Aquatic Chemistry for Engineers

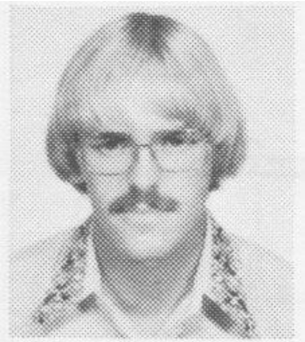
Modeling water treatment trains and processes with PHREEQC

2 April 2015

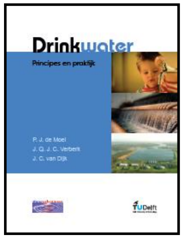
Peter de Moel – Omnisys/TU Delft

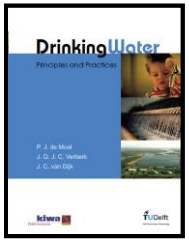
Personal introduction …

Record on water chemistry



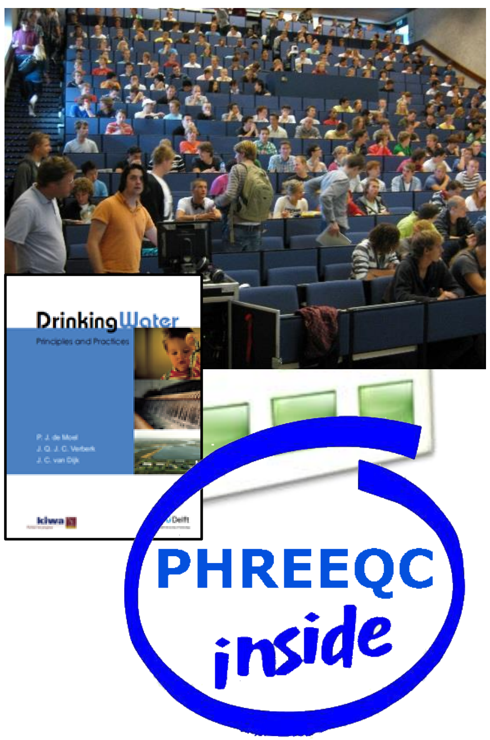
- 1979 - 1980 : KIWA (now KWR)
  - KIWA report and computer program aggressive water
- 1980 - 2000 : DHV (now RHDHV)
  - Patent softening Amsterdam (Graveland cs)
  - Publication / HP41 program on CaCO3 equilibrium
  - Publications / presentations (H2O - JAWWA – Las Vegas)
  - Design and build over 40 water treatment plants, wordwide
- 2000 - present : TU Delft (part-time)
  - BSc / MSc – education
  - OpenCourseWare (2007 - 2014)
  - Aquatic Chemistry 4 Eng (2011 - now)
  - Online MSc (2012 - 2014)
  - edX MOOC (2013 - 2014)





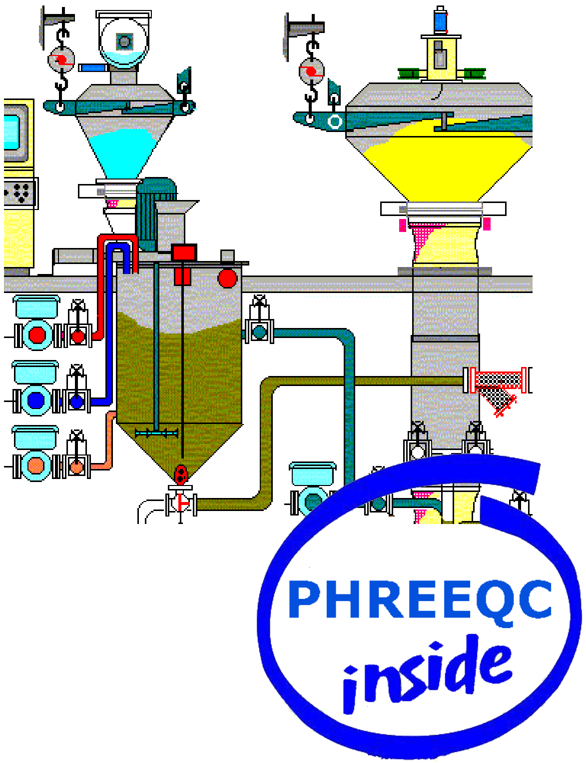
AC4E – Our focus points

Education



Research

Process control

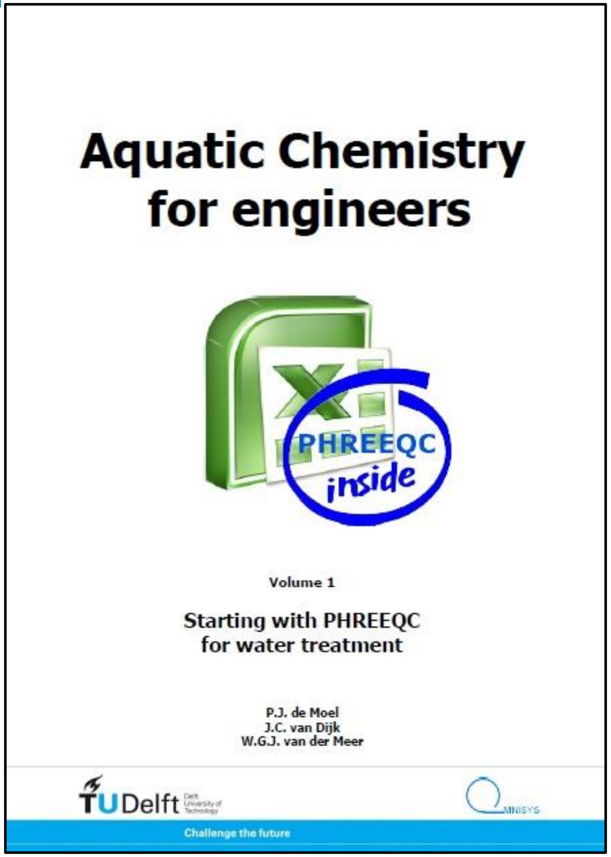


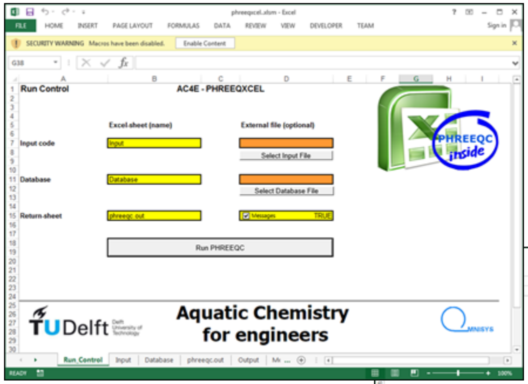
Practical applications for drinking water, waste water and industrial water

PhreeqXcel – PHREEQC in Excel

with Stimela.dat 

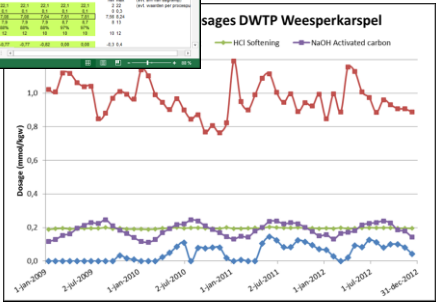
2nd IWA New Developments in IT & Water Conference





