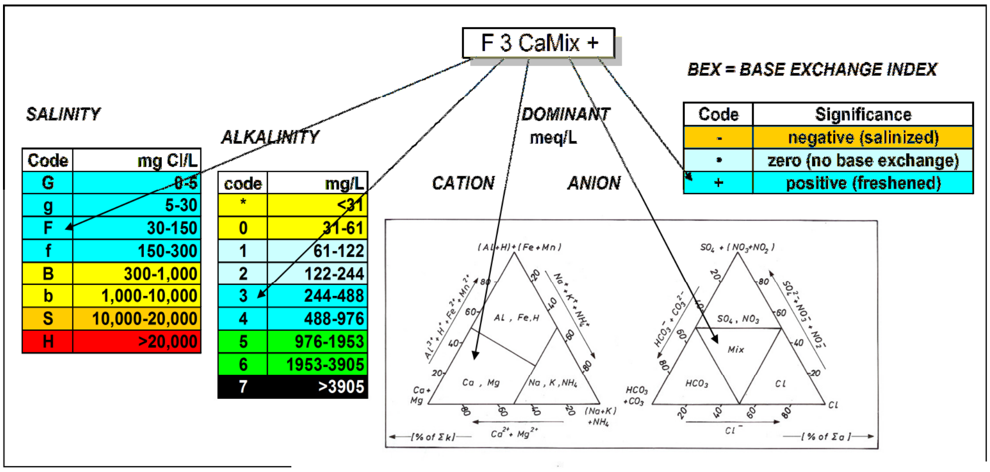
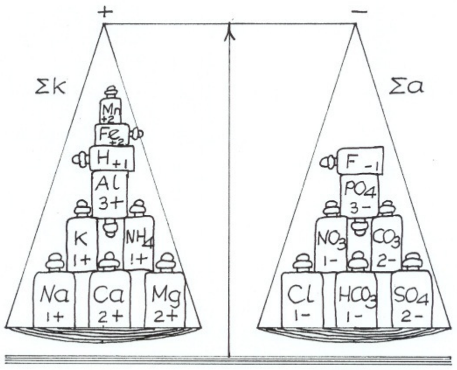
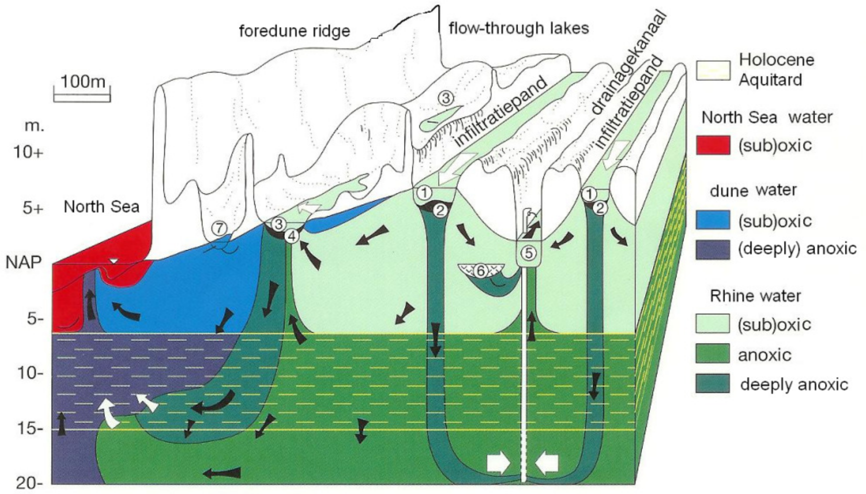


Code	mg Cl/L
G	0-5
g	5-30
F	30-150
f	150-300
B	300-1,000
b	1,000-10,000
S	10,000-20,000
H	>20,000

code	mg/L
*	<31
0	31-61
1	61-122
2	122-244
3	244-488
4	488-976
5	976-1953
6	1953-3905
7	>3905

Code	Significance
-	negative (salinized)
•	zero (no base exchange)
+	positive (freshened)





Hydrogeochemcal (HGC 2.1), for storage, management, control, correction and interpretation of water quality data in Excel® spread sheet

BTO 2012.244(s)

December 2012 (updated in April 2013)

vrije Universiteit amsterdam

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Project numbers
KWR: B111698-002, B111655, etc.
VU: MSc and PhD Hydrogeology education

Clients
BTO, VU University Amsterdam

Quality assurance
Users of previous versions

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Report status:
This report is public domain
Minor update in April 2013.

Preface and Abstract

Hydrogeochemcal (HGC 2.1) is a computer code, which I developed over the years, for storage, management, control, correction and interpretation of water quality data. Older parts of this program have already been pasted into hydrochemical tool boxes or data base programs in the Netherlands, like CHEMCAL (Kiwa; Stuyfzand et al., 1987), CHEMPROC (VU; Biesheuvel et al., 1988), DAWACO (Haskoning), CHEMVB (Lüers, 2000) and HyCA (Mendizabal et al., 2006). HGC features, however, many new options and is easier to use (and modify), as it is fully programmed in Microsoft's Excel® spreadsheet (version 2003 and higher) without need to run macro's and without depending links to other computer programs.

HGC is intended for every professional or student in the field of hydrology, hydrogeochemistry, environmental research, ecology, water treatment and related applied research. It is not intended to compete with computer codes like PHREEQC (Parkhurst & Appelo, 1999), which offer (more) sophisticated tools to calculate among others speciation of solutes, mineral equilibria and reaction transport. Neither is it intended to compete with HyCA (Mendizabal et al., 2006), which offers among others direct ways to plot data on maps and cross sections, to produce Stiff diagrams, Piper diagrams, trend plots and X/Y-plots, and to calculate solute speciation and mineral equilibria via a direct link to PHREEQC-2. HGC is more basic by offering easier input of data from the field and laboratory, more extensive data control methods and many more elaborations that facilitate the interpretation and mapping of water quality data. A link is made with both HyCA and PHREEQC-2 by providing an export file to be directly importable into HyCA. This link is currently under construction.

The report lying in front forms both a manual how to use HGC and a document giving full explanation of the water quality parameters, methods and calculations. Using HGC requires low level spread sheet knowledge of Excel®.

