} = q_{in,1}[X]_{in,1} + q_{in,2}[X]_{in,2} - q_{out}[X], \quad (47)$$

$$\frac{dV}{dt} = q_{in,1} + q_{in,2} - q_{out}. \quad (48)$$

Combining these equations, one gets:

$$[X](q_{in,1} + q_{in,2} - q_{out}) + V \frac{d[X]}{dt} = q_{in,1}[X]_{in,1} + q_{in,2}[X]_{in,2} - q_{out}[X], \quad (49)$$

$$V \frac{d[X]}{dt} = q_{in,1}([X]_{in,1} - [X]) + q_{in,2}([X]_{in,2} - [X]). \quad (50)$$

Equation (50) should be extended to account for the chemical reactions of appearance and disappearance of chemical element  $X$ . It has to be taken into account that the volume may change dynamically in case of imbalance between the input and output flows. The flow  $q_{out}$  is given externally or is defined with  $V$  in the case of hydraulically uncoupled tanks. Also,  $q_{out}$  is defined with current reaction volume  $V_{crv}$  and the next reaction volume in case of hydraulically coupled tanks.

For the case when the volume is fixed, one can write the following equation:

$$\frac{dV}{dt} = 0 \Rightarrow V = \text{const.} \quad (51)$$

In a similar way as described in section 2.1 one can obtain differential equations of concentrations of chemicals with respect to the previously introduced chemical reactions and



coagulation/flocculation. The reaction rates are considered infinite to simplify the model parametrization. In that case the reactions happen instantaneously and stop with the scarcest reactant vanished.

The subscript 'prv' is introduced, with the meaning 'previous reaction volume'. For presentation clarity, the following substitutions are introduced:

$$[\text{MnO}_4^-]_{\text{in,total}} = q_{\text{prv}} \cdot [\text{MnO}_4^-]_{\text{prv}} + q_{\text{KMnO}_4} \cdot [\text{KMnO}_4]_{\text{in}}, \quad (52)$$

$$[\text{K}^+]_{\text{in,total}} = q_{\text{prv}} \cdot [\text{K}^+]_{\text{prv}} + q_{\text{KMnO}_4} \cdot [\text{KMnO}_4]_{\text{in}}, \quad (53)$$

$$[\text{Cl}^-]_{\text{in,total}} = q_{\text{prv}} \cdot [\text{Cl}^-]_{\text{prv}} + q_{\text{Cl}_2} \cdot [\text{Cl}_2]_{\text{in}}, \quad (54)$$

$$[\text{HOCl}]_{\text{eq,in,total}} = q_{\text{prv}} \cdot [\text{HOCl}]_{\text{eq,prv}} + q_{\text{Cl}_2} \cdot [\text{Cl}_2]_{\text{in}}, \quad (55)$$

$$[\text{Ca}^{2+}]_{\text{eq,in,total}} = q_{\text{prv}} \cdot [\text{Ca}^{2+}]_{\text{eq,prv}} + q_{\text{Ca(OH)}_2} \cdot [\text{Ca(OH)}_2]_{\text{in}} - (q_{\text{prv}} + q_{\text{Ca(OH)}_2}) \cdot C, \quad (56)$$

$$C = \max\left(0, \frac{q_{\text{prv}} \cdot [\text{Ca}^{2+}]_{\text{eq,prv}} + q_{\text{Ca(OH)}_2} \cdot [\text{Ca(OH)}_2]_{\text{in}}}{q_{\text{prv}} + q_{\text{Ca(OH)}_2}} - [\text{CaCO}_3]_{\text{limit}}\right) + \max\left(0, \max\left(0, \frac{q_{\text{prv}} \cdot [\text{Ca}^{2+}]_{\text{eq,prv}} + q_{\text{Ca(OH)}_2} \cdot [\text{Ca(OH)}_2]_{\text{in}}}{q_{\text{prv}} + q_{\text{Ca(OH)}_2}} - [\text{CaCO}_3]_{\text{limit}}\right) - [\text{CaSO}_4]_{\text{limit}}\right), \quad (57)$$

$$[\text{H}_2\text{CO}_3]_{\text{eq,in,total}} = q_{\text{prv}} \cdot [\text{H}_2\text{CO}_3]_{\text{eq,prv}} - q_{\text{prv}} \cdot D, \quad (58)$$