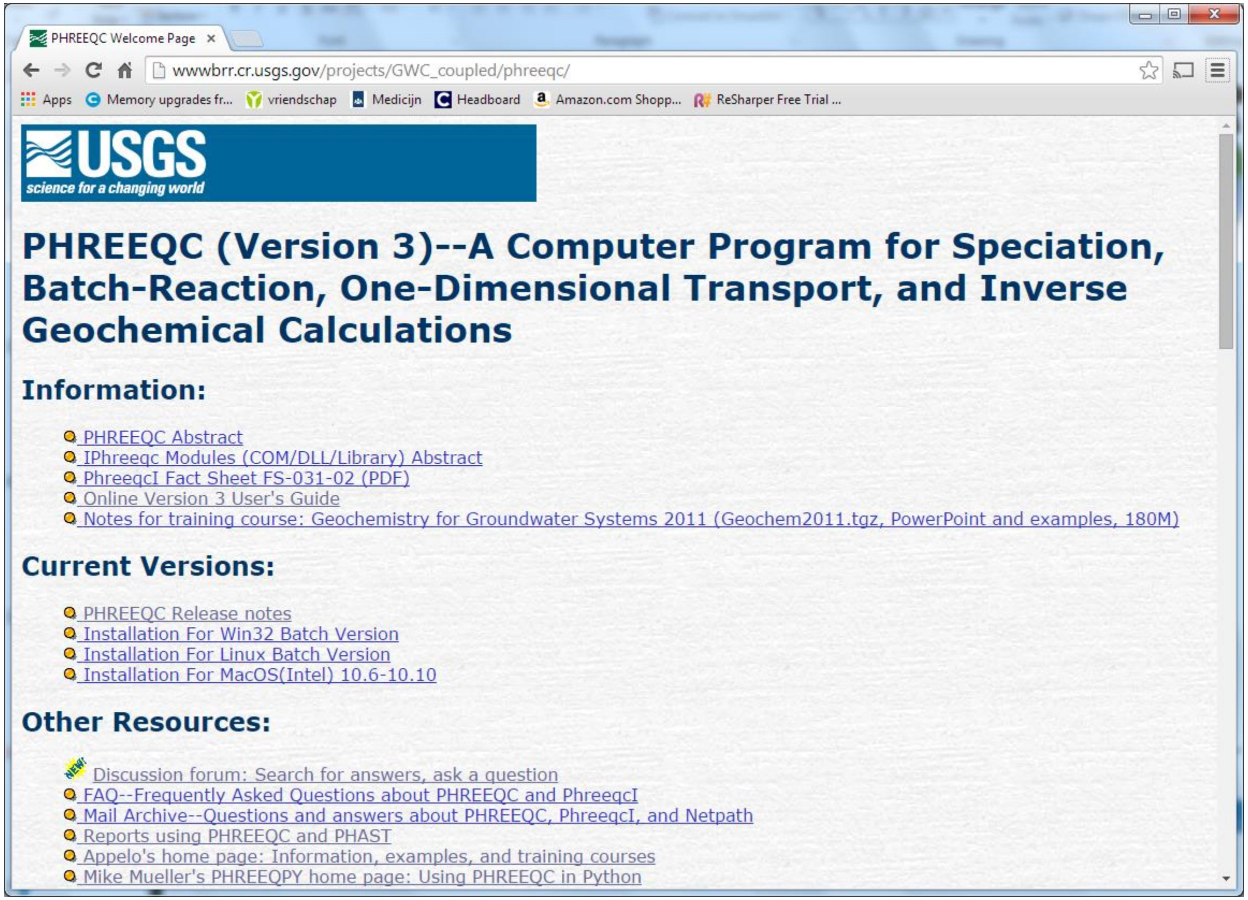
Waterbedrijf Groningen

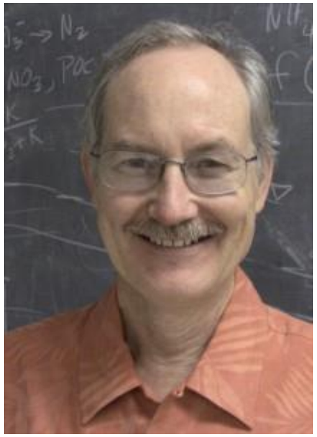
waternet

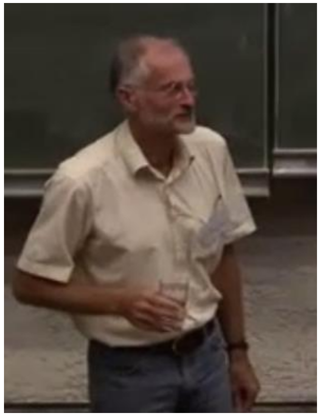


PHREEQC

Development since 1980







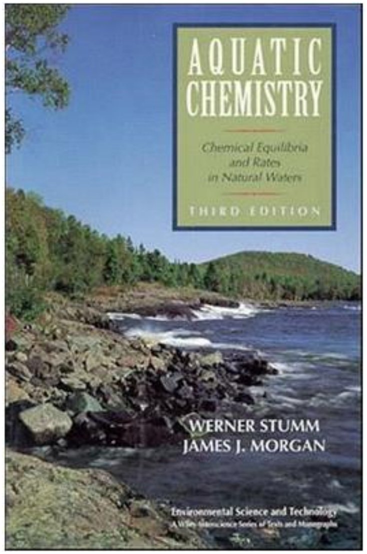
pH - Redox – Equilibrium - Calculations

PHREEQC

pH - Redox - Equilibrium Calculations

• 25 elements	C Ca Mg Na etc
• 21 redox states	C(+4) C(-4) etc
• 180 species	C(+4) : CO2 HCO3 CO3 etc
	C(-4) : CH4 etc
• 72 solid phases	CaCO3 Fe(OH)3 etc
• 8 gas phases	CO2 H2S etc
• + Exchange eq.	(ion-exchange)
• + Surface eq.	(activated carbon)
• + Rates	(kinetics)

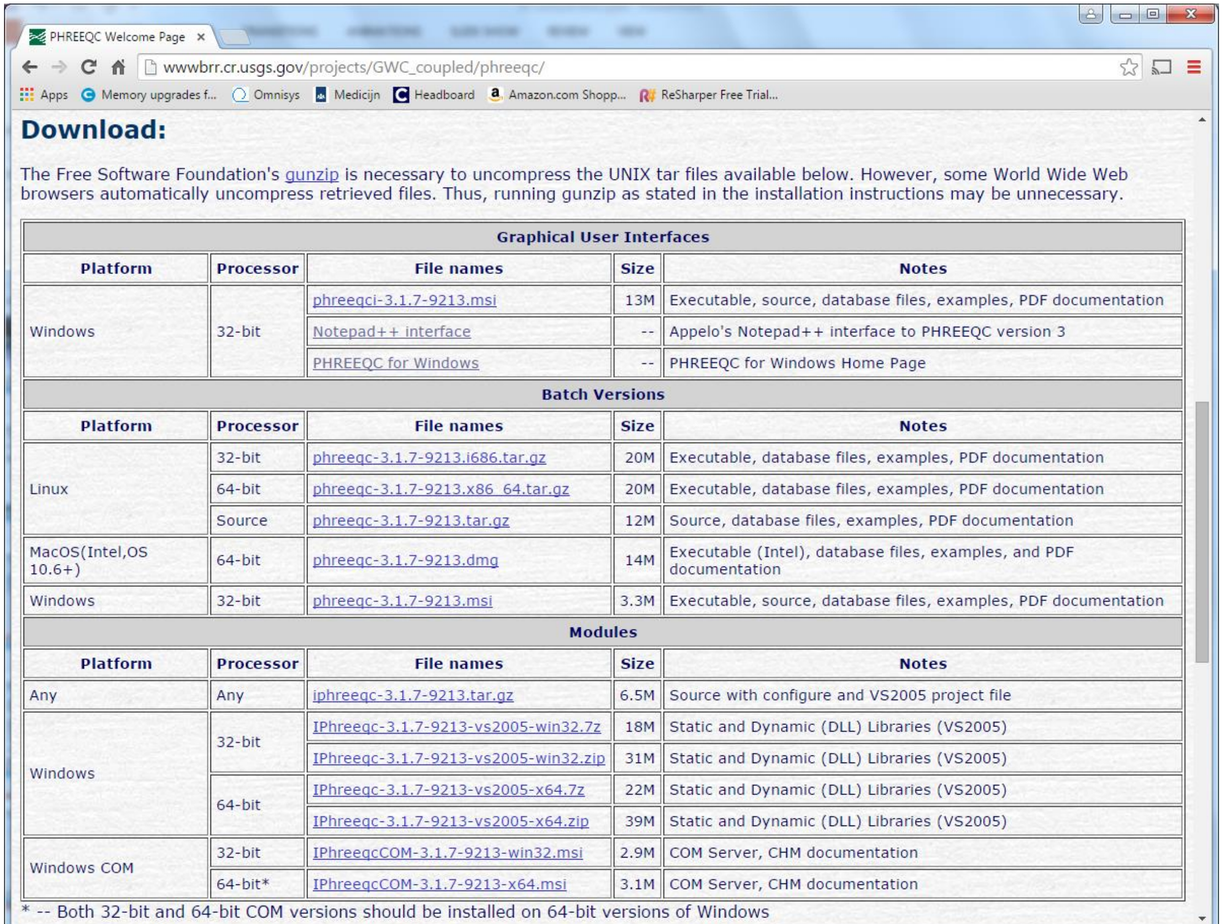
- 8 databases (+ **Stimela.dat**)



Aquatic Chemistry (Stumm & Morgan) in your laptop

PHREEQC

Freely available

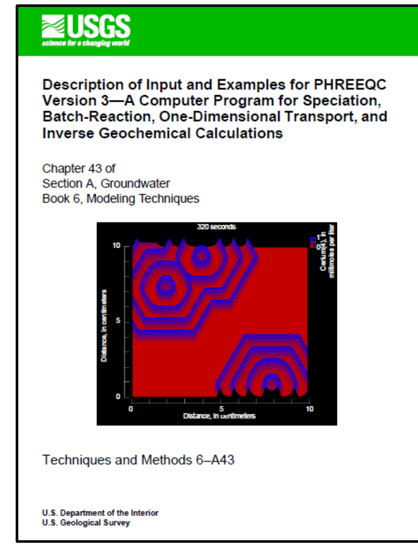


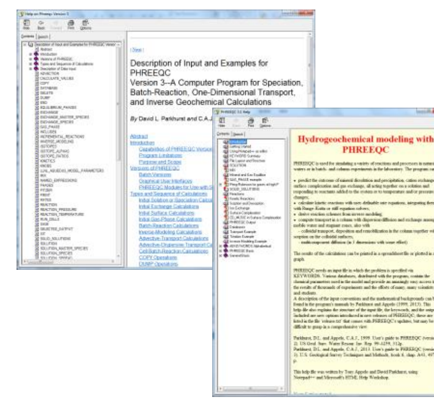
Download:

The Free Software Foundation's gunzip is necessary to uncompress the UNIX tar files available below. However, some World Wide Web browsers automatically uncompress retrieved files. Thus, running gunzip as stated in the installation instructions may be unnecessary.

