

Plant wide chemical water stability modelling with PHREEQC for drinking water treatment

A.W.C. van der Helm^{*/**}, O.J.I. Kramer^{*}, J.F.M. Hoof^{t*} and P.J. de Moel^{***/**}

* Waternet, PO Box 94370, 1090 GJ, Amsterdam, the Netherlands

(E-mail: alex.van.der.helm@waternet.nl, Tel: +31 6 5248 0203)

** Delft University of Technology, Faculty of Civil Engineering and Geosciences, Department of Water Management, PO Box 5048, 2600 GA, Delft, the Netherlands

*** Omnisys, Eiberlaan 23, 3871 TG, Hoevelaken, the Netherlands

Abstract

In practice, drinking water technologists use simplified calculation methods for aquatic chemistry calculations. Recently, the database *stimela.dat* is developed especially for aquatic chemistry for drinking water treatment processes. The database is used in PHREEQC, the standard in geohydrology for calculating chemical equilibria in groundwater. The development of a graphical user interface for PHREEQC in Microsoft Excel has made it possible to easily incorporate complicated chemical calculations for use by technologists of drinking water treatment plants. By making use of PHREEQC the calculations performed are more accurate because of inclusion of ionic strength, ion pairs and most recent determined chemical equilibrium constants. Due to this development it is possible to for instance validate laboratory measurements and on-line sensors. The use of PHREEQC is demonstrated in a simulation of the chemical water stability at drinking water treatment plant Weesperkarspel of Waternet.

Keywords

Chemical equilibrium; drinking water treatment; modelling; phreeqc; stimela

INTRODUCTION

PHREEQC (USGS, 2014) has become the ‘de facto’ standard in geohydrology for calculating chemical equilibria in groundwater. It is developed by the US Geological Survey (USGS), starting in 1980 with regular updates and extensions to date. Major aspects contributed to its success are:

- scientific base, fully traceable;
- adapted to newest scientific knowledge;
- users can modify and extend the basics;
- freely available;
- availability of an MS COM module for communication with e.g. MS Excel.

Recently de Moel et al. (2014) developed the *stimela.dat* database for PHREEQC which is specifically designed for water treatment. The *stimela.dat* database is based on the *phreeqc.dat* database (de Moel et al., 2013) that is available in PHREEQC. Adaptation of the *phreeqc.dat* database is necessary because, on the contrary to geochemistry, in water treatment processes thermodynamic equilibrium of all redox reactions cannot be assumed. Therefore, inert elements are defined for a number of parameters such as:

- non N(+5) oxidation states of nitrogen, with species NH_4^+ , N_2 and NO_2^- ;
- typical anaerobic groundwater species, such as Fe^{2+} , Mn^{2+} and NH_4^+ ;
- all anaerobic gases such as CH_4 , H_2S , NH_3 (already implemented in PHREEQC version 3).

Waternet, the water cycle utility of Amsterdam and surrounding areas in the Netherlands, is adopting the use of stimela.dat in PHREEQC in their operation through the use of a Microsoft Excel user interface with PHREEQC. This paper describes the use of stimela.dat through Excel for calculation of chemical stability in drinking water treatment.

MATERIALS AND METHODS

Data is used from the Loenderveen-Weesperkarspel drinking water treatment, see Figure 1. The pre-treatment Loenderveen consists of an intake of seepage water from the Bethune polder and a consecutive treatment of coagulation and sedimentation, self-purification in a lake-water reservoir and rapid sand filtration. The pre-treated water is transported over 14 kilometers to the Weesperkarspel treatment plant without chlorination. The first process at the treatment plant Weesperkarspel is ozonation for disinfection purpose and oxidation of organic matter. Thereafter, pellet reactors are used to reduce hardness (softening) and biological activated carbon filtration is applied to remove natural organic matter and organic micro-pollutants. The last step in the treatment is slow sand filtration. The drinking water is transported and distributed without residual chlorine.

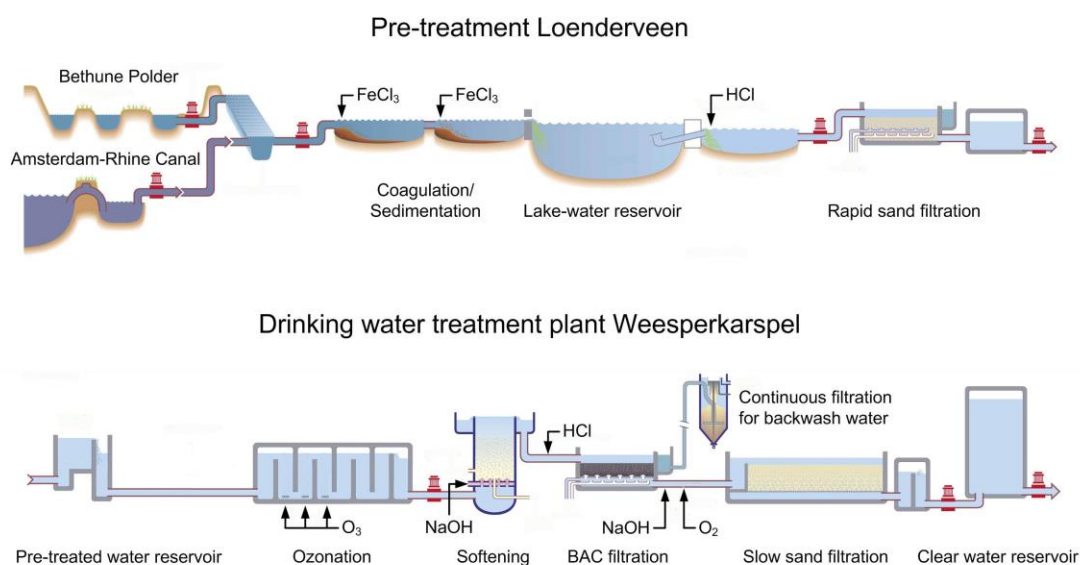


Figure 1 Process scheme of drinking water treatment plant Loenderveen-Weesperkarspel of Waternet