$$D = \max(0, [\text{H}_2\text{CO}_3]_{\text{eq,prv}} - [\text{CaCO}_3]_{\text{limit}}), \quad (59)$$

$$[\text{Al}^{3+}]_{\text{eq,in,total}} = q_{\text{prv}} \cdot [\text{Al}^{3+}]_{\text{eq,prv}} + 2 \cdot q_{\text{Al}_2(\text{SO}_4)_3} \cdot [\text{Al}_2(\text{SO}_4)_3]_{\text{in}} - (q_{\text{prv}} + 2 \cdot q_{\text{Al}_2(\text{SO}_4)_3}) \cdot \text{DOSE}, \quad (60)$$

$$\text{DOSE} = \max\left(0, \frac{q_{\text{prv}} \cdot [\text{Al}^{3+}]_{\text{prv}} + 2 \cdot q_{\text{Al}_2(\text{SO}_4)_3} \cdot [\text{Al}_2(\text{SO}_4)_3]_{\text{in}}}{q_{\text{prv}} + 2 \cdot q_{\text{Al}_2(\text{SO}_4)_3}} - [\text{Al}^{3+}]_{\text{eq,in}}([\text{H}^+]_{\text{prv}})\right), \quad (61)$$

$$[\text{SO}_4^{2-}]_{\text{in,total}} = q_{\text{prv}} \cdot [\text{SO}_4^{2-}]_{\text{prv}} + 3 \cdot q_{\text{Al}_2(\text{SO}_4)_3} \cdot [\text{Al}_2(\text{SO}_4)_3]_{\text{in}} - (q_{\text{prv}} + 3 \cdot q_{\text{Al}_2(\text{SO}_4)_3}) \cdot E, \quad (62)$$

$$E = \max\left(0, \frac{q_{\text{prv}} \cdot [\text{SO}_4^{2-}]_{\text{prv}} + 3 \cdot q_{\text{Al}_2(\text{SO}_4)_3} \cdot [\text{Al}_2(\text{SO}_4)_3]_{\text{in}}}{q_{\text{prv}} + 3 \cdot q_{\text{Al}_2(\text{SO}_4)_3}} - [\text{CaSO}_4]_{\text{limit}}\right), \quad (63)$$

$$q_{\text{in,total}} = q_{\text{prv}} + q_{\text{KMnO}_4} + q_{\text{Cl}_2} + q_{\text{Ca(OH)}_2} + q_{\text{Al}_2(\text{SO}_4)_3}. \quad (64)$$

Variable  $[\text{Al}^{3+}]_{\text{eq,in}}$  is the function of  $[\text{H}^+]_{\text{prv}}$  and represents the dissolved aluminium at the inlet to a reaction volume. Quantities  $[\text{CaCO}_3]_{\text{limit}}$  and  $[\text{CaSO}_4]_{\text{limit}}$  represent the limiting concentrations for precipitation to start, in accordance with (19) and (20). The precipitation conditions were not

met for the set of living laboratory input concentrations evaluated in this paper, hence the variables  $C$ ,  $D$ , and  $E$  are zero. The differential equations of the concentrations are provided next.

$$\begin{aligned} \frac{d[\text{MnO}_4^-]}{dt} = & \frac{1}{V} \left( (\max(0; [\dot{\text{MnO}}_4^-]_{\text{in,total}} - \frac{1}{3}[\text{Fe}^{2+}]_{\text{in}} \cdot q_{\text{prv}} - \frac{2}{3}[\text{Mn}^{2+}]_{\text{in}} \cdot q_{\text{prv}}) \right. \\ & - q_{\text{in,total}} \cdot [\text{MnO}_4^-]) - \frac{1}{3}[\text{Fe}^{2+}] \cdot \delta(f_2([\text{Fe}^{2+}], [\text{MnO}_4^-])) \\ & \left. - \frac{2}{3}[\text{Mn}^{2+}] \cdot \delta(f_2([\text{Mn}^{2+}], [\text{MnO}_4^-])) \right). \end{aligned} \quad (65)$$