Platform	Processor	File names	Size	Notes
Graphical User Interfaces				
Windows	32-bit	phreeqci-3.1.7-9213.msi	13M	Executable, source, database files, examples, PDF documentation
		Notepad++ interface	--	Appelo's Notepad++ interface to PHREEQC version 3
		PHREEQC for Windows	--	PHREEQC for Windows Home Page
Batch Versions				
Linux	32-bit	phreeqc-3.1.7-9213.i686.tar.gz	20M	Executable, database files, examples, PDF documentation
	64-bit	phreeqc-3.1.7-9213.x86_64.tar.gz	20M	Executable, database files, examples, PDF documentation
	Source	phreeqc-3.1.7-9213.tar.gz	12M	Source, database files, examples, PDF documentation
MacOS(Intel,OS 10.6+)	64-bit	phreeqc-3.1.7-9213.dmg	14M	Executable (Intel), database files, examples, and PDF documentation
Windows	32-bit	phreeqc-3.1.7-9213.msi	3.3M	Executable, source, database files, examples, PDF documentation
Modules				
Any	Any	iphreeqc-3.1.7-9213.tar.gz	6.5M	Source with configure and VS2005 project file
Windows	32-bit	IPhreeqc-3.1.7-9213-vs2005-win32.7z	18M	Static and Dynamic (DLL) Libraries (VS2005)
		IPhreeqc-3.1.7-9213-vs2005-win32.zip	31M	Static and Dynamic (DLL) Libraries (VS2005)
	64-bit	IPhreeqc-3.1.7-9213-vs2005-x64.7z	22M	Static and Dynamic (DLL) Libraries (VS2005)
		IPhreeqc-3.1.7-9213-vs2005-x64.zip	39M	Static and Dynamic (DLL) Libraries (VS2005)
Windows COM	32-bit	IPhreeqcCOM-3.1.7-9213-win32.msi	2.9M	COM Server, CHM documentation
	64-bit*	IPhreeqcCOM-3.1.7-9213-x64.msi	3.1M	COM Server, CHM documentation

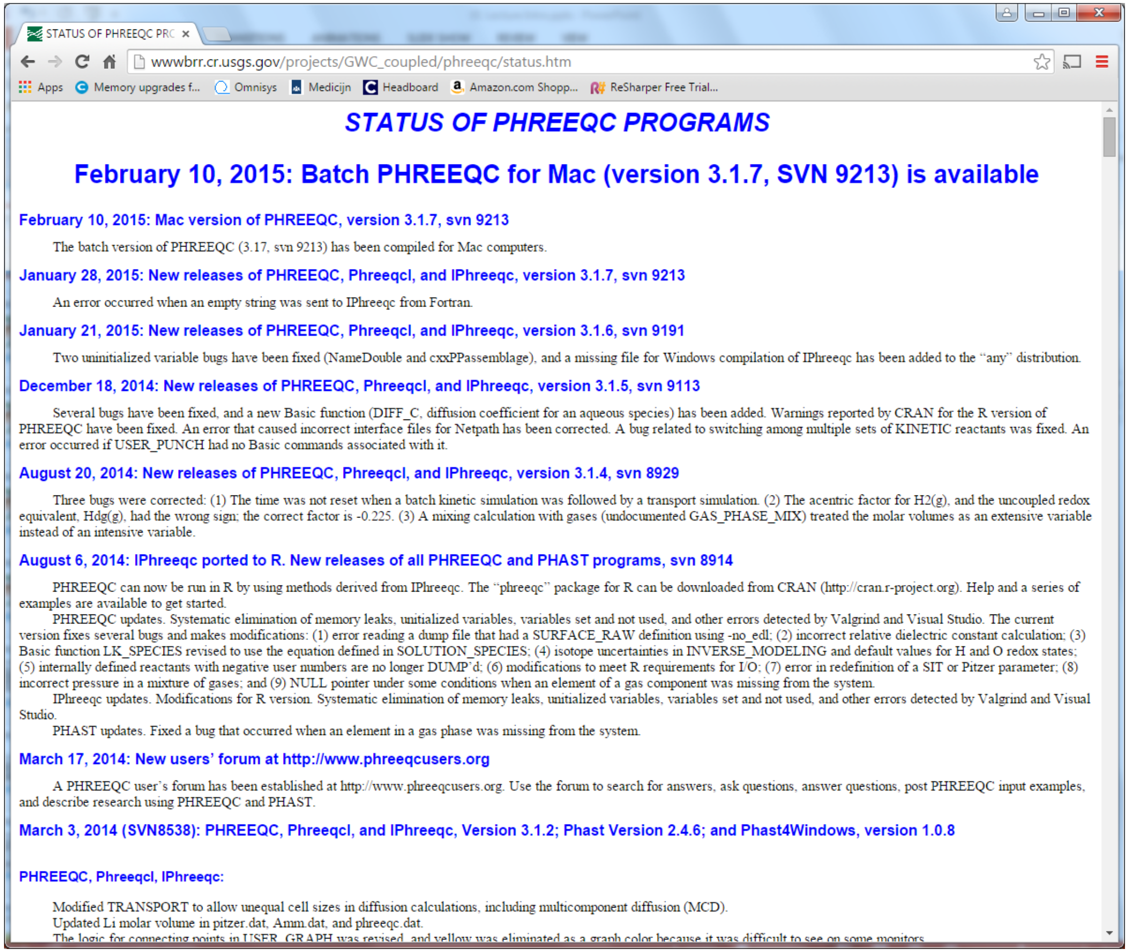
* -- Both 32-bit and 64-bit COM versions should be installed on 64-bit versions of Windows





PHREEQC

Latest release PHREEQC: 1.5 months ago



STATUS OF PHREEQC PROGRAMS

February 10, 2015: Batch PHREEQC for Mac (version 3.1.7, SVN 9213) is available

February 10, 2015: Mac version of PHREEQC, version 3.1.7, svn 9213

The batch version of PHREEQC (3.17, svn 9213) has been compiled for Mac computers.

January 28, 2015: New releases of PHREEQC, Phreeqcl, and IPhreeqc, version 3.1.7, svn 9213

An error occurred when an empty string was sent to IPhreeqc from Fortran.

January 21, 2015: New releases of PHREEQC, Phreeqcl, and IPhreeqc, version 3.1.6, svn 9191

Two uninitialized variable bugs have been fixed (NameDouble and cxxPPassemblage), and a missing file for Windows compilation of IPhreeqc has been added to the "any" distribution.

December 18, 2014: New releases of PHREEQC, Phreeqcl, and IPhreeqc, version 3.1.5, svn 9113

Several bugs have been fixed, and a new Basic function (DIFF_C, diffusion coefficient for an aqueous species) has been added. Warnings reported by CRAN for the R version of PHREEQC have been fixed. An error that caused incorrect interface files for Netpath has been corrected. A bug related to switching among multiple sets of KINETIC reactants was fixed. An error occurred if USER_PUNCH had no Basic commands associated with it.

August 20, 2014: New releases of PHREEQC, Phreeqcl, and IPhreeqc, version 3.1.4, svn 8929

Three bugs were corrected: (1) The time was not reset when a batch kinetic simulation was followed by a transport simulation. (2) The acentric factor for H2(g), and the uncoupled redox equivalent, Hdg(g), had the wrong sign; the correct factor is -0.225. (3) A mixing calculation with gases (undocumented GAS_PHASE_MIX) treated the molar volumes as an extensive variable instead of an intensive variable.

August 6, 2014: IPhreeqc ported to R. New releases of all PHREEQC and PHAST programs, svn 8914

PHREEQC can now be run in R by using methods derived from IPhreeqc. The "phreeqc" package for R can be downloaded from CRAN (http://cran.r-project.org). Help and a series of examples are available to get started.

PHREEQC updates. Systematic elimination of memory leaks, unitialized variables, variables set and not used, and other errors detected by Valgrind and Visual Studio. The current version fixes several bugs and makes modifications: (1) error reading a dump file that had a SURFACE_RAW definition using -no_edl; (2) incorrect relative dielectric constant calculation; (3) Basic function LK_SPECIES revised to use the equation defined in SOLUTION_SPECIES; (4) isotope uncertainties in INVERSE_MODELING and default values for H and O redox states; (5) internally defined reactants with negative user numbers are no longer DUMP'd; (6) modifications to meet R requirements for I/O; (7) error in redefinition of a SIT or Pitzer parameter; (8) incorrect pressure in a mixture of gases; and (9) NULL pointer under some conditions when an element of a gas component was missing from the system.

IPhreeqc updates. Modifications for R version. Systematic elimination of memory leaks, unitialized variables, variables set and not used, and other errors detected by Valgrind and Visual Studio.

PHAST updates. Fixed a bug that occurred when an element in a gas phase was missing from the system.

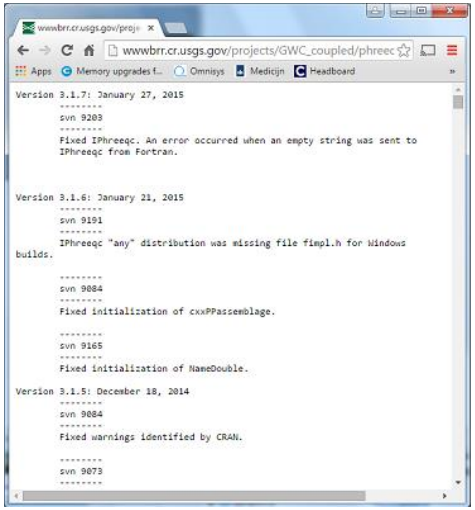
March 17, 2014: New users' forum at http://www.phreeqcusers.org

A PHREEQC user's forum has been established at http://www.phreeqcusers.org. Use the forum to search for answers, ask questions, answer questions, post PHREEQC input examples, and describe research using PHREEQC and PHAST.