In the model, the water from the lake-water reservoir, with a detention time of about 100 days, is used as influent. The used laboratory measurements are temperature, pH, calcium, magnesium, alkalinity, ammonium, sodium, potassium, total iron, chloride, sulfate, nitrate, ortho-phosphate, oxygen, silicate, total organic carbon and Electrical Conductivity (EC-20). In Table 1 an overview is given of the relevant chemical reactions within the treatment plants. All these chemical reactions are defined within the PHREEQC/Stimela database, as equilibrium reactions with all related equilibrium constants and compound characteristics.

Table 1 Chemical reactions relevant for this PHREEQC/Stimela water treatment model

Process	Item	Reaction
pH control	HCl-dosing	$\text{HCO}_3^- + \text{H}^+ + \text{Cl}^- \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Cl}^-$
Filtration	NH ₄ -oxidation	$\text{NH}_4^+ + 2 \text{O}_2 + 2 \text{HCO}_3^- \rightarrow \text{NO}_3^- + 2 \text{CO}_2 + 3 \text{H}_2\text{O}$
Ozone	O ₃ -reduction	$2 \text{O}_3 \rightarrow 3 \text{O}_2$
Softening	NaOH-dosing	$\text{CO}_2 + \text{OH}^- + \text{Na}^+ \rightarrow \text{HCO}_3^- + \text{Na}^+$
	NaOH-dosing	$\text{HCO}_3^- + \text{OH}^- + \text{Na}^+ \rightarrow \text{CO}_3^{2-} + \text{Na}^+$
	CaCO ₃ -crystallization	$\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3(\text{s})$
pH control	HCl-dosing	$\text{CO}_3^{2-} + \text{H}^+ + \text{Cl}^- \rightarrow \text{HCO}_3^- + \text{Cl}^-$
AC filtration	DOC/TOC-oxidation	$\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
pH control	NaOH-dosing	$\text{CO}_2 + \text{OH}^- + \text{Na}^+ \rightarrow \text{HCO}_3^- + \text{Na}^+$
O ₂ control	O ₂ -dosing	$\text{O}_2 \rightarrow \text{O}_2$
SS filtration	DOC/TOC-oxidation	$\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$

The input file for the model only defines the quantity of dosed chemicals or the quantity of the converted compounds. In this case the operation of the plant is simulated for the caustic soda and hydrochloric acid dosages at Loenderveen and Weesperkarspel based on the set-points used in the plants for the calcium carbonate saturation index (SI) and total hardness (TH) after pellet softening. The calculated dosages are obtained within the model by iterative calculations, by specific algorithms or by 'normal' functionality of PHREEQC.

The output of the model is fully in compliance with all related equilibria as defined within the chemical database. The model calculates the content of all compounds, after each treatment step, as well as typical calculated values for e.g. pH, SI and electrical conductivity.

The model set-up allows for the incorporation of non-chemical compounds such as turbidity and UV-extinction. In this particular model these non-chemical compounds were not included, as the prime goal for this model was the prediction of acid and base dosing levels.

The computer program PHREEQC version 3.1.4 (phreeqci-3.1.4-8929.msi) was used to solve the mathematical equations which are generated from the chemical database stimela.dat and an input file (.pqi), both adjustable by the user (Parkhurst and Appelo, 2013). For use of PHREEQC through Excel the communication module version 3.0.6 (IphreeqcCOM-3.1.4-8929-win32.msi) was used.

RESULTS

Raw water quality

The quality of the water abstracted from the process reservoir ('Waterleidingplas') reflects the rather constant quality of the original seepage water, the effect of pre-treatment with coagulation, and the typical yearly variation caused by natural processes in the reservoir. Figure 2 shows the stable concentrations of the major ionic components (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , Cl^- , SO_4^{2-} , NO_3^- , ortho- PO_4^{3-}), Figure 3 shows the remarkable yearly variation of some typical reservoir parameters (temperature, O_2 , NH_4^+) and Figure 4 shows the remaining parameters used as input for the modelling (SiO_2 , TOC, Fe-total, EC-20) with the exception of pH which is shown in Figure 6.

For this reservoir, total organic carbon (TOC, unfiltered) was 0.0-0.2 mg/l higher than dissolved organic carbon (DOC, filtered), and total-PO₄ was 0.00-0.05 mg/l higher than ortho-PO₄.

All this data was obtained from the monthly water quality sampling program (2009-2013).