The function  $f_n(x)$  is defined as:

$$f_n(x_1, x_2, \dots, x_n) = \begin{cases} \neq 0 & \text{if any } x_i \leq 0, \\ 0 & \text{if all } x_i > 0. \end{cases} \quad (66)$$

$$\begin{aligned} \frac{d[\text{Cl}^-]}{dt} = & \frac{1}{V} \left( ([\dot{\text{Cl}}^-]_{\text{in,total}} + \min(\frac{1}{1}[\text{Mn}^{2+}]_{\text{in}} \cdot q_{\text{prv}}; \frac{1}{1}[\dot{\text{HOCl}}]_{\text{eq,in,total}}) \right. \\ & + \min(\frac{1}{2}[\text{Fe}^{2+}]_{\text{in}} \cdot q_{\text{prv}}; \frac{1}{1}[\dot{\text{HOCl}}]_{\text{eq,in,total}}) - q_{\text{in,total}} \cdot [\text{Cl}^-]) \\ & + \min(\frac{1}{1}[\text{Mn}^{2+}]; \frac{1}{1}[\text{HOCl}]_{\text{eq}}) \cdot \delta(f_2([\text{Mn}^{2+}], [\text{HOCl}]_{\text{eq}})) \\ & + \min(\frac{1}{2}[\text{Fe}^{2+}]; \frac{1}{1}[\text{HOCl}]_{\text{eq}}) \cdot \delta(f_2([\text{Fe}^{2+}], [\text{HOCl}]_{\text{eq}})) \\ & \left. + k_d[\text{HOCl}]_{\text{eq}}, \right) \end{aligned} \quad (67)$$

$$\begin{aligned} \frac{d[\text{Mn}^{2+}]}{dt} = & \frac{1}{V} \left( (\max(0; [\text{Mn}^{2+}]_{\text{in}} \cdot q_{\text{prv}} - \frac{1}{1}[\dot{\text{HOCl}}]_{\text{eq,in,total}} - \frac{3}{2}[\dot{\text{MnO}}_4^-]_{\text{in,total}}) \right. \\ & - q_{\text{in,total}} \cdot [\text{Mn}^{2+}]) - \frac{1}{1}[\text{HOCl}]_{\text{eq}} \cdot \delta(f_2([\text{HOCl}]_{\text{eq}}, [\text{Mn}^{2+}])) \\ & \left. - \frac{3}{2}[\text{MnO}_4^-] \cdot \delta(f_2([\text{MnO}_4^-], [\text{Mn}^{2+}])) \right), \end{aligned} \quad (68)$$

$$\begin{aligned} \frac{d[\text{Fe}^{2+}]}{dt} = & \frac{1}{V} \left( (\max(0; [\text{Fe}^{2+}]_{\text{in}} \cdot q_{\text{prv}} - \frac{3}{1}[\dot{\text{MnO}}_4^-]_{\text{in,total}} - \frac{2}{1}[\dot{\text{HOCl}}]_{\text{eq,in,total}}) - q_{\text{in,total}} \right. \\ & \cdot [\text{Fe}^{2+}]) - \frac{3}{1}[\text{MnO}_4^-] \cdot \delta(f_2([\text{MnO}_4^-], [\text{Fe}^{2+}])) \\ & \left. - 2[\text{HOCl}]_{\text{eq}} \delta(f_2([\text{HOCl}]_{\text{eq}}, [\text{Fe}^{2+}])) \right), \end{aligned} \quad (69)$$

$$\frac{d[\text{Ca}^{2+}]_{\text{eq}}}{dt} = \frac{1}{V} ([\dot{\text{Ca}}^{2+}]_{\text{eq,in,total}} - q_{\text{in,total}} \cdot [\text{Ca}^{2+}]_{\text{eq}}), \quad (70)$$

$$\frac{d[\text{Mg}^{2+}]_{\text{eq}}}{dt} = \frac{1}{V} ([\dot{\text{Mg}}^{2+}]_{\text{eq,in}} \cdot q_{\text{prv}} - q_{\text{in,total}} \cdot [\text{Mg}^{2+}]_{\text{eq}}), \quad (71)$$

$$\begin{aligned} \frac{d[\text{H}_2\text{CO}_3]_{\text{eq}}}{dt} = & \frac{1}{V} \left( (\max(0; [\dot{\text{H}}_2\dot{\text{C}}\text{O}_3]_{\text{eq,in,total}} \cdot q_{\text{prv}} - 3 \cdot (q_{\text{prv}} + 2 \cdot q_{\text{Al}_2(\text{SO}_4)_3_{\text{in}}}) \cdot \text{DOSE}) \right. \\ & \left. - q_{\text{in,total}} \cdot [\text{H}_2\text{CO}_3]_{\text{eq}} \right), \end{aligned} \quad (72)$$