March 3, 2014 (SVN8538): PHREEQC, Phreeqcl, and IPhreeqc, Version 3.1.2; Phast Version 2.4.6; and Phast4Windows, version 1.0.8

PHREEQC, Phreeqcl, IPhreeqc:

Modified TRANSPORT to allow unequal cell sizes in diffusion calculations, including multicomponent diffusion (MCD).
Updated Li molar volume in pitzer.dat, Amm.dat, and phreeqc.dat.
The logic for connecting points in USER_GRAPH was revised, and yellow was eliminated as a graph color because it was difficult to see on some monitors.



```
Version 3.1.7: January 27, 2015
        --------
        svn 9203
        --------
        Fixed IPhreeqc. An error occurred when an empty string was sent to
        IPhreeqc from Fortran.

Version 3.1.6: January 21, 2015
        --------
        svn 9191
        --------
        IPhreeqc "any" distribution was missing file fimpl.h for Windows
builds.

        --------
        svn 9084
        --------
        Fixed initialization of cxxPPassemblage.

        --------
        svn 9165
        --------
        Fixed initialization of NameDouble.

Version 3.1.5: December 18, 2014
        --------
        svn 9084
        --------
        Fixed warnings identified by CRAN.

        --------
        svn 9073
        --------
```

PHREEQE (1980)

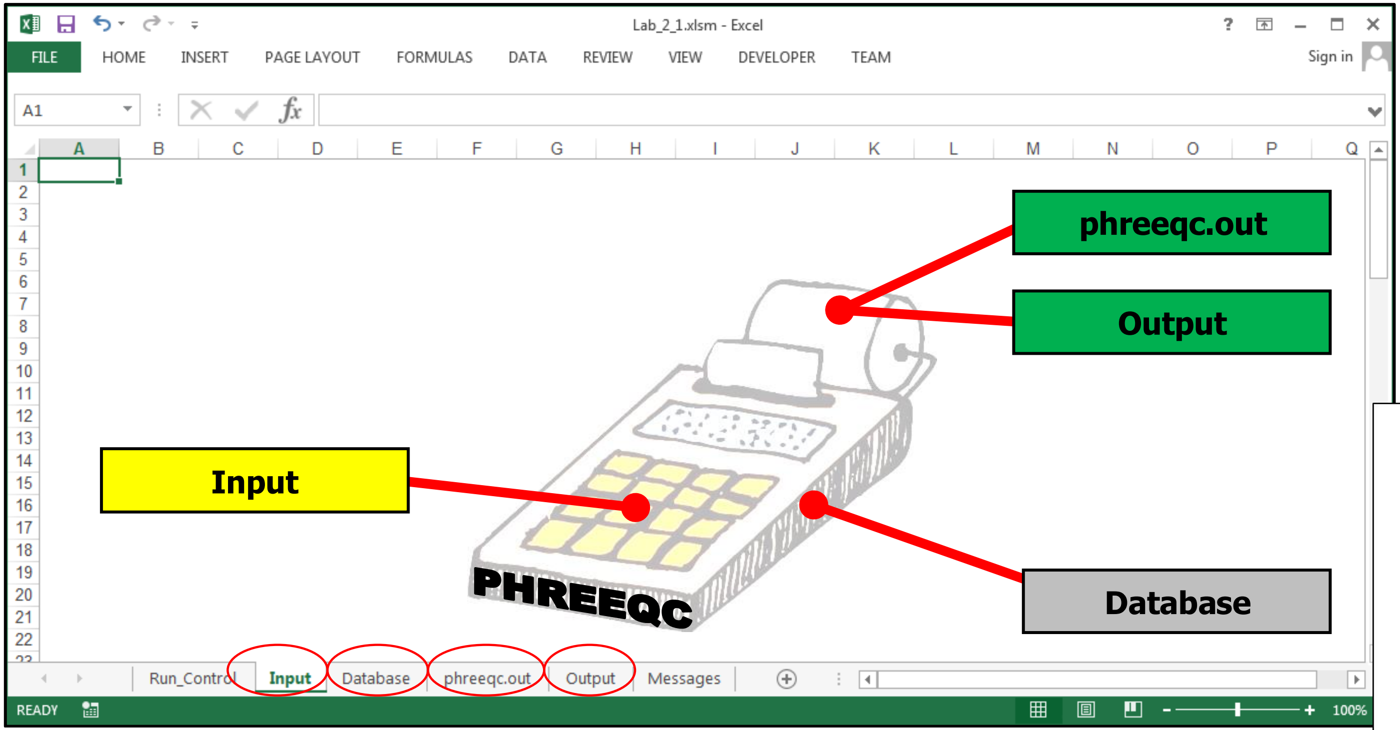
PHREEQC v1 (1995)

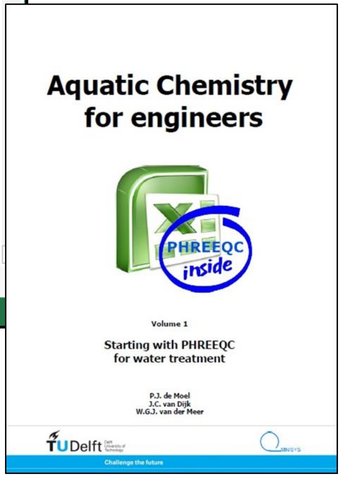
PHREEQC v2 (1999)

PHREEQC v3 (2013)