Work in progress is indicated as such, while ideas are welcomed. Please, help to improve manual and program by informing me about errors and omissions. Enjoy working with HGC while learning about the different ways of elaborating and interpreting your data!

Pieter J. Stuyfzand, December 2012.

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Contents

1 Introduction

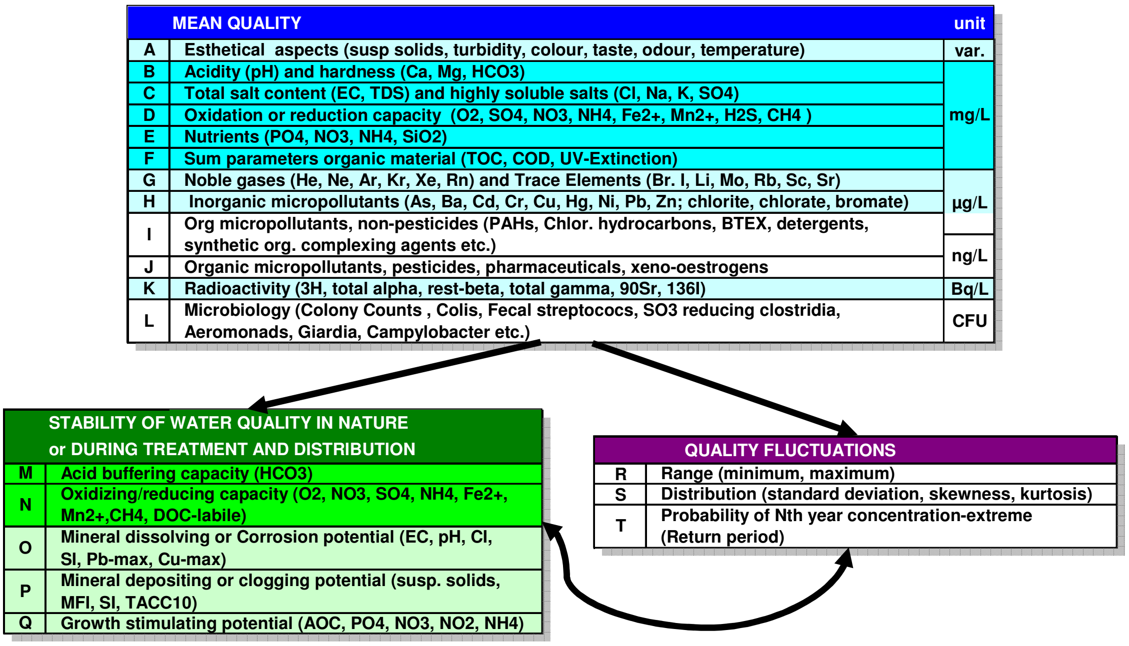
1.1 Genesis and capabilities of Hydrogeochemcal

Hydrogeochemcal (HGC 2.1) is a computer code, which I developed over the years, for storage, management, control, correction and interpretation of water quality data. Water quality consists of all aspects shown in Fig.1.1, and many of them are addressed by HGC. The organic chemistry is less addressed, however, only the sum parameters TOC or DOC (Total or Dissolved Organic Carbon), COD (Chemical Oxygen Demand as measured by $KMnO_4$ consumption), UVA_{254} (Ultraviolet absorbance at 254 nm), colour, 26 organic micropollutants (OMPs) and 3 microbiological parameters are standard considered (which is the top of an iceberg).

Older parts of this program have already been pasted into hydrochemical tool boxes or data base programs in the Netherlands, like CHEMCAL (Kiwa; Stuyfzand et al., 1987), CHEMPROC (VU; Biesheuvel et al., 1988), DAWACO (Haskoning), CHEMVB (Lüers, 2000) and HyCA (Mendizabal et al., 2006). HGC features, however, many new options and is easier to use (and modify), as it is fully programmed in Excel spreadsheet without need to run macro's and without links to other computer programs.

Table 1.1 presents an overview of HGC output with subdivision into 10 categories. These are also the chapters 3-12 where parameters, methods and calculations are fully explained. Chapter 2 is devoted to explaining how HGC is structured and how to use it.

→ Running HGC is easy: just click on HGC.xls and fill in all the data in worksheet #2 (2-RAW), either directly or by using optional input sheets 2A-2D which are tailored to the input from specific labs. The resulting output of all calculations is automatically added to the data in worksheet #6 (6-Best), via #3, #4 and #5. If corrections are needed for either bird droppings in rain water or filtration bias, then select 5 instead of 3 in cell A10 of sheet #6. For more information see Ch.2.



	MEAN QUALITY	unit
A	Esthetical aspects (susp solids, turbidity, colour, taste, odour, temperature)	var.
B	Acidity (pH) and hardness (Ca, Mg, HCO3)	mg/L
C	Total salt content (EC, TDS) and highly soluble salts (Cl, Na, K, SO4)	
D	Oxidation or reduction capacity (O2, SO4, NO3, NH4, Fe2+, Mn2+, H2S, CH4)	
E	Nutrients (PO4, NO3, NH4, SiO2)	
F	Sum parameters organic material (TOC, COD, UV-Extinction)	
G	Noble gases (He, Ne, Ar, Kr, Xe, Rn) and Trace Elements (Br. I, Li, Mo, Rb, Sc, Sr)	µg/L
H	Inorganic micropollutants (As, Ba, Cd, Cr, Cu, Hg, Ni, Pb, Zn; chlorite, chlorate, bromate)	
I	Org micropollutants, non-pesticides (PAHs, Chlor. hydrocarbons, BTEX, detergents, synthetic org. complexing agents etc.)	ng/L
J	Organic micropollutants, pesticides, pharmaceuticals, xeno-oestrogens	
K	Radioactivity (3H, total alpha, rest-beta, total gamma, 90Sr, 136I)	Bq/L
L	Microbiology (Colony Counts , Colis, Fecal streptococs, SO3 reducing clostridia, Aeromonads, Giardia, Campylobacter etc.)	CFU

	STABILITY OF WATER QUALITY IN NATURE or DURING TREATMENT AND DISTRIBUTION
M	Acid buffering capacity (HCO3)
N	Oxidizing/reducing capacity (O2, NO3, SO4, NH4, Fe2+, Mn2+,CH4, DOC-labile)
O	Mineral dissolving or Corrosion potential (EC, pH, Cl, SI, Pb-max, Cu-max)
P	Mineral depositing or clogging potential (susp. solids, MFI, SI, TACC10)
Q	Growth stimulating potential (AOC, PO4, NO3, NO2, NH4)

	QUALITY FLUCTUATIONS
R	Range (minimum, maximum)
S	Distribution (standard deviation, skewness, kurtosis)
T	Probability of Nth year concentration-extreme (Return period)

FIG 1.1. Aspects of water quality. HGC addresses aspects A-H, K and M-Q, of which the dark coloured aspects fully and the lighter coloured aspects partly. The other aspects are addressed only very lightly.