$$\frac{d[\text{K}^+]}{dt} = \frac{1}{V} ([\dot{\text{K}}^+]_{\text{in,total}} - q_{\text{in,total}} \cdot [\text{K}^+]), \quad (73)$$

$$\frac{d[\text{TOC}]}{dt} = \frac{1}{V} \left[ [\text{TOC}]_{\text{in}} \cdot q_{\text{prv}} - h(K_1, K_2, x_1, x_2, x_3, \text{DOSE}, \text{pH}, [\text{TOC}]_{\text{in}} \cdot \frac{q_{\text{prv}}}{q_{\text{prv}} + q_{\text{Al}_2(\text{SO}_4)_3}_{\text{in}}}) \cdot q_{\text{in,total}} \right], \quad (74)$$

where  $h$  denotes the function defined in subsection 2.3,

$$\begin{aligned} \frac{d[\text{HOCl}]_{\text{eq}}}{dt} = & \frac{1}{V} \left( \max(0; [\text{HOCl}]_{\text{eq,in,total}} - \frac{1}{1} [\text{Mn}^{2+}]_{\text{in}} \cdot q_{\text{prv}} - \frac{1}{2} [\text{Fe}^{2+}]_{\text{in}} \cdot q_{\text{prv}}) \right. \\ & - q_{\text{in,total}} \cdot [\text{HOCl}]_{\text{eq}} - \frac{1}{1} [\text{Mn}^{2+}] \delta(f_2([\text{Mn}^{2+}], [\text{HOCl}]_{\text{eq}})) \\ & \left. - \frac{1}{2} [\text{Fe}^{2+}] \delta(f_2([\text{Fe}^{2+}], [\text{HOCl}]_{\text{eq}})) - k_d [\text{HOCl}]_{\text{eq}} \right), \end{aligned} \quad (75)$$

$$\frac{d[\text{Al}^{3+}]_{\text{eq}}}{dt} = \frac{1}{V} ([\text{Al}^{3+}]_{\text{eq,in,total}} - q_{\text{in,total}} \cdot [\text{Al}^{3+}]_{\text{eq}}), \quad (76)$$

$$\frac{d[\text{SO}_4^{2-}]}{dt} = \frac{1}{V} ([\text{SO}_4^{2-}]_{\text{in,total}} - q_{\text{in,total}} \cdot [\text{SO}_4^{2-}]), \quad (77)$$

$$\frac{dV}{dt} = q_{\text{in,total}} - q_{\text{out}}. \quad (78)$$

### 3.2 pH modelling

Besides the concentrations, an important output of the model will also be the pH value established in the reaction volume. It is modelled by starting with the dissociation equation for water [17]:

$$[\text{H}^+] \cdot [\text{OH}^-] = k_w = 10^{-14}. \quad (79)$$

From charge balance one can obtain:

$$[\text{H}^+] - [\text{OH}^-] = r_{\text{net}}, \quad (80)$$

where:

$$\begin{aligned} r_{\text{net}} = & [\text{HCO}_3^-]([\text{H}^+], [\text{H}_2\text{CO}_3]_{\text{eq}}) + 2[\text{CO}_3^{2-}]([\text{H}^+], [\text{H}_2\text{CO}_3]_{\text{eq}}) + [\text{Cl}^-] + [\text{MnO}_4^-] \\ & + 2[\text{SO}_4^{2-}] + [\text{ClO}^-]([\text{H}^+], [\text{HOCl}]_{\text{eq}}) - 2[\text{Ca}^{2+}]([\text{H}^+], [\text{Ca}^{2+}]_{\text{eq}}) \\ & - 2[\text{Mg}^{2+}]([\text{H}^+], [\text{Mg}^{2+}]_{\text{eq}}) - 2[\text{Fe}^{2+}] - 2[\text{Mn}^{2+}] - [\text{K}^+] \\ & - [\text{CaOH}^+]([\text{H}^+], [\text{Ca}^{2+}]_{\text{eq}}) - [\text{MgOH}^+]([\text{H}^+], [\text{Mg}^{2+}]_{\text{eq}}) - c_{\text{avg}}[\text{Al}^{3+}]_{\text{eq}}, \end{aligned} \quad (81)$$

where  $c_{\text{avg}} = -0.1937$ , denoting the average charge of the dissolved aluminium species at pH 7 to simplify the calculation. After substituting (35), (36), (38), (42), (43), (45), (46), (79) and (81) into (80) one gets the equation for  $[\text{H}^+]$  with a ninth order polynomial which is not written here because of the length of its notation. The concentration of  $(\text{H}^+)$  ions obtained from the solution to it is used to calculate the pH value.