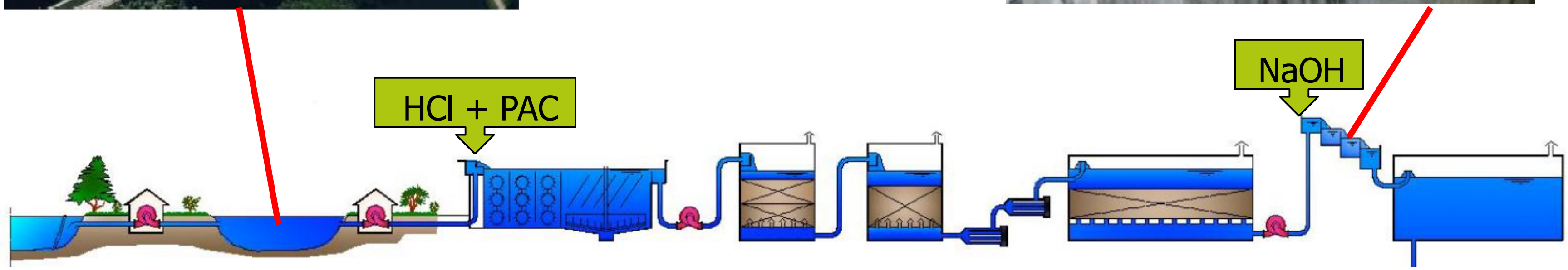
PHREEQXCEL

Excel with IphreeqcCOM for Windows + Stimela.dat



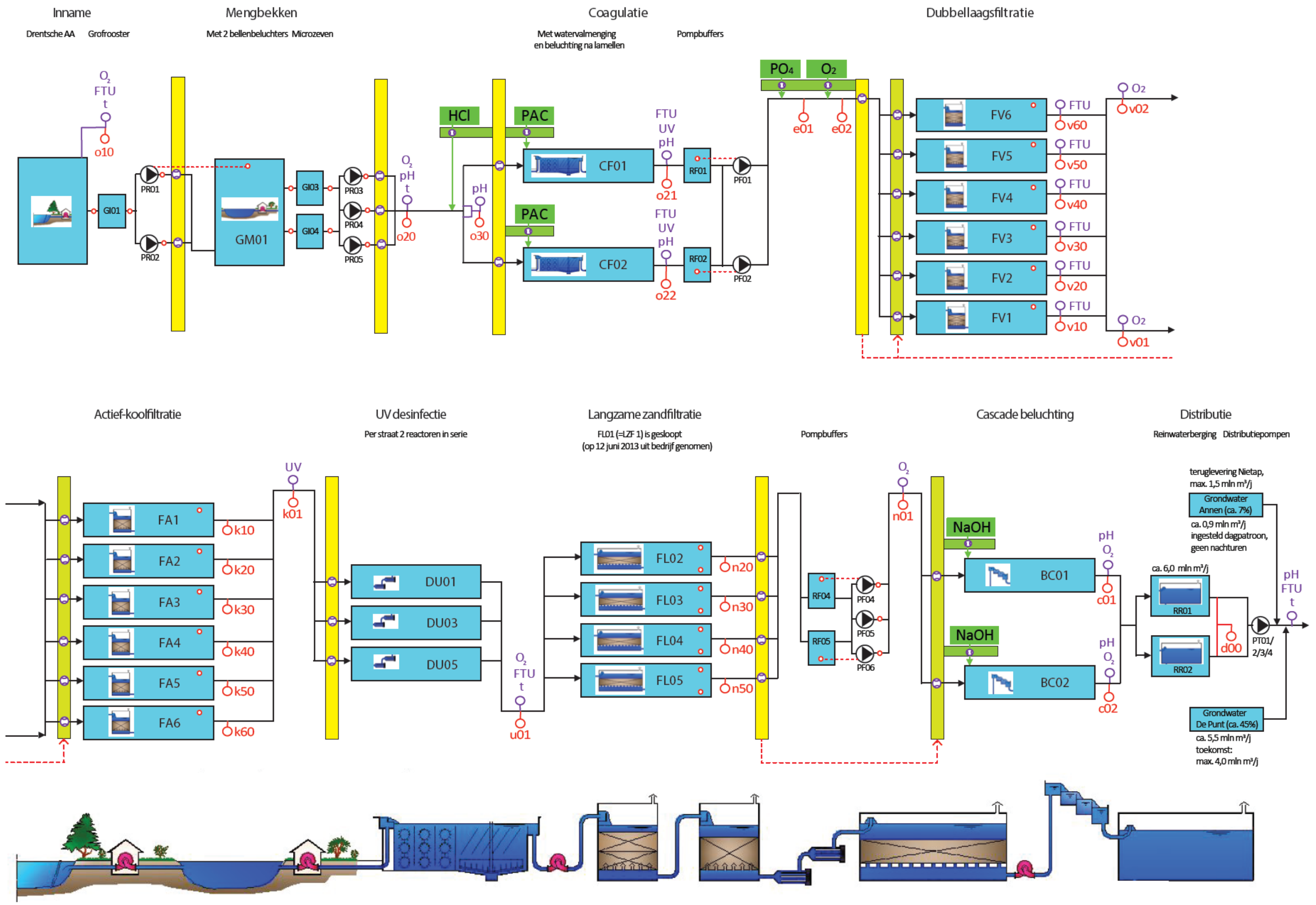


Drinking water - De Punt

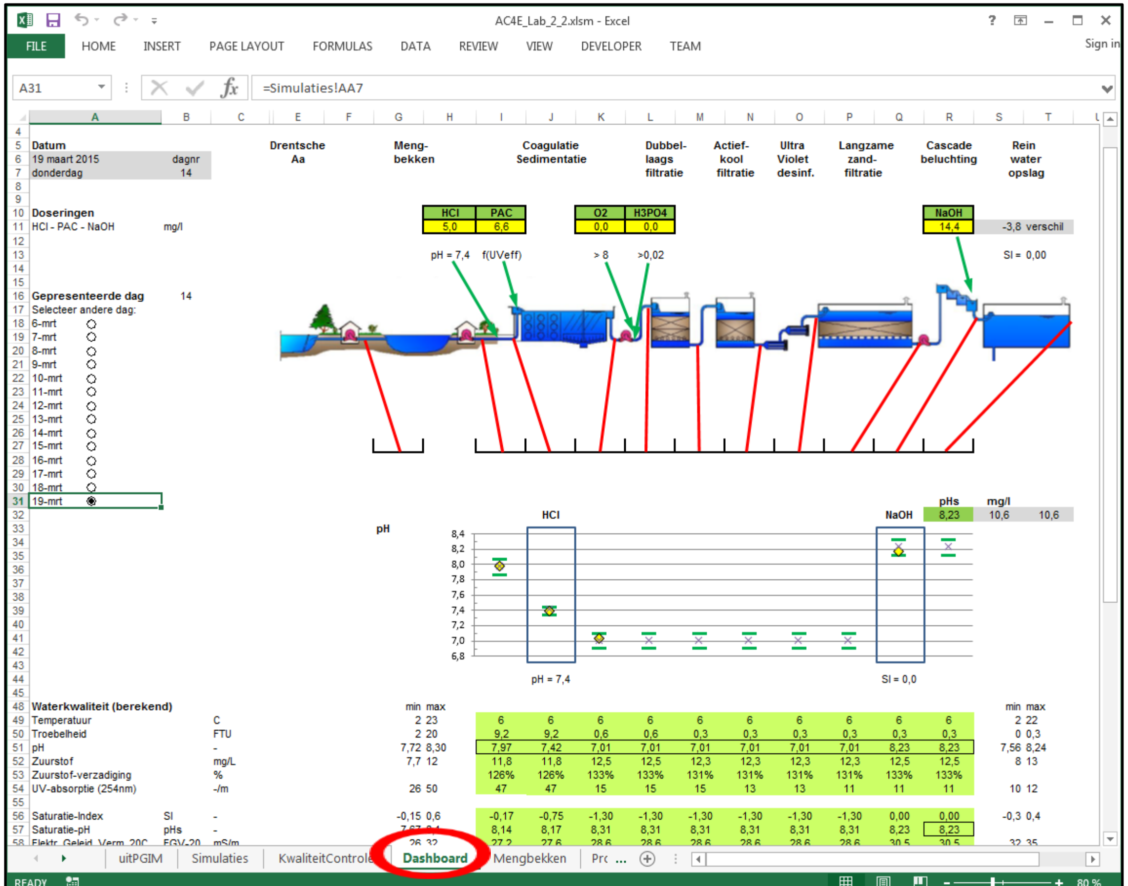


Waterbedrijf Groningen

Drinking water - De Punt



Drinking water - De Punt



Modeling for 'day-average' values

10 process/sample points

31 water quality parameters

14 days

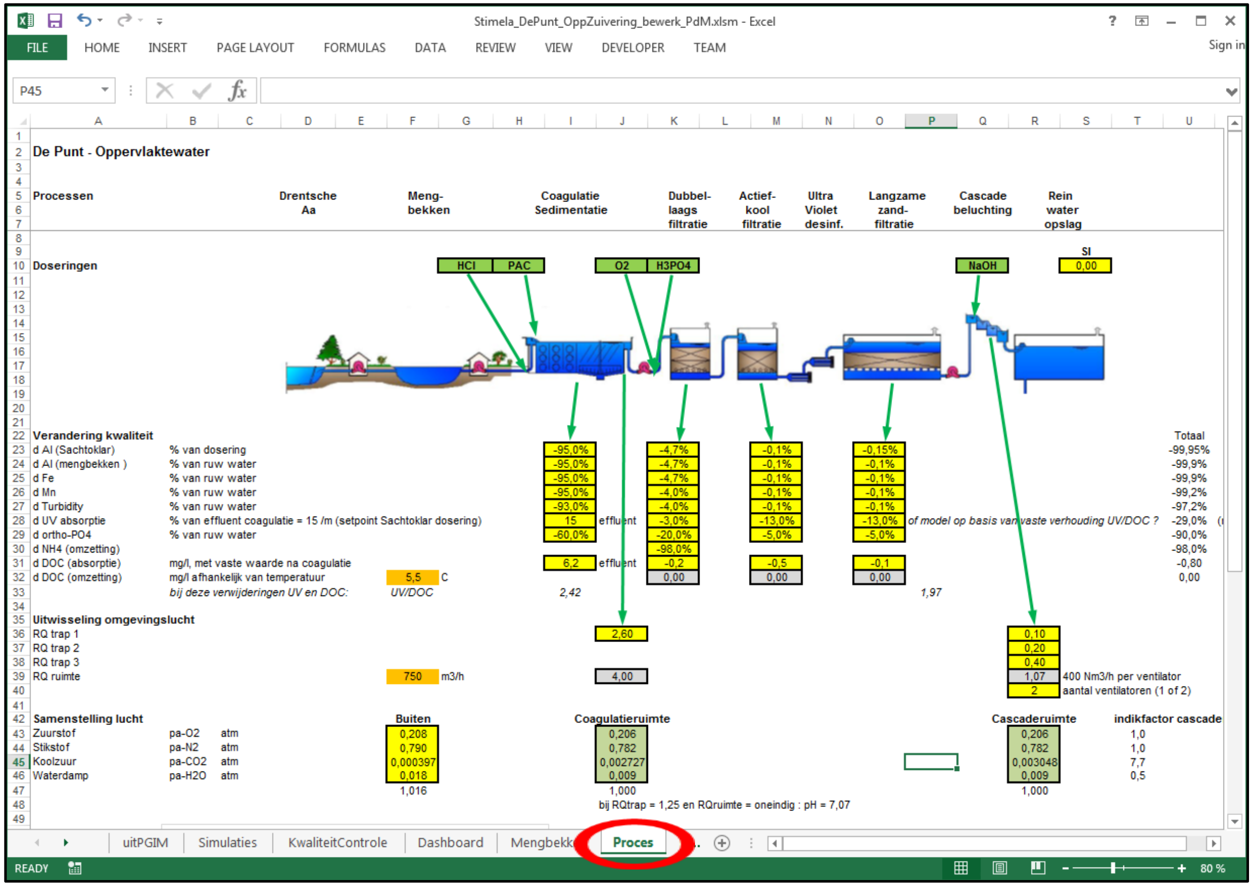
=

4,340 numbers / batch

Selected per day for presentation

Drinking water - De Punt

Waterbedrijf Groningen



Removal efficiencies from historical data

4 removal processes
2 gas exchange processes

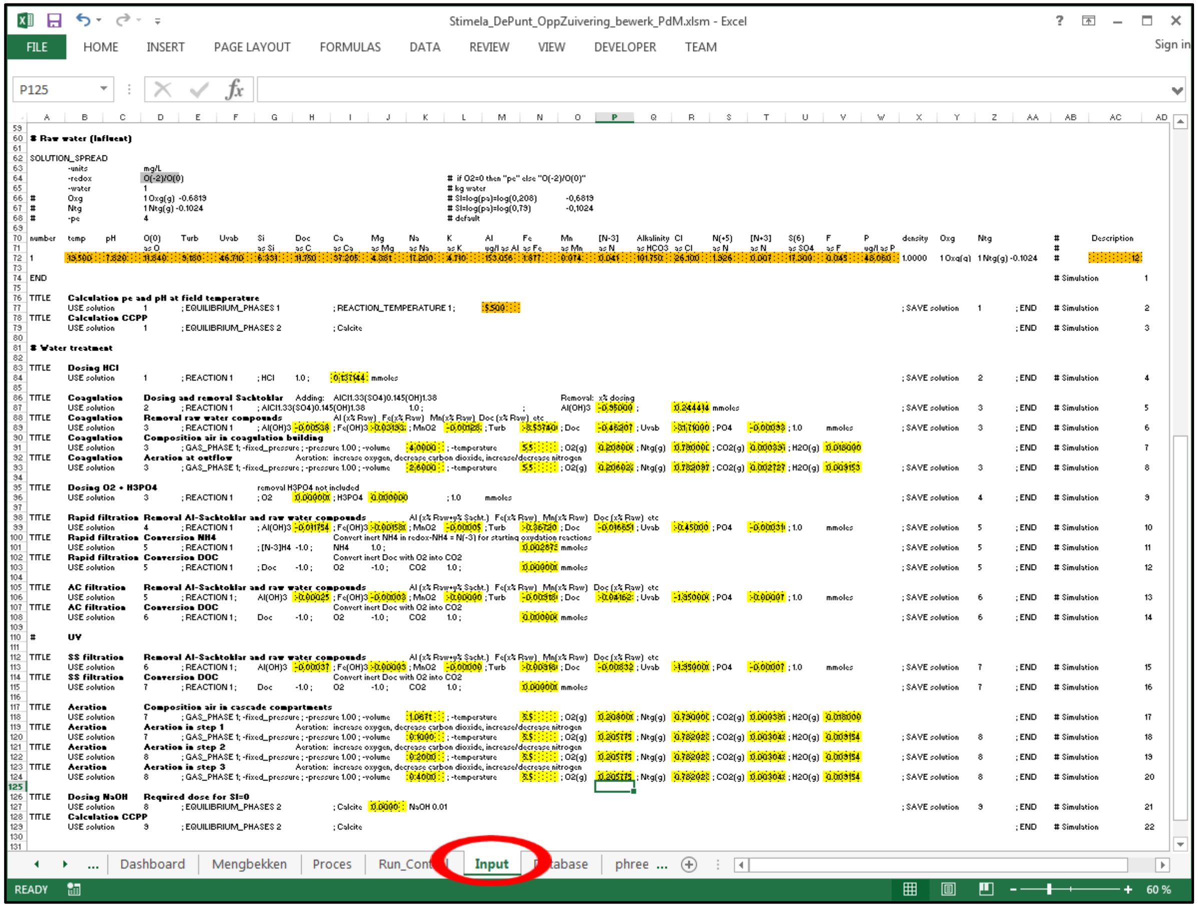
10 water quality parameters
4 gas/air quality parameters