TABLE 1.1. Overview of the various calculations performed by HGC.

Ch.	Category	Parameters involved
3	Data control	conversion to standard unit, values <MDL, IB, EC, missing values, bird dropping correction (BDC), filtration bias correction (FBC)
4	Base exchange and nonmarine concentrations	BEX, Na, K, Ca, Mg, Cl, SO4, B, Br, F, I, Li, Mo, Rb, Sr, 18O
5	Chemical watertype	Chlorinity, alkalinity, dominant cation & anion, BEX
6	Mineral equilibria	Saturation index for calcite, dolomite, siderite, rhodochrosite, gypsum, barite, fluorite; TIC, CO2
7	Ratios	Cl/Br, Cl/Na, Ca/Mg, Ca/Sr, HCO3/Ca, HCO3/ΣA, Fe/Mn, COD/TOC, MONC, SUVA, 2H/18O
8	Hydrochemical facies	pH-class, redox index, BEX, pollution index WAPI
9	TDS contributing processes	TDS, %Marine, %Atm pollution, %Bulk Organic Matter, %Mineral dissolution (silicates and carbonates)
10	Various calculated parameters	O2-sat, oxid capacity, trace element groups, Wirdum, SAR, ESR, EPI, water density, viscosity, O-18 corrected for salinity effects
11	Normalization of analytical data	Spider plot, WAPI radar plot, norm exceedance
12	Complexation of 2+ trace metals in fresh water	free conc., inorg and org complexed: Ba, Cd, Co, Cu, Ni, Pb, Zn

BEX = Base Exchange index; EC = Electrical conductivity; IB = Ionic Balance; MDL = Minimum Detection Limit; MOC = Modified Oxidation/reduction Capacity; NA = Not Available; SAR = Sodium Adsorption Ratio; SI = Saturation Index; TDS = Total Dissolved Solids; TIC = Total Inorganic Carbon; TIN = Total Inorganic Nitrogen ions; TotH = Total Hardness; WAPI = WAter Pollution Index;

1.2 Unit conversions

In Hydrogeochemistry various unit conversions may be needed. The most frequent ones are those to convert concentration units: mg/L, ppm, mmol/L, meq/L and mol/kg. How to convert these units and how to calculate the ionic balance, electrical conductivity and density is indicated in Table 1.2. This table is supplied as an auxiliary tool in HGC, as Excel worksheet #15 (15-Conc Unit Exerciser).
A second auxiliary tool in HGC, as Excel worksheet #16 (16-Elem Converter) helps to rapidly convert elements into specific molecules (like P into PO_4) or into minerals (like Ca into $CaCO_3$) and vice versa. And a third auxiliary tool in HGC, as Excel worksheet #17 (17-Unit Converter) helps to rapidly convert various units (length, surface, volume, length/time, volume/time, weight, fluxes, pressure, heat/temperature, and chemistry).

TABLE 1.2. Concentration unit conversions and calculation of elementary parameters (turquoise cells) from input (yellow cells). Available as Excel worksheet #15 (Conc Unit Exerciser).

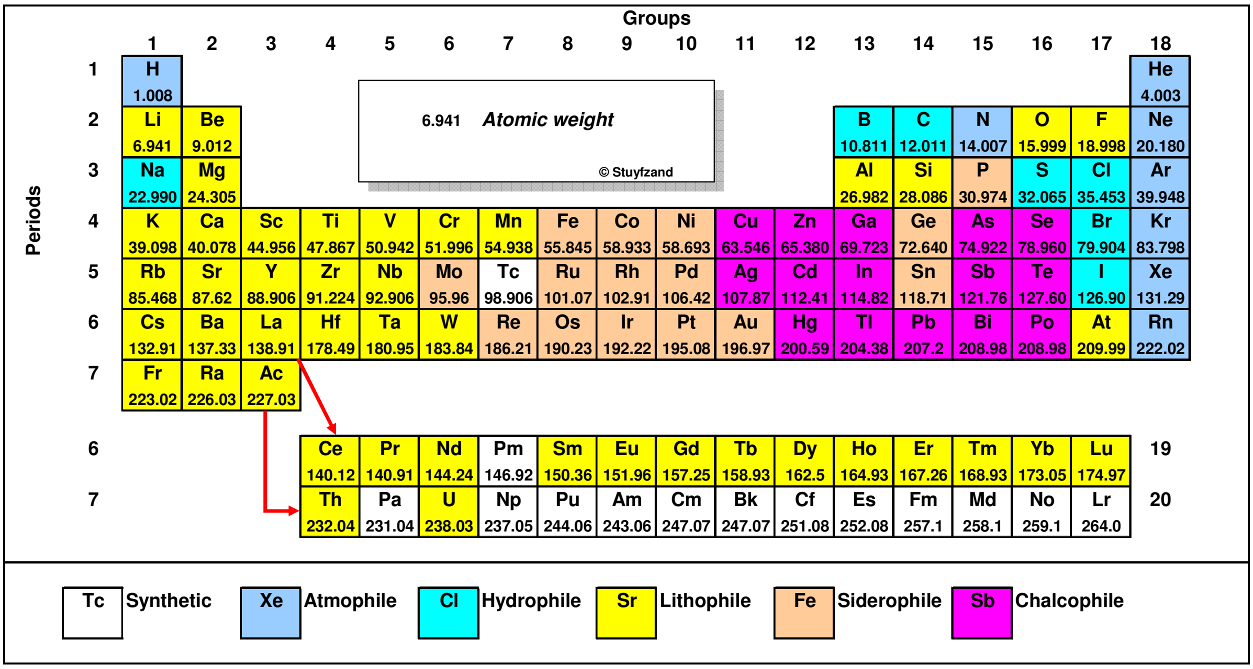
Solution:	temp =	10	oC	EC =	16195	uS/cm	ρ =	1.008	kg/L
Compound	unit	Cations				Anions			
		Na	K	Ca	Mg	Cl	SO4	HCO3	NO3
GFW	g / mol	22.99	39.1	40.08	24.312	35.453	96.06	61.02	62.0
Z		1	1	2	2	-1	-2	-1	-1
Concentration	mg/L	3460.0	80.0	600.0	300.0	6500.0	545.0	300.0	2.0
	ppm	3431.6	79.3	595.1	297.5	6446.7	540.5	297.5	2.0
	mmol/L	150.50	2.05	14.97	12.34	183.34	5.67	4.92	0.03
	meq/L	150.50	2.05	29.94	24.68	183.34	11.35	4.92	0.03
	M = mol/kg	0.149	0.002	0.015	0.012	0.182	0.006	0.005	0.00003
Ionic Balance	%	IB =	1.85	Σk =	207.17	meq/L	Σa =	199.64	meq/L