Now one can determine pH using the following expression:

$$\text{pH} = -\log[\text{H}^+]. \quad (82)$$

## 4 VALIDATION ON CASE STUDY

### 4.1 Description

Dynamical model for fast reactions was implemented and simulated in the Matlab/Simulink development environment. The raw water quality, i.e. the concentration of each element in raw water obtained by laboratory analysis of samples from a real DWTP is set as in Table 2. All subsequent concentrations will be presented in (mg/L) for easier comparison of results with the measurements.

Table 2 Raw water quality. The concentrations are expressed in mg/L

[Mn <sup>2+</sup> ]	[Fe <sup>2+</sup> ]	[Ca <sup>2+</sup> ]	[Mg <sup>2+</sup> ]	[H <sub>2</sub> CO <sub>3</sub> ] <sub>eq</sub>	[TOC]
0.543	0.308	41	4.5	175	6.12

The doses of each of the reagents added to each reaction volume are shown in Table 3.

Table 3 Doses of each reagent. The reagent dosages are expressed in mg/L (the unit L refers to the litre of the treated water stream here)

	RV <sub>1</sub>	RV <sub>2</sub>	RV <sub>3</sub>	RV <sub>4</sub>
[KMnO <sub>4</sub> ] <sub>in</sub>	0.5	-	-	-
[Ca(OH) <sub>2</sub> ] <sub>in</sub>	5	-	-	3
[Cl <sub>2</sub> ] <sub>in</sub>	-	6.8	-	1
[Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ] <sub>in</sub>	-	-	80	-

### 4.2 Mathematical model simulation

The obtained concentration of each element and pH value responses at the outlet of the fourth reaction volume are shown in Fig. 2. In it the first two responses show how much reagent is dosed and when in each reaction volume. Here it can be observed that the iron concentration was reduced to zero while the manganese concentration was reduced to approximately half of the initial value after the addition of potassium permanganate. By adding chlorine in the second reaction volume, the manganese concentration is reduced to zero. In the third reaction volume, coagulation/flocculation processes take place since aluminium sulfate is added as a coagulant with the concentration from Table 3. The main goal of adding aluminium sulfate is to reduce the TOC concentration, i.e. to reduce the presence of organic matter and fifth response in Fig. 2 clearly shows that this has been achieved. In the fourth reaction volume free chlorine is achieved in the required concentration, while the addition of lime regulates the pH also on the required level.