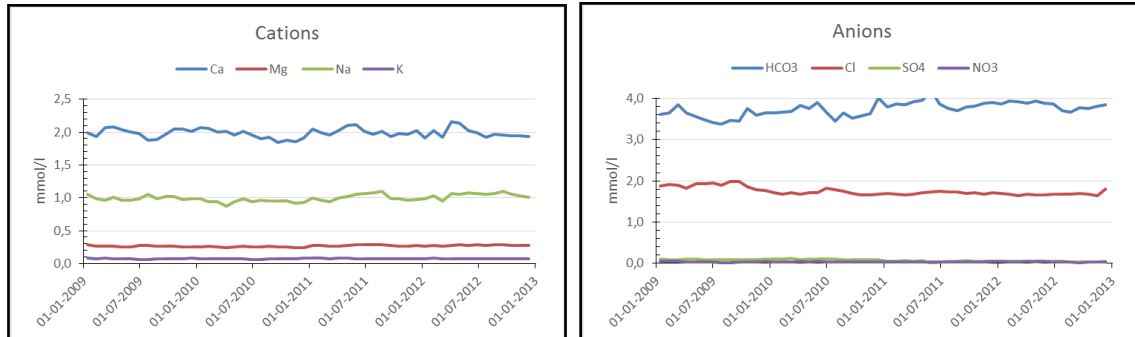


Figure 2 Concentrations of major ionic compounds in the reservoir water (2009-2013)

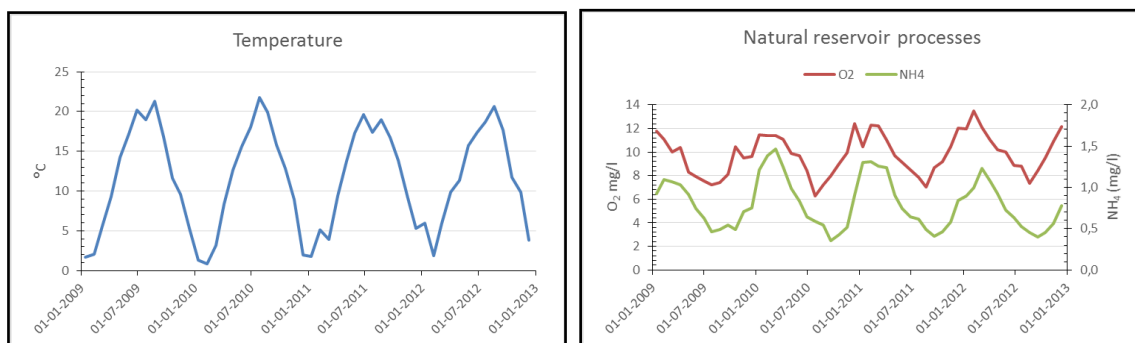


Figure 3 Variation in water quality caused by natural processes (2009-2013)

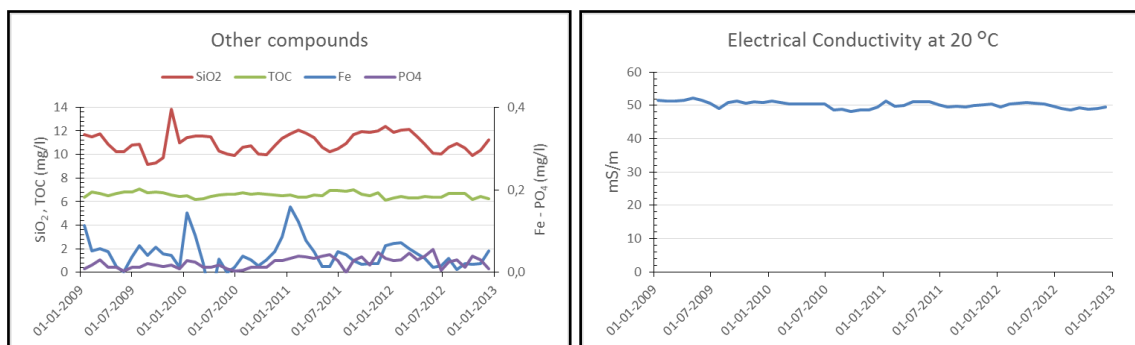


Figure 4 Other water quality parameters used in the model (2009-2013)

Evaluation and validation of raw water quality

The laboratory data was further evaluated and validated by means of PHREEQC calculations.

Figure 5 shows the evaluation for the contents of oxygen (O₂) and carbon dioxide (CO₂). The contents of these gases are largely determined by biological processes in the reservoir and by gas exchange with the atmosphere.

For all samples the O₂ saturation concentration in the reservoir water was calculated with PHREEQC from the partial pressure of oxygen in atmospheric air (0.2 bar). The

presented O₂ saturation ratios were calculated from the measured O₂ content divided by the saturation concentration. The O₂ saturation ratio shows a yearly pattern with algae growth in the reservoir. Large algae blooms are prevented by phosphate removal in the pre-treatment and by air bubble columns which avoids stratification in this deep reservoir.

The CO₂ concentration was not part of the laboratory measuring program. For all samples the concentration was calculated by PHREEQC, in which pH, Alkalinity and temperature are the most relevant parameters. The CO₂ content reflects the reduction of the intake depth in 2009. Since 2010 the CO₂ content is nearly constant at 0.06 mmol/l (2.6 mg/l) being slightly higher than the CO₂ content in equilibrium with atmospheric air.