mmol/L = [mg/L] / GFW = [ppm ρ] / GFW = [meq/L] / abs(Z)   N = eq/L H2O
ppm = [mg/L] / ρ   meq/L = [mmol/L] * abs(Z)   mol/kg = [mmol/L] / [1000 ρ]

Σk = Na+K+Ca+Mg+.....
Σa = Cl+SO4+HCO3+NO3+....   **IB = 100(Σk-Σa)/(Σk+Σa)**
EC = If Σa < 3: 100 Σa; If Σa > 30: 133.605 $\Sigma a^{0.9058}$;
else: 71.027 (0.94+1.38207 Cl+SO4+NO3+0.95721 HCO3)
ρ = f(temp, EC), see Eq.10.20 (manual Hydrogeochemcal)

1.3 Periodic table of elements and their concentrations in various compartments

The periodical table of elements is reproduced in Fig.1.2, together with their hydrogeochemical classification and atomic weight. The classification is based on Goldschmidt's geochemical grouping with a modification by Stuyfzand (1993) to also discern hydrophilic elements. The notation of groups has been changed to run consecutively from 1 to 18 across the table (following Hitchon et al. 1999).
This periodic table is included as an auxiliary tool in HGC, as Excel worksheet #18 (18-Period). It gives tabulated information on a.o. each element's chemical character, state, concentration in different geochemical and hydrochemical compartments, dominant dissolved species, norms etc. An abbreviated list is given as Table 1.3.



Groups

Periods	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 1.008																	He 4.003
2	Li 6.941	Be 9.012											B 10.811	C 12.011	N 14.007	O 15.999	F 18.998	Ne 20.180
3	Na 22.990	Mg 24.305											Al 26.982	Si 28.086	P 30.974	S 32.065	Cl 35.453	Ar 39.948
4	K 39.098	Ca 40.078	Sc 44.956	Ti 47.867	V 50.942	Cr 51.996	Mn 54.938	Fe 55.845	Co 58.933	Ni 58.693	Cu 63.546	Zn 65.380	Ga 69.723	Ge 72.640	As 74.922	Se 78.960	Br 79.904	Kr 83.798
5	Rb 85.468	Sr 87.62	Y 88.906	Zr 91.224	Nb 92.906	Mo 95.96	Tc 98.906	Ru 101.07	Rh 102.91	Pd 106.42	Ag 107.87	Cd 112.41	In 114.82	Sn 118.71	Sb 121.76	Te 127.60	I 126.90	Xe 131.29
6	Cs 132.91	Ba 137.33	La 138.91	Hf 178.49	Ta 180.95	W 183.84	Re 186.21	Os 190.23	Ir 192.22	Pt 195.08	Au 196.97	Hg 200.59	Tl 204.38	Pb 207.2	Bi 208.98	Po 208.98	At 209.99	Rn 222.02
7	Fr 223.02	Ra 226.03	Ac 227.03															
6				Ce 140.12	Pr 140.91	Nd 144.24	Pm 146.92	Sm 150.36	Eu 151.96	Gd 157.25	Tb 158.93	Dy 162.5	Ho 164.93	Er 167.26	Tm 168.93	Yb 173.05	Lu 174.97	19
7				Th 232.04	Pa 231.04	U 238.03	Np 237.05	Pu 244.06	Am 243.06	Cm 247.07	Bk 247.07	Cf 251.08	Es 252.08	Fm 257.1	Md 258.1	No 259.1	Lr 264.0	20

Tc Synthetic	Xe Atmophile	Cl Hydrophile	Sr Lithophile	Fe Siderophile	Sb Chalcophile

FIG. 1.2. Classification of elements according to the geochemical classification of Goldschmidt with modifications by Stuyfzand (1993). Taken from worksheet #18.

TABLE 1.3. Inorganic constituents of water, subdivided into major compounds and trace elements, both in alphabetical order. Based on worksheet #18 (18-Period).