Biological TOC conversion depends on water temperature

Parameter to be determined/modified by process engineer (yearly ?)
Future: self learning system

Drinking water - De Punt

Waterbedrijf Groningen



PHREEQC input code

Simulation per day

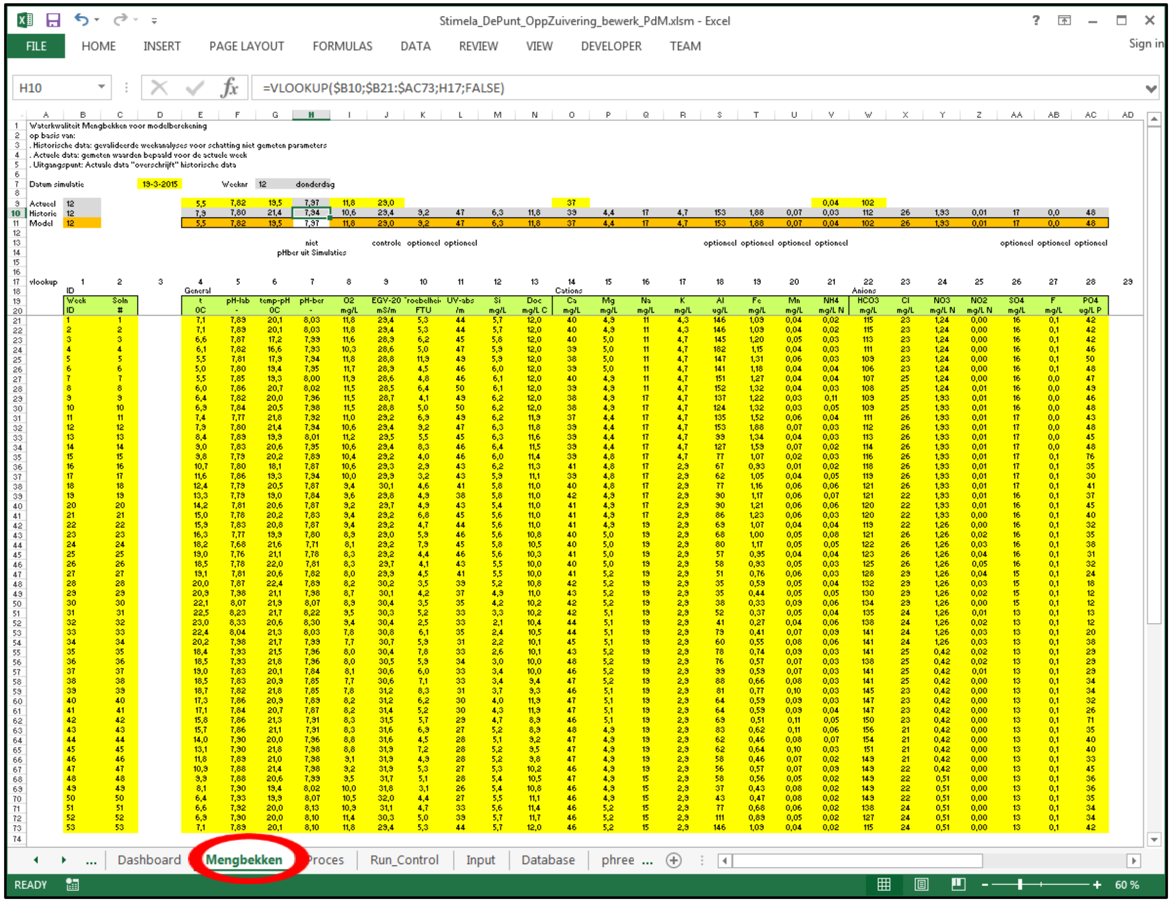
Orange cells:
Raw water quality
from reservoir
(from sheet Mengbekken)

Yellow cells:
Process parameters
(from sheet Proces)

1-3 program code lines
per treatment process
(22 PHREEQC calculations)

Drinking water - De Punt

Waterbedrijf Groningen



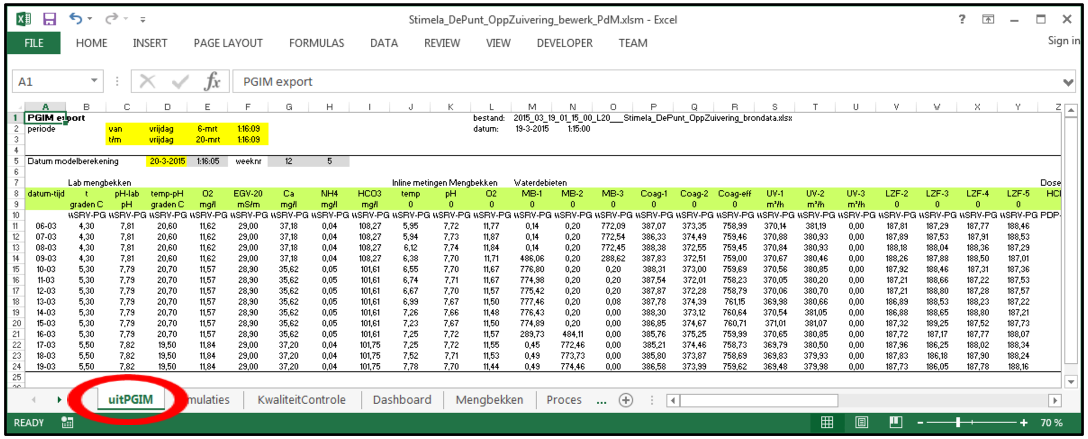
Actual and historical water quality from reservoir

9 actual quality parameters (weekly sampling)
25 historical quality parameters
from previous year(s)

Actual overrules historical
Actual compared with historical

Validation checks

Drinking water - De Punt



PGIM export											bestand:	2015_03_19_01_15_00_L20___Stimela_DePunt_OppZuivering_brondata.xlsx	
periode		van	vrijdag	6-mrt	1:16:09						datum:	19-3-2015	1:15:00
		t/m	vrijdag	20-mrt	1:16:09								
Datum modelberekening			20-3-2015	1:16:05	weeknr	12	5						

	Lab mengbekken								Inline metingen Mengbekken			Waterdebieten													Dose
datum-tijd	t	pH-lab	temp-pH	O2	EGV-20	Ca	NH4	HCO3	temp	pH	O2	MB-1	MB-2	MB-3	Coag-1	Coag-2	Coag-eff	UV-1	UV-2	UV-3	LZF-2	LZF-3	LZF-4	LZF-5	HCl
	graden C	pH	graden C	mg/l	mS/m	mg/l	mg/l	mg/l	0	0	0	0	0	0	0	0	0	m³/h	m³/h	m³/h	0	0	0	0	
	\\SRV-PG	\\SRV-PG	\\SRV-PG	\\SRV-PG	\\SRV-PG	\\SRV-PG	\\SRV-PG	\\SRV-PG	\\SRV-PG	\\SRV-PG	\\SRV-PG	\\SRV-PG	\\SRV-PG	\\SRV-PG	\\SRV-PG	\\SRV-PG	\\SRV-PG	\\SRV-PG	\\SRV-PG	\\SRV-PG	\\SRV-PG	\\SRV-PG	\\SRV-PG	\\SRV-PG	PDP-
06-03	4,30	7,81	20,60	11,62	29,00	37,18	0,04	108,27	5,95	7,72	11,77	0,14	0,20	772,09	387,07	373,35	758,99	370,14	381,19	0,00	187,81	187,29	187,77	188,46	
07-03	4,30	7,81	20,60	11,62	29,00	37,18	0,04	108,27	5,94	7,73	11,87	0,14	0,20	772,54	386,33	374,49	759,46	370,88	380,93	0,00	187,89	187,53	187,91	188,53	
08-03	4,30	7,81	20,60	11,62	29,00	37,18	0,04	108,27	6,12	7,74	11,84	0,14	0,20	772,45	388,38	372,55	759,45	370,84	380,93	0,00	188,18	188,04	188,36	187,29	
09-03	4,30	7,81	20,60	11,62	29,00	37,18	0,04	108,27	6,38	7,70	11,71	486,06	0,20	288,62	387,83	372,51	759,00	370,67	380,46	0,00	188,26	187,88	188,50	187,01	
10-03	5,30	7,79	20,70	11,57	28,90	35,62	0,05	101,61	6,55	7,70	11,67	776,80	0,20	0,20	388,31	373,00	759,69	370,56	380,85	0,00	187,92	188,46	187,31	187,36	
11-03	5,30	7,79	20,70	11,57	28,90	35,62	0,05	101,61	6,74	7,71	11,67	774,98	0,20	0,20	387,54	372,01	758,23	370,05	380,20	0,00	187,21	188,66	187,22	187,53	
12-03	5,30	7,79	20,70	11,57	28,90	35,62	0,05	101,61	6,67	7,70	11,57	775,42	0,20	0,20	387,87	372,28	758,79	370,06	380,70	0,00	187,21	188,80	187,28	187,57	
13-03	5,30	7,79	20,70	11,57	28,90	35,62	0,05	101,61	6,99	7,67	11,50	777,46	0,20	0,08	387,78	374,39	761,15	369,98	380,66	0,00	186,89	188,53	188,23	187,22	
14-03	5,30	7,79	20,70	11,57	28,90	35,62	0,05	101,61	7,26	7,66	11,48	776,43	0,20	0,00	388,30	373,12	760,64	370,54	381,05	0,00	186,88	188,65	188,80	187,21	
15-03	5,30	7,79	20,70	11,57	28,90	35,62	0,05	101,61	7,23	7,67	11,50	774,89	0,20	0,00	386,85	374,67	760,71	371,01	381,07	0,00	187,32	189,25	187,52	187,73	
16-03	5,30	7,79	20,70	11,57	28,90	35,62	0,05	101,61	7,25	7,72	11,57	289,73	484,11	0,00	385,76	375,25	759,99	370,65	380,85	0,00	187,72	187,17	187,77	188,07	
17-03	5,50	7,82	19,50	11,84	29,00	37,20	0,04	101,75	7,25	7,72	11,55	0,45	772,46	0,00	385,21	374,46	758,73	369,79	380,50	0,00	187,96	186,25	188,02	188,34	
18-03	5,50	7,82	19,50	11,84	29,00	37,20	0,04	101,75	7,52	7,71	11,53	0,49	773,73	0,00	385,80	373,87	758,69	369,83	379,93	0,00	187,83	186,18	187,90	188,24	
19-03	5,50	7,82	19,50	11,84	29,00	37,20	0,04	101,75	7,78	7,70	11,44	0,49	774,46	0,00	386,58	373,99	759,62	369,48	379,98	0,00	187,73	186,05	187,78	188,16	