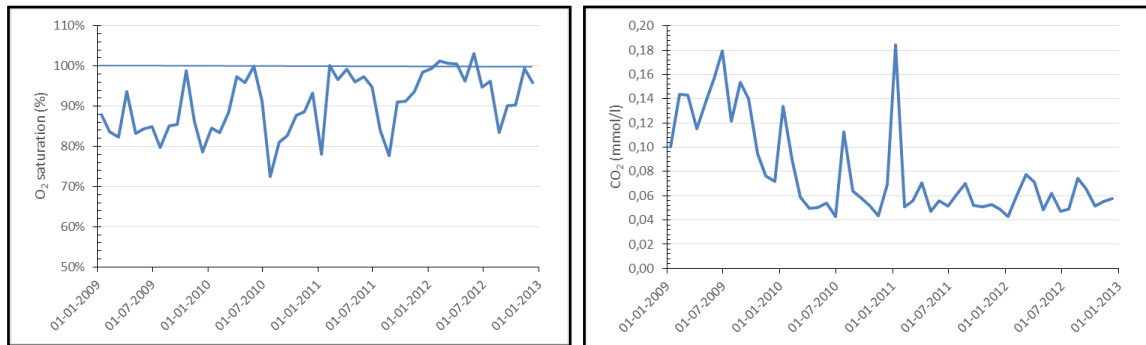


Figure 5 Content of gases in reservoir water - O₂ saturation ratio (left) and CO₂ (right) (2009-2013)

Figure 6 shows the evaluation of the Saturation Index (SI) and the Calcium Carbonate Precipitation Potential (CCPP). These parameters were calculated for all samples by PHREEQC.

The low CO₂ content results in a rather high pH, as typical for most surface waters. This reservoir water has a permanent scaling potential for calcium carbonate as shown by its SI and CCPP. In practice only minor calcium precipitation is observed in the reservoir, resulting in a yearly variation in Ca-content of some 0.1-0.2 mmol/l, with the maximum content in winter months.

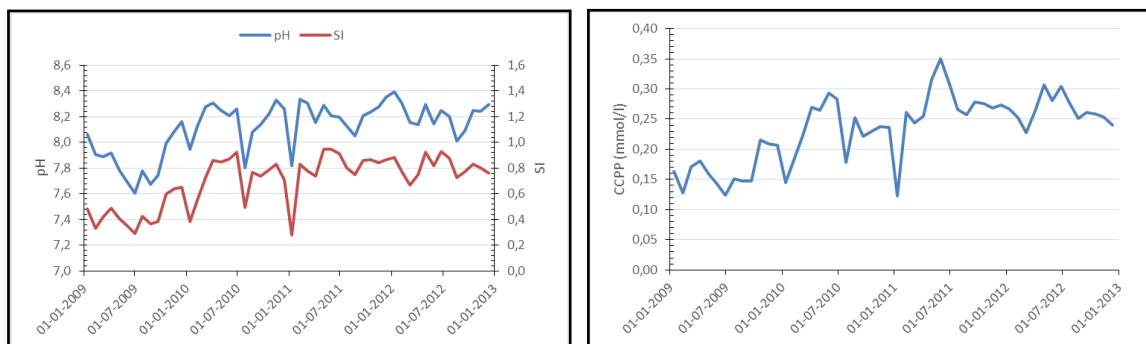


Figure 6 CO₂ release results in supersaturation for calcite – SI (left) and CCPP (right) (2009-2013)

Validation of laboratory analyses were done in PHREEQC by calculating both the ionic charge balance as well as the Electrical Conductivity (EC). Proper laboratory analyses show only a low imbalance in ionic charge and similar values for measured and calculated EC, with guideline values according to Standard Methods 1030E.

Figure 7 shows that the observed variation in ionic balance has not always been within the accepted range of 2%. The EC-ratio was always very well within the acceptable range of 0.9 to 1.0.

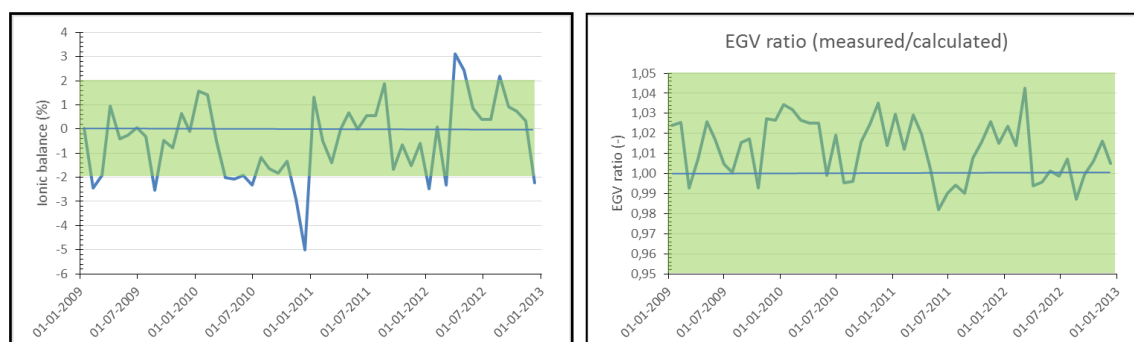


Figure 7 Validation of analyses – Ionic balance (left) and EC-ratio (right) (2009-2013)

Changes in water quality

The effect of dosing chemicals can easily be calculated in PHREEQC by using its build-in function REACTION, in which defined amounts of chemical components can be added to a 'solution'. PHREEQC calculates the effect on all species defined in the applied chemical database, including related parameters such as pH, EC, activity coefficients etc., while keeping track of all mass balances. This functionality can also be applied by calculating the effect of chemical reactions in a treatment process. In this case the reacted amount should be either known, estimated or calculated by kinetic process modelling.