Symbol	Name	Mass	Geochem	Up.Earth	Unit	Ocean	Rain	Rhine	Meuse	Mean	MPC	Predominant
		g/mol	Classif	Crust	in	SMOW	water	water	water	ground-	drinking	dissolved species
			Mod	ppm	water		Neths.	80-83	80-83	water ##	water	in water
Ar	Argon	39.948	At	3.5	mg/L	0.636						Ar
C	Carbon	12.011	At	3240	mg HCO3/L	145	0.7	155	161	198	>60	HCO_3^-, H_2CO_3
Ca	Calcium	40.078	Li	29,400	mg/L	422	1.3	77.8	64.6	67.6	150	Ca2+
Cl	Chlorine	35.453	Hy	640	mg/L	19,805	15	151	54	35.0	150	Cl-
Fe	Iron	55.845	Si	30,859	mg/L	0.002	0.05	0.0051	0.82	3.44	0.2	Fe2+, Fe3+
H	Hydrogen	1.008	Hy	1400	pH	8.22	4.85			7.19		H2O
He	Helium	4.003	At	0.008	mg/L	0.0072						He
K	Potassium	39.098	Li	28,700	mg/L	408	0.31	6.2	5.1	3.24	12	K+
Mg	Magnesium	24.305	Hy	13,508	mg/L	1,322	1.0	11.6	7.4	7.5	50	Mg2+
Mn	Manganese	54.938	Li	527	mg/L	0.0002	0.03	0.05	0.12	0.22	0.05	Mn2+, Mn4+
N	Nitrogen	14.007	At	83	mg NH4/L	0.03	1.21	0.85	0.82	2.83	0.2	N2, NO3-, NH4+
Na	Sodium	22.990	Hy	25,700	mg/L	11,020	8.3	83.1	33.4	23.5	120	Na+
Ne	Neon	20.180	At	0.005	mg/L	0.164						Ne
O	Oxygen	15.999	Hy	460,000	mg O2/L	8.3	11	8.3	9.6	1.5	>2	H2O, O2
P	Phosphorus	30.974	Si	665	mg PO4/L	0.06	0.05	1.16	0.98	0.71	6.1	PO43-
S	Sulfur	32.065	Hy	953	mg SO4/L	2,775	3.6	71	57	28.2	150	SO42-
Si	Silicon	28.086	Li	303,365	mg SiO2/L	4.4	0.1	2.4	3.4	18.4		H4SiO4
Ac	Actinium	227.028		5.5E-10	µg/L							Ac3+
Ag	Silver	107.868	Ch	0.055	µg/L	0.04	<0.05	<1	<1	<0.05	10	Ag+
Al	Aluminium	26.982	Li	77,400	µg/L	5	8	135		8.2	200	Al3+
As	Arsenic	74.922	Ch	2	µg/L	2.5	0.2	2.4	2.7	1.7	50	AsO2-, AsO43-
At	Astatine	209.987	Li	3E-20	µg/L							At-
Au	Gold	196.967	Si	0.0018	µg/L	0.011				<0.05		Au+
B	Boron	10.811	Hy	17	µg/L	4,600	3.5	122	120	43	1,000	B(OH)3
Ba	Barium	137.327	Li	668	µg/L	30	1.5	86	62	43.94	500	Ba2+
Be	Beryllium	9.012	Li	3.1	µg/L	0.0006	0.006	0.01	0.0251	0.037		Be2+
Bi	Bismuth	208.980	Ch	0.123	µg/L	0.00003				0.026		Bi3+
Br	Bromine	79.904	Hy	1.6	µg/L	67,300	52.2	230	130	95		Br-
Cd	Cadmium	112.411	Ch	0.102	µg/L	0.11	0.08	0.33	0.5	0.036	5	Cd2+
Ce	Cerium	140.116	Li	65.7	µg/L	0.0052	0.31			0.16		Ce3+,Ce4+
Co	Cobalt	58.933	Si	11.6	µg/L	0.1	0.34	0.8	0.251	0.4		Co2+
Cr	Chromium	51.996	Li	35	µg/L	0.2	0.16	2.6	1.6	0.9	50	Cr3+, CrO42-
Cs	Caesium	132.905	Li	5.8	µg/L	0.3	0.09			0.01		Cs+
Cu	Copper	63.546	Ch	14.3	µg/L	0.9	1.7	4.1	5.6	2.5	100	Cu2+, Cu+
Dy	Dysprosium	162.500	Li	2.9	µg/L	0.00112				0.024		Dy3+
Er	Erbium	167.259	Li	2.3	µg/L	0.0012				0.016		Er3+
Eu	Europium	151.964	Li	0.95	µg/L	0.00013	0.02			0.009		Eu3+, Eu2+
F	Fluorine	18.998	Li	611	µg/L	1,300	26	240	378	101	1,100	F-
Fr	Francium	223.020		3E-17	µg/L							Fr+
Ga	Gallium	69.723	Ch	14	µg/L	0.0012				0.03		Ga3+
Gd	Gadolinium	157.250	Li	2.8	µg/L	0.00092				0.031		Gd3+
Ge	Germanium	72.640	Si	1.4	µg/L	0.05				0.04		H4GeO4
Hf	Hafnium	178.490	Li	5.8	µg/L	<0.008				0.010		Hf4+
Hg	Mercury	200.590	Ch	0.056	µg/L	0.03	0.04	0.04	0.13	0.051	1	Hg22+, Hg2+, Hg0
Ho	Holmium	164.930	Li	0.62	µg/L	0.00037	0.02			0.009		Ho3+
I	Iodine	126.904	Li	1.4	µg/L	60	4	8	7	8.0		I-, IO3-
In	Indium	114.818	Ch	0.061	µg/L	0.00001				0.005		In3+
Ir	Iridium	192.217	Si	0.00002	µg/L	1E-06				0.028		Ir3+
Kr	Krypton	83.798	At	0.0001	µg/L	0.32						Kr
La	Lanthanum	138.905	Li	32.3	µg/L	0.012	0.06			0.08		La3+
Li	Lithium	6.941	Li	22	µg/L	170	0.14	18	8	8.3		Li+
Lu	Lutetium	174.967	Li	0.27	µg/L	0.00015				0.006		Lu3+
Mo	Molybdenum	95.960	Si	1.4	µg/L	10	0.008	2		0.41		MoO42-
Nb	Niobium	92.906	Li	26	µg/L	0.0046				0.007		Nb5+
Nd	Neodymium	144.242	Li	25.9	µg/L	0.0092				0.078		Nd3+
Ni	Nickel	58.693	Si	18.6	µg/L	0.7	0.1	4.3	6.2	1.7	50	Ni2+
Os	Osmium	190.230	Si	0.00005	µg/L	1.7E-06				0.025		Os4+
Pb	Lead	207.200	Ch	17	µg/L	0.03	1.3	1.5	3.5	0.14	50	Pb2+
Pd	Palladium	106.420	Si	0.0005	µg/L	4.3E-05				0.100		Pd2+
Po	Polonium	208.982	Ch	2E-10	µg/L	1.5E-11						Po2+
Pr	Praseodymium	140.908	Li	6.3	µg/L					0.022		Pr3+
Pt	Platinum	195.084	Si	0.0004	µg/L	0.00005				0.005		Pt2+
Ra	Radium	226.025		9E-07	µg/L	1.3E-07						Ra2+
Rb	Rubidium	85.468	Li	110	µg/L	120	0.09			1.88		Rb+
Re	Rhenium	186.207	Si	0.0004	µg/L	0.0074				0.007		ReO4-
Rh	Rhodium	102.906	Si	0.00006	µg/L	0.08				0.005		Rh3+
Rn	Radon	222.018	At	4E-13	µg/L	6E-13						Rn
Ru	Ruthenium	101.070	Si	0.0001	µg/L	0.0007				0.025		Ru4+
Sb	Antimony	121.760	Ch	0.31	µg/L	0.3	0.89	0.3		0.045	10	Sb(OH)30, Sb(OH)6-
Sc	Scandium	44.956	Li	7	µg/L	0.0007	0.012			3.0		Sc3+
Se	Selenium	78.960	Ch	0.083	µg/L	0.09	0.0801	0.35	0.301	0.47	10	SeO32-, SeO42-
Sm	Samarium	150.360	Li	4.7	µg/L	0.00045	0.06			0.024		Sm2+, Sm3+
Sn	Tin	118.710	Si	2.5	µg/L	0.8				0.051		Sn2+, Sn4+
Sr	Strontium	87.620	Li	316	µg/L	8,100	6.3	450		261		Sr2+
Ta	Tantalum	180.948	Li	1.5	µg/L	0.0025				0.010		Ta5+
Tb	Terbium	158.925	Li	0.5	µg/L	0.00014				0.008		Tb3+
Te	Tellurium	127.600	Ch	0.005	µg/L	0.03				0.025		Te2+, Te4+, Te6+
Th	Thorium	232.038	Li	10.3	µg/L	0.0004	<0.03	-	-	0.028		Th4+
Ti	Titanium	47.867	Li	3,117	µg/L	1	3.8			<5		TiO2+
Tl	Thallium	204.383	Ch	0.75	µg/L	0.013				0.006		Tl+, Tl3+
Tm	Thulium	168.934	Li	0.33	µg/L	0.0002				0.006		Tm3+
U	Uranium	238.029	Li	2.5	µg/L	3.3	0.02	0.9	-	0.12		UO2+
V	Vanadium	50.942	Li	53	µg/L	1.9	1	2	2.8	0.4		V(OH)30, VO2+, VO43-
W	Tungsten	183.840	Li	1.4	µg/L	0.1		0.09		0.067		WO42-
Xe	Xenon	131.293	At	0.00003	µg/L	0.065						Xe
Y	Yttrium	88.906	Li	20.7	µg/L	0.015				0.17		Y3+
Yb	Ytterbium	173.054	Li	1.5	µg/L	0.00082				0.014		Yb2+, Yb3+
Zn	Zinc	65.380	Ch	52	µg/L	2	7	26	48	10.2	100	Zn2+
Zr	Zirconium	91.224	Li	237	µg/L	0.012				0.09		Zr4+