Daily export from process computer (automated)

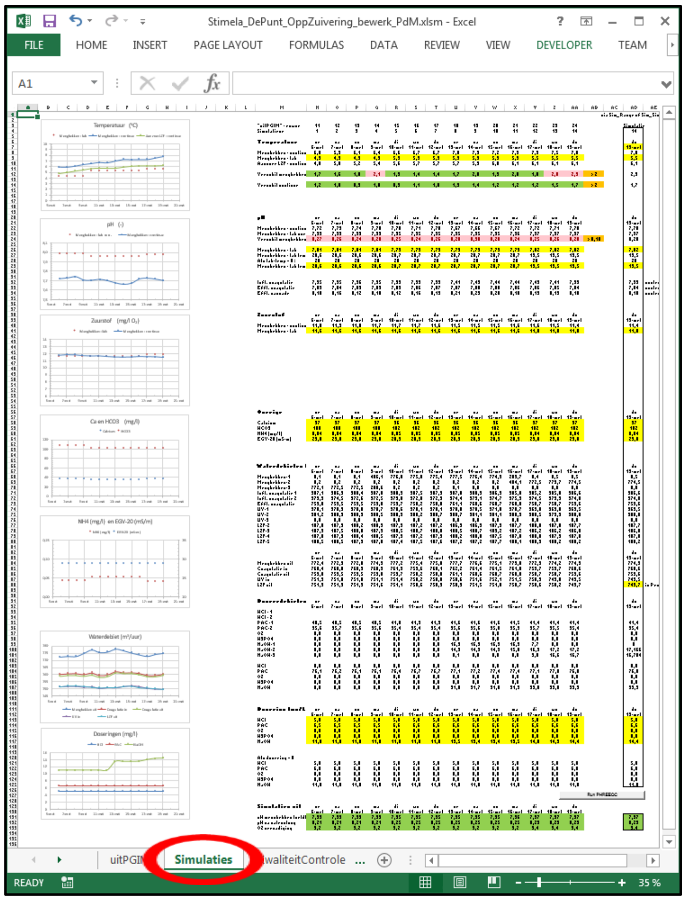
14 days
'day-average' values

Each day:
8 water quality parameters (measured by lab)
27 online water quality parameters/location
9 online flow measurements (water)
13 online flow measurements (chemicals)

672 numbers / batch

Drinking water - De Punt

Waterbedrijf Groningen



Simulations per day

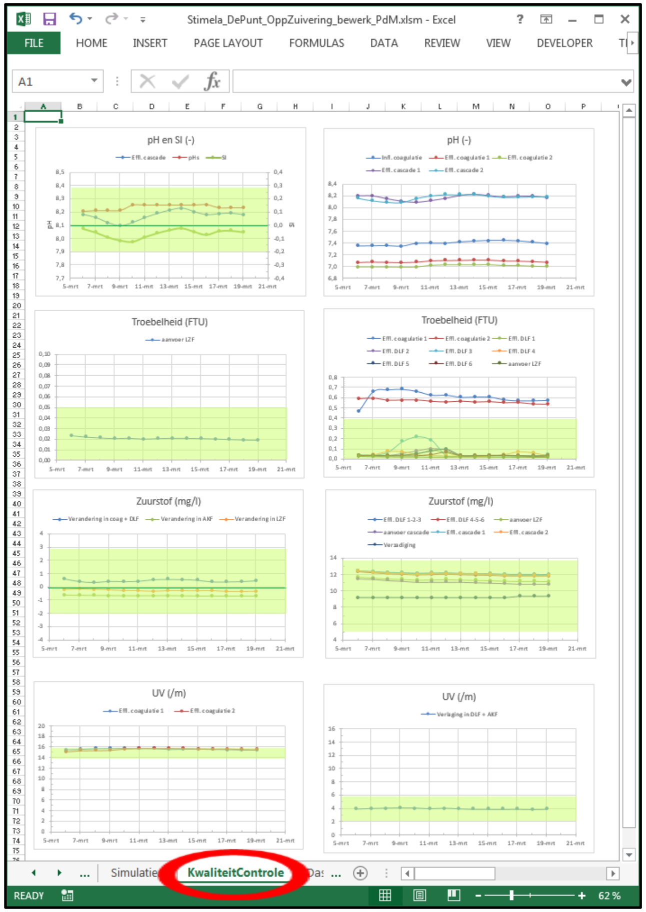
14 days
'day-average' values

Model input for:
Water flows
Chemical flows

Calculated:
Dosing levels
pH at actual temperature
O2-saturation (%)
pHs (setpoint NaOH)

Graphical presentation

Drinking water - De Punt



Quality control for operators

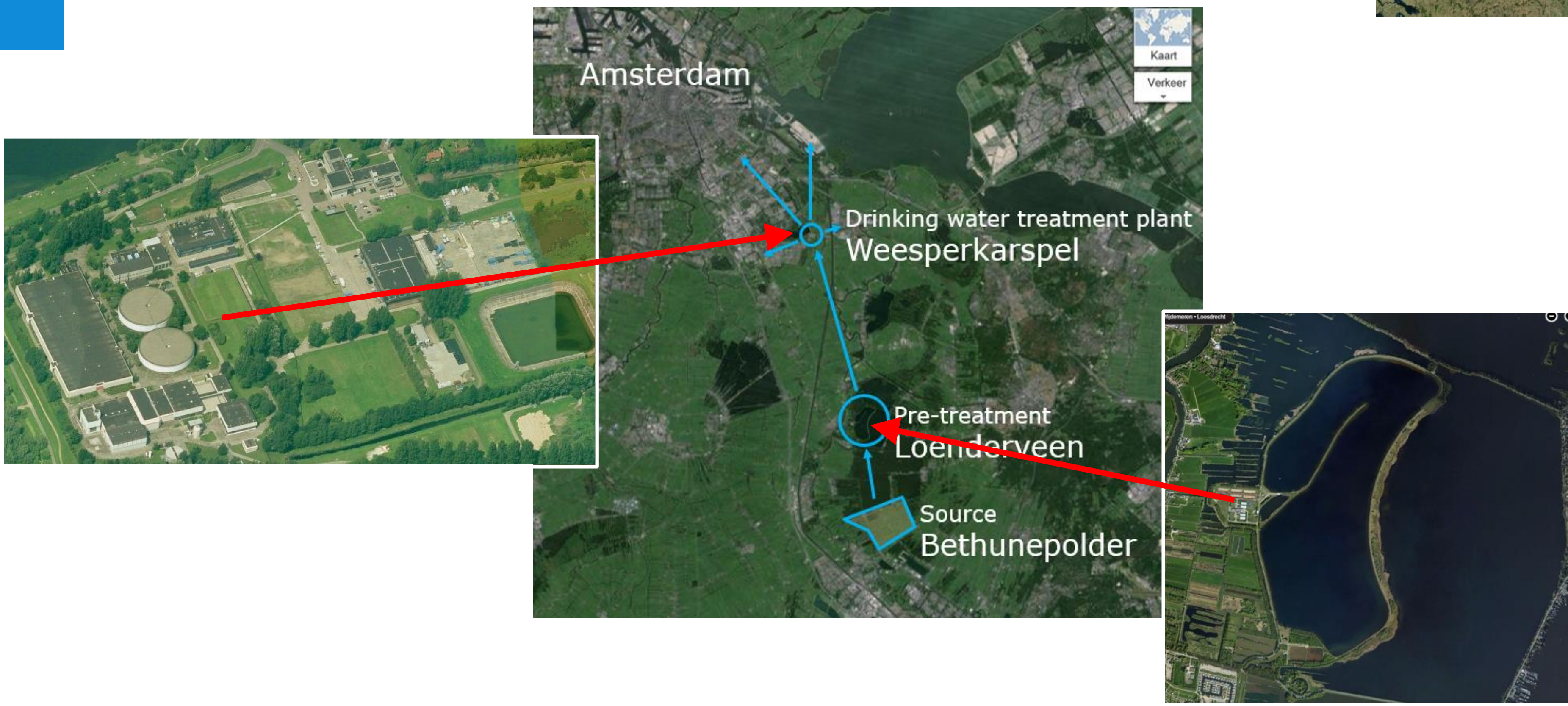
14 days overview

'Green zones'
for acceptable values

Accessible for modifications by operators, supervisors, process engineers, etc...
- no specific skills
- no proprietary equipment