Alternatively PHREEQC can calculate the amount of a chemical needed to obtain a specific Saturation Index by using its build-in function EQUILIBRIUM_PHASES. This functionality can be used when set-points for SI has been given. The latter is largely the case in these treatment plants, with defined SI set-point on several process locations:

- before the transportation mains (SI to be reduced to +0.3 to prevent scaling)
- before activated carbon filtration (SI to be reduced to -0.05 for proper adsorption)
- before distribution (SI to be increased to +0.35 to obtain the highest achievable pH).

The SI set-point for distribution has been defined to prevent metal corrosion and uptake of copper, lead, nickel and zinc from metal pipes and pipe appurtenances but still preventing scaling in the distribution network and in consumers installations.

To achieve these distribution goals the water is softened in the treatment plant by softening reactors in which calcium carbonate is crystallized in a fluid bed, with caustic soda applied as chemical reagent. Waternet has defined a set-point for Total hardness of 1.49 mmol/l in their produced drinking water. This set-point can be obtained by the varying the caustic soda dose with variable feed water quality. The applied dose needs to be some 0.1-0.2 mmol/l higher than equilibrium conditions, based on operational experiences. In PHREEQC this constant total hardness is obtained by an iterative calculation method in which the caustic soda dose is gradually increased.

In these treatment plant water quality is not only changed by dosing chemicals but also by the treatment processes itself. With respect to water stability (pH, SI, Ca-hardness, Alkalinity) two more processes are important:

- oxidation of ammonium (NH_4^+ raw water 0.02-0.08 mmol/l)
- oxidation of Total Organic Carbon (TOC raw water 0.51-0.59 mmol/l C).

Practical experiences have given proper estimates for the amount of these compounds which are oxidized in each process. NH_4^+ is always fully oxidized (>99%) in the rapid sand filters in Loenderveen. TOC is oxidized in the biological activated carbon filters between 0.02 (at 2 °C) and 0.11 (at 20 °C) mmol/l, and in the slow sand filters between 0.003 (at 2 °C) and 0.014 (at 20 °C) mmol/l. TOC removal by adsorption is found in the activated carbon filters only, between 0.06 (at 2 °C) and 0.02 (at 20 °C) mmol/l. However, adsorption has no effect on pH or oxygen content and therefore not on the dosing levels for NaOH and O_2 .

Oxidation of ammonium and TOC at a known amount of conversion can be modelled in the Stimela concept of PHREEQC by altering the converted amounts of the inert phases of ammonium and TOC into reactive phases, after which the chemical reactions are 'automatically' obtained in the related PHREEQC calculation/simulation.

Applied PHREEQC code

The PHREEQC code applied for the modelling of this treatment plants is shown in Figure 8. Each relevant process is defined in 2 to 3 lines of program code. The orange marked cells contain the raw water quality as defined in the raw water data set, the yellow marked cells contain the data which can be altered by the process engineer or operator in the 'process dashboard'. Because of the Excel linking to this PHREEQC program code lines, these model users are not puzzled by such program code lines. On the other hand these code lines can easily be understood by a water treatment engineer or operator, which allow for a proper understanding of the whole treatment model.