2 Running Hydrogeochemcal (HGC 2.1)

2.1 General information

The software Hydrogeochemcal (HGC) and the manual are both free domain; they can be downloaded from ?? The computer code is set in Microsoft's Excel® spreadsheet (Windows Excel 2003). The user therefore needs some acquaintance with Excel.

A blue print of the programme is given in Fig.2.1, showing interconnection of worksheets 1-18, data flow and data elaborations. The normal data flow is from the data you have to the data input in HGC (using 2-Raw either directly or via optional sheets 2A-2D), via the data output without (3-ALL) or with corrections for bird droppings or filtration bias (4-COR + 5-ALLcor) to worksheet #6. There, you find a.o. the analytical data which have been converted (if needed) and corrected (in case you used worksheets 3A, 4 and 5), and all calculated parameters, with options to vary the units (mg/L, ug/L, mmol/L, umol/L, mg NO_3-N/L etc.).

Input and output data can be formatted (number of decimals) by selecting the appropriate cells of row 2 and [copy paste special formats] these to rows ≥11 (11 down to final row #). Each water sample forms one row, on which the data are fixed in specific columns.

Warning: copy rows (9 or 11), not columns because columns are unique and should remain as such!!

Row 9 in worksheets 2-6 is a *back up or restore row*: it contains formulas that may need to be copied to the first sample row (#11) up to the final sample row, if you lost or mutilated somehow row 11. It is recommended to restrict this copying to the total number of samples in the data set, in order to reduce Excel speed losses. Thus, if row 11 (first sample) is somehow mutilated, then row 9 serves as a restore/back up row by copying it back to row 11.

Cell colouring is in general as follows: yellow = cell for data entry; no colour = cell contains formula; other colours = cell contains information / explanation.

Columns can be added or hidden; removal may have desastrous impacts on the proper working of HGC.