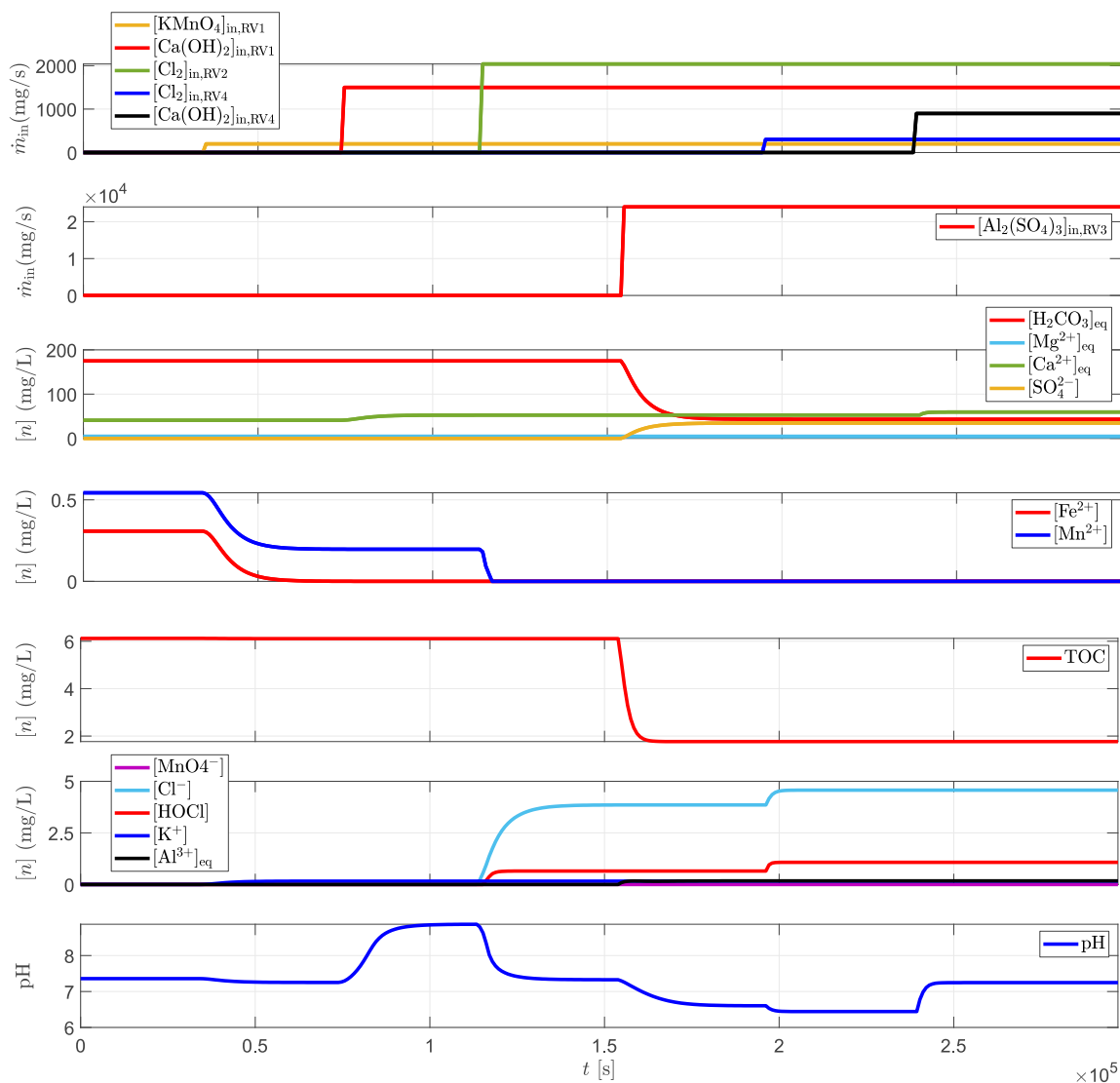


Figure 2 The concentration of each element and pH value at the outlet of the fourth reaction volume

### 4.3 Comparison of the model results with living lab measurements

Table 4 compares the measurements taken at the DWTP's output, i.e. at the fourth reaction volume's output, to the values calculated using the proposed model.

Table 4 Comparison of measurements to the model results. The concentrations are expressed in (mg/L)

	[HOCl] <sub>eq</sub>	[Fe <sup>2+</sup> ]	[Mn <sup>2+</sup> ]	[TOC]	pH
Measurement	1.1	<0.032	0.009	1.63	7.3
Model	1.08	0	0	1.77	7.3

The model yielded a concentration of 0.177 (mg/L) of aluminium at the fourth reaction volume's outlet. Because the concentration of dissolved aluminium is highly dependent on pH, and its value is irrelevant in determining the model's accuracy, there was no comparison of aluminium with the real measurements. However, the concentration is within the DWTP's allowed limits, with a maximum dissolved aluminium of 0.2 (mg/L). A comparison of the results for this preliminary

validation shows a satisfactory model accuracy with the maximum deviation from the actual measurements being 8.6%, for the case of TOC.

## 5 CONCLUSIONS

A model of a general reaction volume of a drinking water treatment plant (DWTP) is presented in the paper. The DWTP under consideration is divided into four reaction volumes, each with its own set of chemical processes, all considered as fast chemical reactions. The model implementation is simplified with only a couple of known parameters required. The model is simulated in the Matlab/Simulink development environment and the expected values of drinking water quality parameters are obtained at the output. It includes a bicarbonate buffer system that prevents pH levels from fluctuating drastically when chemicals are added. The Edwards model was also used, which resembles the TOC removal with good accuracy when compared to the real measurement. A comparison of measurements on an actual DWTP and the model results was made. For this preliminary validation, the comparison shows a good model accuracy with the maximum deviation from the actual measurement of 8.6%, presenting a good indicator of the model reliability.

## 6 ACKNOWLEDGMENT

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