SOLUTION_SPREAD		mg/L		# # O2=0 then "pe" else "O(-2)/O(0)"																										
number	temp	pH	Ca	Mg	Alkalinity [N-3]	Na	K	Fe	Cl	S(6)	N(5)	P	O(0)	Si	Org_c	density	Org	Nrg												
			as Ca	as Mg	as HCO3	as NH4	as Na	as K	as Fe	as Cl	as SO4	as NO3	as PO4	as O	as SiO2	as C														
1	8.800	8.298	79.640	8.509	236.470	0.778	23.280	2.954	0.059	84.019	4.878	2.466	0.069	12.360	11.209	8.254	1.000324	1	Org(g) - (1)Nrg(g) -0.1024											
END	# Simulation	1																												
TITLE	Berekening pe	Batch-reaction for calculating pe (redox equilibrium) (dummy calculation)																												
USE solution	1	EQUILIBRIUM_PHASES 1;																												
TITLE	Berekening TACC / CCPP	Batch reaction for calculating CalciumCarbonate Precipitation Potential																												
USE solution	2	EQUILIBRIUM_PHASES 2; Calcite																												
TITLE	Bepaling HCl dosering	Eerst reactie van NH4, daarna HCl dosering tot setpoint-SI, indien noodzakelijk (voorwaarde via comment marker #)																												
USE solution	22	REACTION; [N-3]H4-1 NH4 t; 0.042633; mmoles																												
USE solution	22	EQUILIBRIUM_PHASES 3; Calcite																												
USE solution	22	EQUILIBRIUM_PHASES 3; HCl; 0.001																												
TITLE	HCl dosering	Berekende dosering = Cl (sim5-sim4) in mol/kgw (voor CO2: ook onderdeel Verbruik in Bedieningspaneel aanpassen)																												
USE solution	2	REACTION; HCl; 1; 0.0434; mmoles																												
USE solution	3	EQUILIBRIUM_PHASES; Calcite																												
TITLE	Snelfiltratie - NH4 oxidatie	(zonder TOC omzetting)																												
USE solution	3	REACTION; [N-3]H4-1 NH4 t; 0.042633; mmoles																												
USE solution	4	EQUILIBRIUM_PHASES; Calcite																												
TITLE	Ozon dosering	(bijbehorende reacties zoals bromaatvorming niet gedaan)																												
USE solution	4	REACTION; O3 t; 0.009000; mmoles																												
USE solution	5	EQUILIBRIUM_PHASES; Calcite																												
TITLE	Ontharding - stap 1	Dosering en neerslag tot evenwicht																												
PRINT; -selected_output false	# uitvoer naar Selected output UIT (tussenresultaten DoseTH niet nodig in Output)																													
USE solution	5	KINETICS; DoseTH; -formula NaOH; 10; -parms 1.3400; ; m0 10.0; -bad_step_max 100; -ovode true; -steps 10 s in 10 steps																												
PRINT; -selected_output true	# uitvoer naar Selected output AAN (met alsnog uitvoer van laatste step)																													
USE solution	6	EQUILIBRIUM_PHASES;																												
TITLE	Ontharding - stap 2	Toevoegen CaCO3 voor TTAC																												
USE solution	6	REACTION; CaCO3 t; 0.1500; mmoles																												
USE solution	7	EQUILIBRIUM_PHASES; Calcite																												
TITLE	HCl dosering	Zuurdosering tot setpoint SI (voor CO2 een andere Excel ontwikkelen)																												
USE solution	7	EQUILIBRIUM_PHASES 4; Calcite																												
USE solution	8	EQUILIBRIUM_PHASES; Calcite																												
TITLE	Koelfiltratie - TOC omzetting	TOC omzetting: Org_C + O2 -> CO2																												
USE solution	8	REACTION; Org_c-t; CO2 t; 0.0781; mmoles																												
USE solution	9	EQUILIBRIUM_PHASES; Calcite																												
TITLE	Bepaling NaOH dosering	Eerst reactie van TOC (vorming CO2), daarna NaOH dosering tot setpoint-SI																												
USE solution	9	REACTION; CO2; 0.0004; ; 1.00 mmol																												
USE solution	9	EQUILIBRIUM_PHASES 5; Calcite																												
USE solution	9	EQUILIBRIUM_PHASES 5; NaOH; 0.001																												
TITLE	NaOH dosering	Berekende dosering = Na (sim20-sim19) in mol/kgw																												
USE solution	9	REACTION; NaOH; 0.1958; ; O2																												
USE solution	10	EQUILIBRIUM_PHASES; Calcite																												
TITLE	Langzame zandfiltratie - TOC c	TOC omzetting: Org_C + O2 -> CO2																												
USE solution	10	REACTION; Org_c-t; CO2 t; 0.0004; mmoles																												
USE solution	11	EQUILIBRIUM_PHASES; Calcite																												

Figure 8 PHREEQC code for the applied water quality model

Process dashboard

The process dashboard is shown in Figure 9. The orange cell contains the selected date for raw water quality, the yellow cells contain the set-points and process parameters.

The simulation for the selected date, set-points and process parameter can be initiated by the 'Run PHREEQC' button.

The calculated dosing levels and actual set-point values are presented in the green cells (PHREEQC output) and the gray cells (post-calculated in Excel).

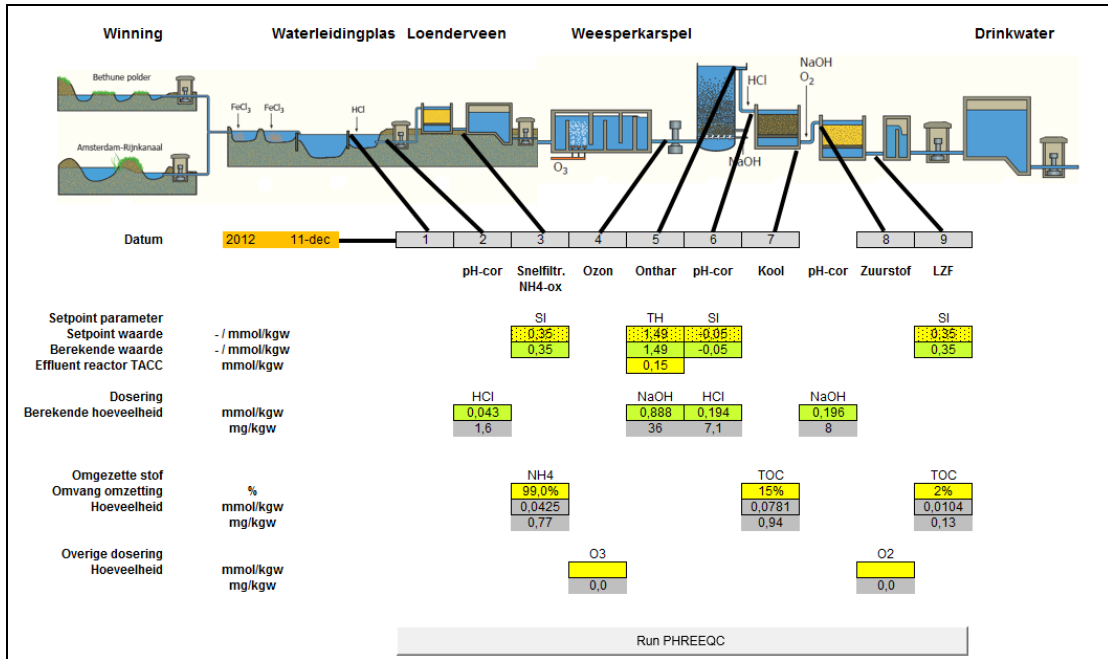


Figure 9 Process dashboard for the applied water quality model (operator section)

The calculated results on water quality can be presented in a graphical form using standard Excel graphs, as is shown in Figure 10. The calculated values for Total hardness and SI are presented in the central part (yellow dots) together with the acceptable range for practical operations (green marker lines) at all stages of the treatment plant. For references the output graphs are flanked by pictures for the long-time variation of these parameters, on the left for raw water, on the right for produced drinking water.