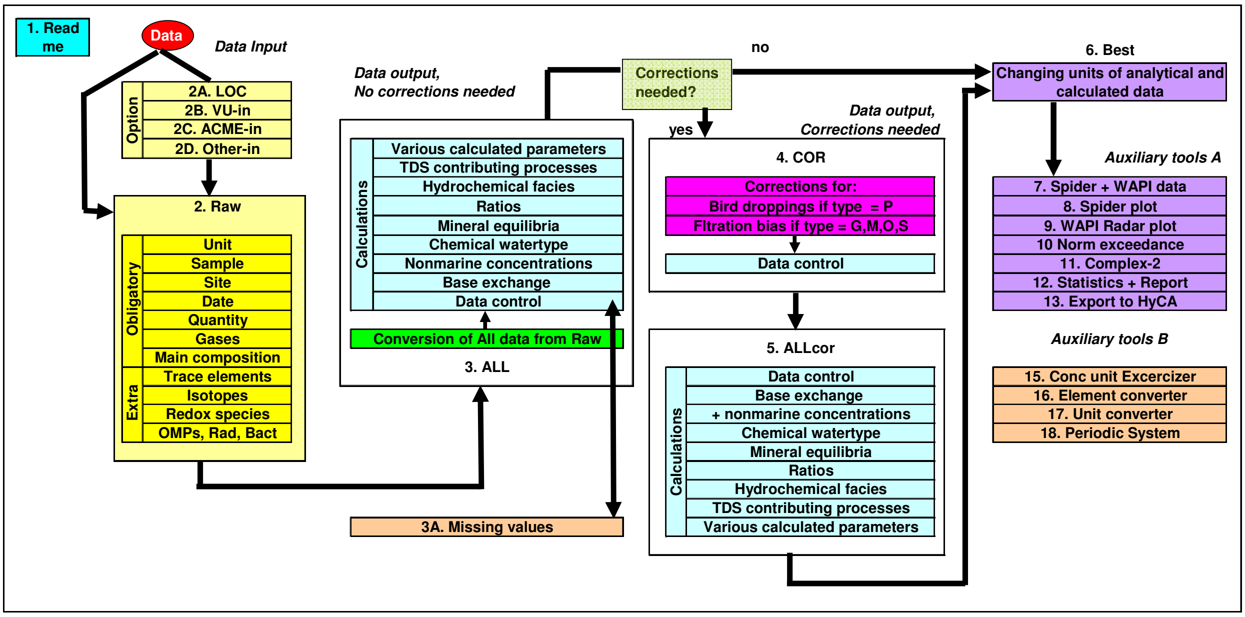


FIG. 2.1. Blue print of HGC, showing interconnection of worksheets 1-18, data flow and data elaboration. Worksheets 15-18 are not connected (independent). Worksheets 3A, 10-13 under construction.

2.2 Data input (sheet #2)

Data input is to be done in Worksheet #2 (2-Raw). This can be done directly by filling in its yellow coloured cells. Remember that cells without colour contain formulas !

Information on Row 9 is invisible, because it contains formulas (showing no results because there are no data) that can be copied into any row below row #10. Row 9 contains formulas also for the yellow cells, in case use is made of option A, B, C or D (specified below).

→ So, if option A, B, C or D is chosen, then copy in '2 RAW' as many rows as needed from the last row already present (Row # ≥11), or otherwise from rescue row 9. Then select -- in cell A10 -- which lab data (1 = B, 2 = C or 3 = D) to take. This will automatically paste the data from the appropriate worksheet into '2 RAW'. When you select 0 in cell A10, the colour of the cells on and below row 11 remain yellow, indicating that input should be done there. When you selected 1, 2 or 3 this colour disappears indicating that the data are imported via formulas in the cells on row numbers ≥11 in #2.

Units

It is obligatory to Indicate the data input units in '2 Raw' in the yellow cells on rows 6 and 8. For instance, by filling in 1, 2 or 3 for Na we obtain mg/L, µg/L and mmol/L respectively. The resulting unit is displayed in the cell below. All calculations in HGC are based on the standard internal unit (mostly mg/L and µg/L), which is indicated in Table 3.1.

NB: The data you are entering should have the same unit for each parameter (column)! If not, then first change the data involved to the one unit you prefer for all samples for that particular parameter.

Location data

→ Option A1: Utilizing worksheet #2A (2A LOC)

Inserting your location data directly into worksheet #2 (2A-LOC) is advantageous, if same locations were sampled more frequently. It contains various data (Table 2.1) of which the type is most essential because some calculations pertain to a specific type of water. Other Location information can be added to the right of the table displayed below.

In 2-Raw you need to insert the site's abbreviated code in column A, which should be identical to one code in column A of #2A. If so, via Excel's lookup function the site's location data are automatically copied from 2A-LOC into 2-Raw. The first 8 columns (A:H) as well as columns of Table 2.1 are copied then, the others not.

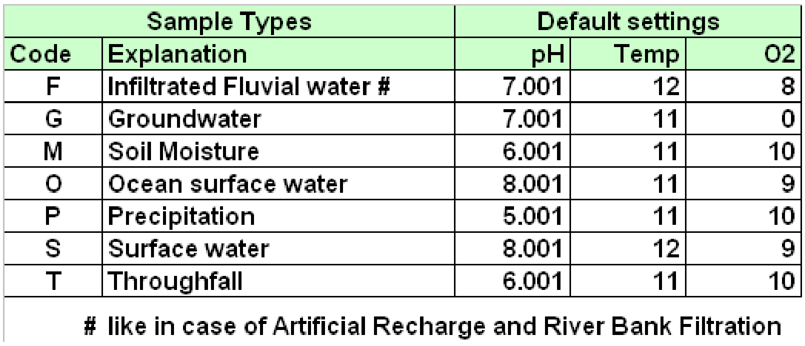
→ Option A2: Not utilizing worksheet #2A (2A-LOC)

Just type or copy paste your data directly into columns A:H of worksheet #2 (2-Raw). Remember the sample type always needs to be filled in, because some calculations pertain to a specific type of water. The type codes are given in Table 2.2.

TABLE 2.1. Standard information in worksheet '2A LOC' which is partly copied to '2 Raw' if Site Code abbrev in column A is filled in there.

SAMPLE			SITE					DETAILS SAMPLE			DETAILS SITE	
Sample		Type	Depth	Coordinates		Land	Depth to	Quantity	Measurements		Site's	Vegetation
Site	Code	P = Precip	Below	X	Y	Surface	Ground		Start	End	or Area's	
Code	in	G = Grwater	Ground Level			Altitude	Water Table	mL	dd-mm-yy	dd-mm-yy	Name	
abbrev	full	S = Surf water	m BGL	m	m	m+SL	m BGL	or m3/h				
KB1	KB1 WK1 001	P	-1.5	98739	493484	4	2.5	5500	02-09-10	09-09-10	Kattendel	mosses
WB2	WB2 WK1 002	P	-1.5	99289	493561	5	0.5	5750	02-09-10	09-09-10	Wieringen	grasses
P1	P1 WK2	T	-0.4	100179	493329	15	11.0	3550	09-09-10	30-05-11	Pine forest	pine
P2	P2 WK2	T	-0.4	100148	493268	16	12.3	3260	09-09-10	30-05-11	Pine forest	pine
M1	SP1	M	0.2	98632	493444	8	6.6				Kattendel west	mosses
M2	SP2	M	0.4	98770	493488	9	7.2				Kattendel east	mosses
D	BD 001	G	2.1	98624	493480	2	1.5				Beach, spiral	bare
E	K 002	G	3.5	98748	493480	3	1.5				Kattendel spiral	mosses
S1	HSW 005	S	0.0	99085	493820	2	0				Houtglop Lake	reeds
S2	KSW 006	S	0.0	98725	493299	2.5	0				Kattendel lake	reeds
needed		copied	copied	copied	copied	copied	copied	copied		copied		

TABLE 2.2. Sample types and their default settings if data are lacking (not entered). If F (infiltrated river, lake or canal water, in saturated zone) and G (infiltrated local rain water in saturated zone, brackish or (hyper)saline groundwater) cannot be discerned, then fill in G.