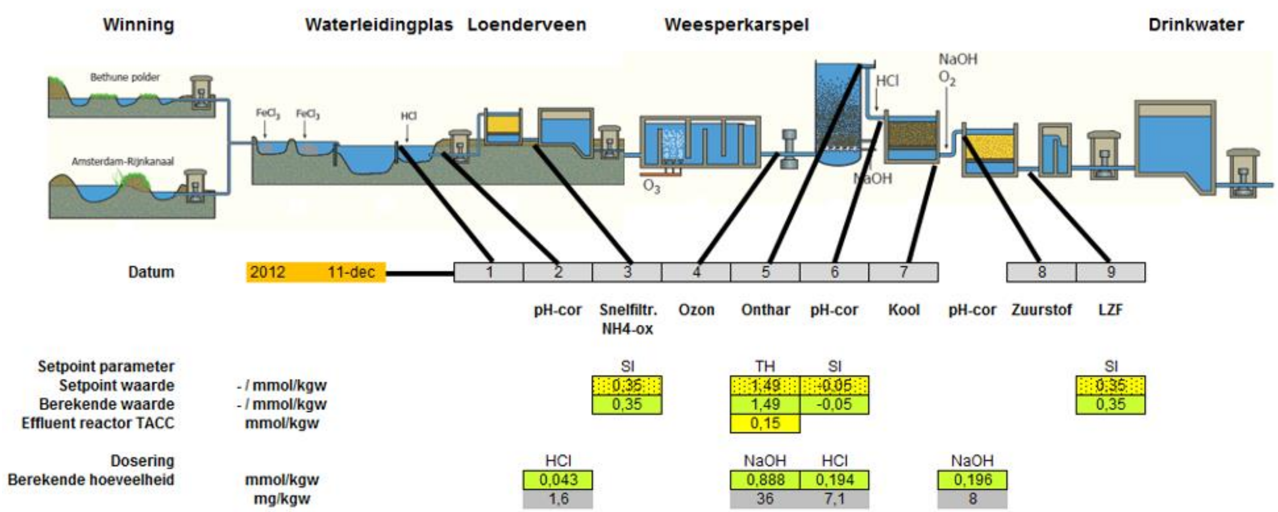
Graphical presentation

Drinking water - Weesperkarspel



Drinking water - Weesperkarspel

/innovation SI and Total Hardness (TH)

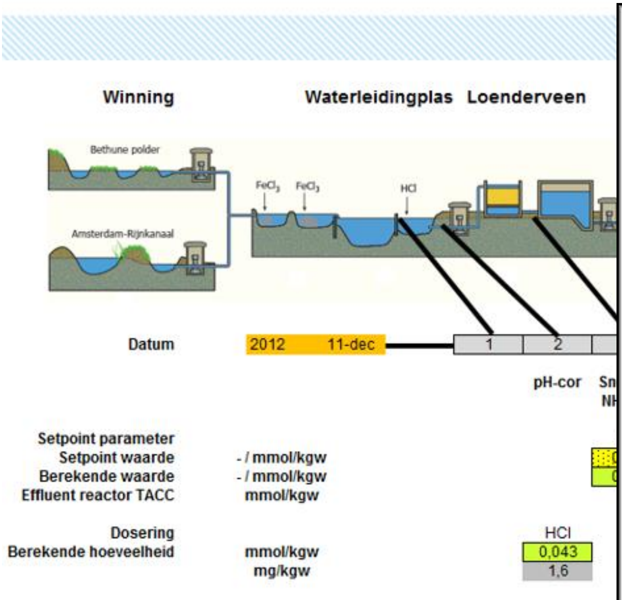


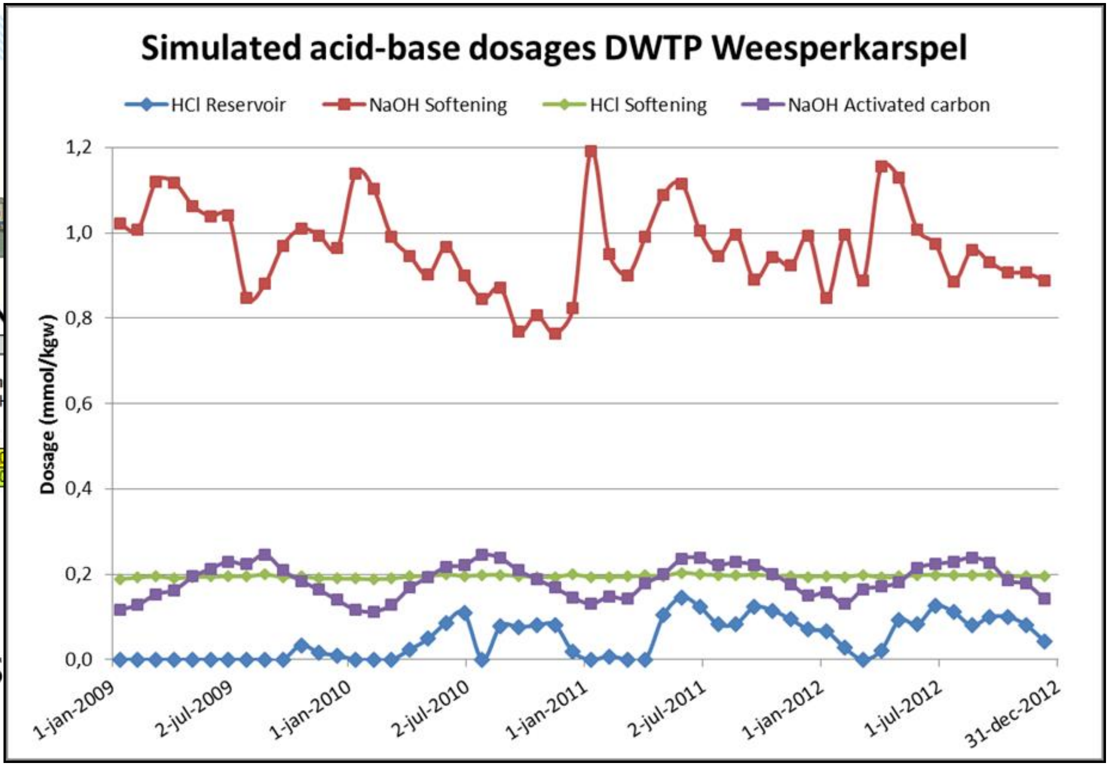
4 influencing processes in the treatment

Drinking water - Weesperkarspel

/innovation

SI and Total Hardness (TH)

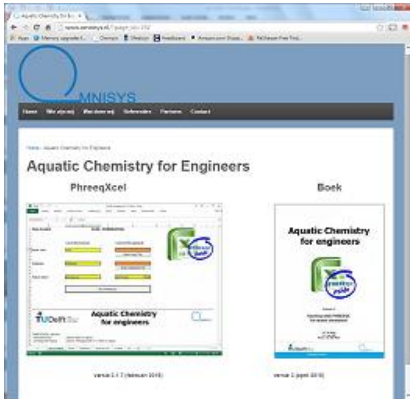




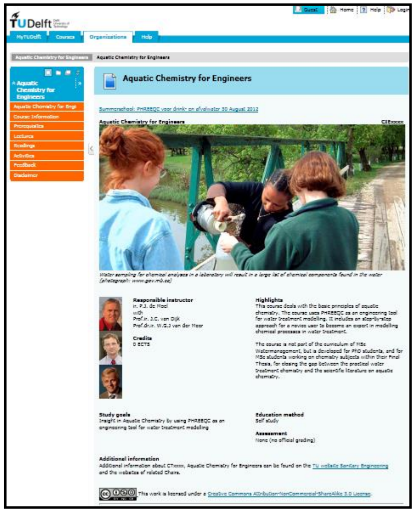
4 influencing process

Aquatic Chemistry for Engineers
Further information

OpenCourseWare website
- http://drinkwater.citg.tudelft.nl/AquaticChemistry
- http://www.omnisys.nl



Contains
- Lectures
- Readings
- Activities (Labs and Tests)
- New developments



- Database stimela.dat
  (phreeqc.dat for Water Treatment, updated)

PHREEQC

Drinking water in PHREEQC – in the cloud

Drinking water - Conductivity + Charge balance

Conductivity (EC) + Charge balance

Steps to do:
- Fill in water quality data
- Press Run Phreeqc
- Wait a few seconds for (updated) output
- optional: Change input values and re-Run Phreeqc
- optional: if email-address is filled: Send Excel file (full version) by email
- optional: if email-address is not filled: Download and Save Excel file (full version)

General

Temperature	t	° C	11,5
Oxygen	O_2	mg/L	11,0
pH			7,91
Conductivity (EC 20 ° C)		mS/m	38,4

Cations

Calcium	Ca	mg/L	40,5
Magnesium	Mg	mg/L	5,30
Sodium	Na	mg/L	49,7
Potassium	K	mg/L	2,0

Anions

Hydrogen carbonate	HCO_3	mg/L	199
Chloride	Cl	mg/L	28
Nitrate	NO_3	mg/L	7,0
Sulfate	SO_4	mg/L	7,9

Run Phreeqc

Run Phreeqc

Overall parameters

Cations	meq/kgw	4,61
Anions	meq/kgw	4,26
Conductivity (EC at t)	mS/m	31,4
Total dissolved solids (TDS)	mg/L	339
Ionic strength	mmol/kgw	5,7
Total hardness	mmol/kgw	1,23

Redox conditions

pe (electron activity)		13,92
Redox potential	mV	785

Correctness checks

Charge difference	meq/kgw	0,34
Percentage error (100*(Cat-|An|)/(Cat+|An|)		3,85 %
EC ratio, calculated/measured		1,01
pH change by electron balancing (Phreeqc)		0,000

Carbon equilibrium

pH (Hydrogen activity)		7,91
Alkalinity	meq/kgw	3,26
Total inorganic carbon (TIC)	mmol/kgw	3,34
CO_2	mmol/kgw	0,10
HCO_3 -	mmol/kgw	3,19
CO_3 2-	mmol/kgw	0,01
dpH by 0.1 mmol HCl / kgw		-0,28
Buffer capacity	mmol/kgw /pH	0,28

Calcite equilibrium

SI (calcite)		0,18
Equilibrium-pH (pHs or pH-Langelier)		7,73
Calcite Precipitation Potential	mmol/kgw	0,05
Calcite Precipitation Potential at 60 C	mmol/kgw	0,20
Calcite Precipitation Potential at 100 C	mmol/kgw	0,46

E-mail address (optional):

Download / Mail Excel

Aquatic Chemistry for Engineers

Modeling water treatment trains and processes with PHREEQC

2 April 2015

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