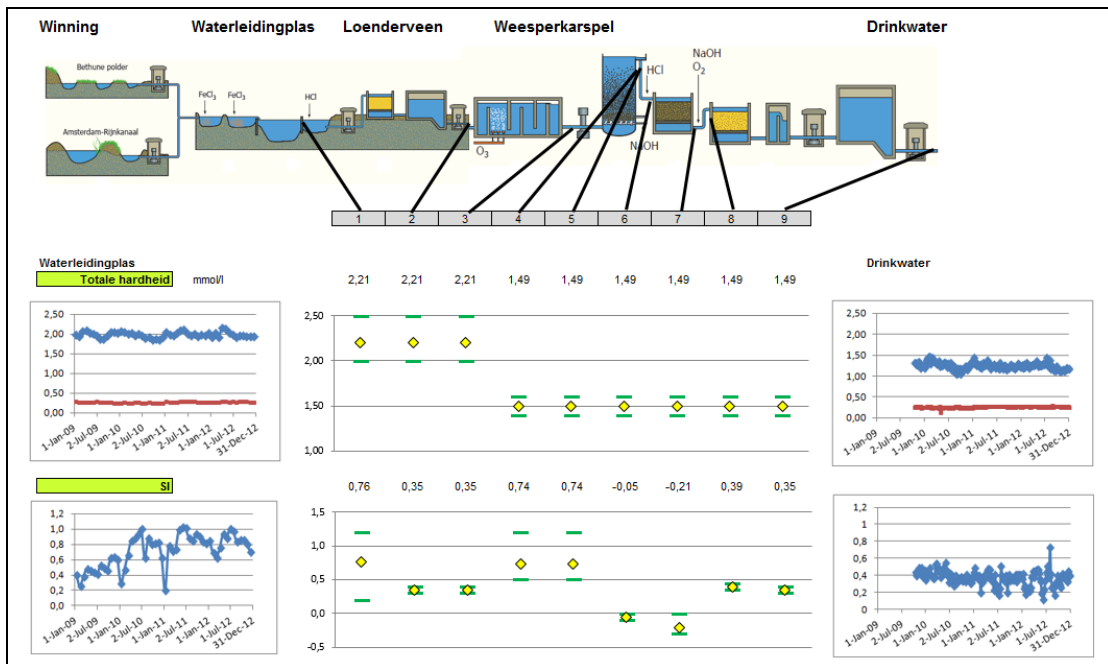


Figure 10 Process dashboard for the applied water quality model (water quality section)

Multiple simulations for long term process evaluation

Using the data set for raw water quality and the selected set-points for water quality goals multiple simulations can be done, resulting in required dosing levels over several years, as shown in Figure 11. This set-up allows for evaluating the effects of different set-point levels for Total hardness, and/or SI, as well as the effect of using different chemicals such as CO₂ as a replacement for HCl etc. The latter has actually been done for the reservoir dosing in August 2010.

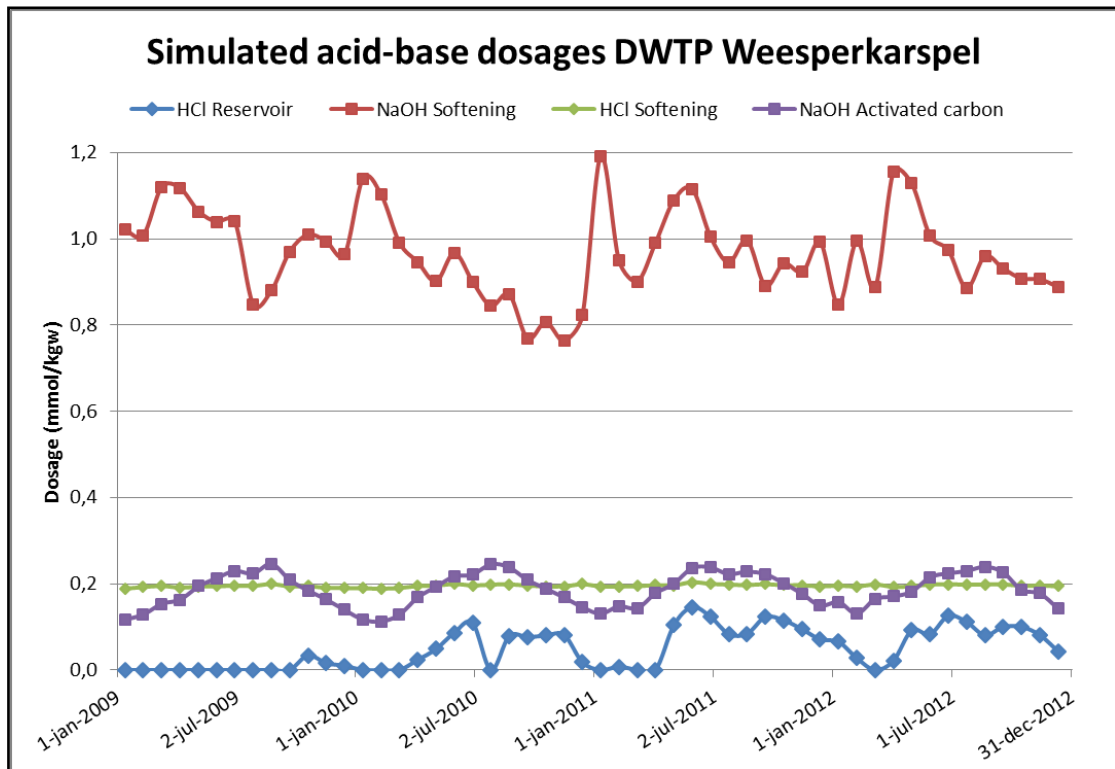


Figure 11 Required dosing levels for normal operational set-points (2009-2013)

Next to the required dosing levels also the quality of the produced drinking water is calculated allowing for presentation in standards Excel graphs, as shown in Figure 12. These graphs show more variations in the content of Na and Cl than the original raw water because of the variation in dosing levels.

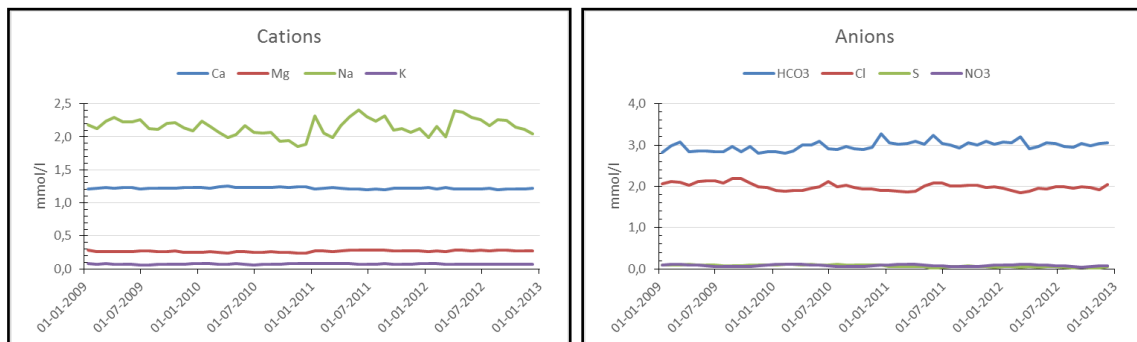


Figure 12 Calculated concentrations of major ionic compounds in the produced drinking water (2009-2013)

The fixed set-point for SI has resulted in a modest variation in pH of the produced drinking water, as shown in Figure 13. This variation is mainly caused by the natural variation in water temperature.

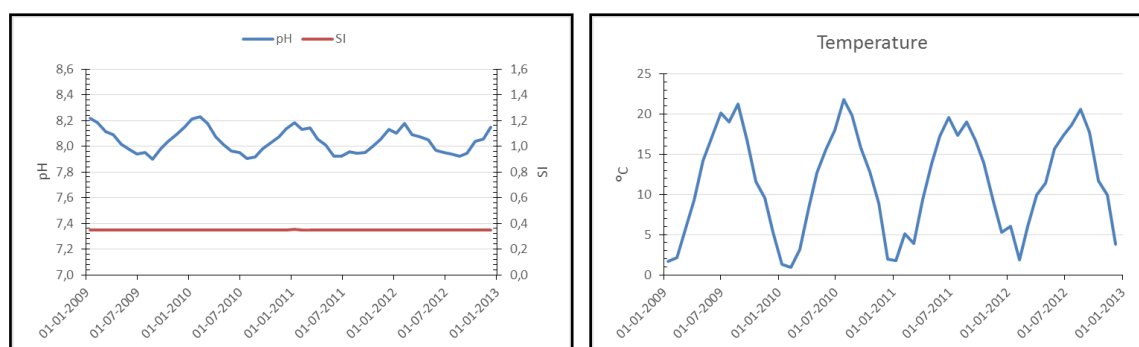


Figure 13 Calculated pH, SI and water temperature of produced drinking water (2009-2013)

CONCLUSIONS

The development of a graphical user interface in Excel has made it possible to incorporate complicated chemical calculations in daily operation of drinking water production for technologists. By using PHREEQC the calculations performed are more accurate, because effects of ionic strength and ion pairs are included and most recent determined chemical equilibrium constants are used. Furthermore the dosing of chemicals with regard to the calcium carbonate saturation can be optimised. Important for practice of technologists is the availability of a tool that can work with data arrays instead of for instance average year values. This gives better insight in the processes and leads to better decisions by process technologists.

REFERENCES

- de Moel, P. J., van der Helm, A.W.C., van Rijn, M., van Dijk, J.C. and van der Meer, W.G.J. (2013). Assessment of calculation methods for calcium carbonate saturation in drinking water for DIN 38404-10 compliance. *Drink. Water Eng. Sci. Discuss.*, 6, 167–198.
- de Moel, P. J., van Dijk, J. C., and van der Meer, W. G. J. (2014). *Aquatic chemistry for engineers, Volume 1, Starting with PHREEQC 3*. Delft University of Technology, Delft, the Netherlands.
- Parkhurst, D. L and Appelo, C. A. J. (2013). *Description of input and examples for PHREEQC version 3—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations*, US Geological Survey, Denver, USA.
- USGS: phreeqci-3.1.4-8929.msi, http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/, last access: 13 October 2014.