Sample Types		Default settings		
Code	Explanation	pH	Temp	O2
F	Infiltrated Fluvial water #	7.001	12	8
G	Groundwater	7.001	11	0
M	Soil Moisture	6.001	11	10
O	Ocean surface water	8.001	11	9
P	Precipitation	5.001	11	10
S	Surface water	8.001	12	9
T	Throughfall	6.001	11	10

like in case of Artificial Recharge and River Bank Filtration

Option B: data import from VU Lab (sheet #2B)

When you receive your analytical results from VU lab, then you can directly copy paste these chemical data into worksheet #2B (2B-VU-in). There are columns for sample code + type, Field data, Ion Chromatography, ICP-OES, Lab analysis of EC, pH and Alkalinity as HCO_3, and Aquachem.

Practically all VU-data are provided in the mg/L unit. The unit setting in #2 must therefore be 1 for main constituents and 1 for trace elements ! **This is automatically taken care of, if you did not alter the light yellow cells on row 6.** These light yellow cells do contain a simple formula (cell6 = cell10), which activates the correct unit via the corresponding cell on row 10 and via your choice in cell A10.

→ To get the data from #2B into sheet #2 (2-Raw), fill in ‘1’ in cell A10 of sheet #2. The yellow cell colouring in #2 dissappears immediately, indicating that the data are imported via formulas in the cells on row numbers ≥11.

Option C: data import from ACME Lab (sheet #2C)

When you receive your analytical results from ACME lab, then you can directly insert these chemical data into worksheet #2C (2C-ACME-in). The ICP-OES + ICP-MS results are ordered in alphabetical order.

All ACME-data are provided in the ug/L unit, Cl and SO_4-S excluded (mg/L). The unit setting must therefore be 2 for most main constituents and 1 for trace elements, Cl and SO_4 ! **This is automatically taken care of, if you did not alter the light yellow cells on row 6 (details ad Option B).**

The conversion of S into SO_4, P into PO_4 and Si into SiO_2 is taken care of during the transfer from #2C to #2 (2-Raw).

→ To get the data from #2C into sheet #2 (2-Raw), fill in ‘2’ in cell A10 of sheet #2. The yellow cell colouring in #2 dissappears immediately, indicating that the data are imported via formulas in the cells on row numbers ≥11.

Option D: data import from Other-in (sheet #2D)

This worksheet can be used for any other data input. It standard contains interesting examples of different environmental watertypes showing a wide spectrum of chemical compositions, ranging from coastal rain water to hypersaline brines, from acidic to basic, oxic to deeply anoxic, unpolluted to polluted. *→ List of examples to be completed.*

Data from this set can be directly copied into worksheet #2 (2-Raw) in case they serve for comparison or reference. **The units are automatically taken care of, if you did not alter the light yellow cells on row 6 (details ad Option B).**

→ To get the data from #2D into sheet #2 (2-Raw), fill in ‘3’ in cell A10 of sheet #2. The yellow cell colouring dissappears immediately, indicating that the data are imported via formulas in the cells on row numbers ≥11 in #2.

TABLE 2.3. Data parameter groups that can be entered in worksheets 2A-2D or directly into the column ranges in '2-Raw', with indication of their total number.

Info		Sample	Site	Date	Quantity	Gases	Main compo-sition	Trace ele-ments	Isotopes	Redox speci-ation	Organic Micro-pollutants	Radio-activity	Micro-biology
Cells in '2 Raw'	Start	A	D	I	K	M	Q	AV	DG	DO	EA	FB	FC
	End	C	H	J	L	P	AU	DF	DN	DZ	FA	FB	FE
	Total No.	3	5	2	2	4	31	63	8	12	27	1	3
Worksheet	2A Loc	3	5	1	1	0	0	0	0	0	0	0	0
	2B VU-in	3	0	0	0	0	22	34	0	0	0	0	0
	2C ACME-in	3	0	0	0	0	10	63	0	0	0	0	0
	2D-Other-in	Exactly as '2-Raw'				Exactly as '2-Raw'							

Date

The date of sampling must be entered in column J, in the format indicated (dd-mm-yyyy). Column I calculates from J the digital date yyyy+d/y: for instance 09-09-2010 = 2010.689. This is convenient when time plots are needed.

2.3 Data output, no corrections needed (sheet #3)

All standard generated data output is given in worksheet #3 (3-ALL). It gives from left (cell A) to right (cell IJ) information on successively the sample (code, XYZ, date, quantity), hydrochemistry (data imported from sheet #2 but converted) and calculated parameters as based on the converted data. Table 2.4 presents a blue-print of sheet #3.
All information in #3 is still without Bird Dropping Corrections (BDC; type P only) and without Filtration Bias Correction (FBC; all types). If these corrections are not needed (which is often the case), then sheet #3 is the one you need to transfer to sheet #6, where you can change output units and from which additional elaborations may be obtained via sheets 7-14 (Fig.2.1).
The data are automatically copied from worksheet #2 (2-Raw) to worksheet #3 (3-ALL), provided you have copied as many rows as needed, from the last row already present (Row # ≥11) or from rescue row 9. This data duplication is accompanied by conversion into the standard data base units (Table 3.1), conversion of <values into 0.501*values (recognizable later), conversion of negative values into 0.502*MDL (recognizable later) if value < -MDL (Minimum Detection Limit) and otherwise eliminated. These conversions are further explained in §3.1-3.2. The calculated parameters, as based on the converted input, are discussed in chapters 3-10.

TABLE 2.4. Blue print of worksheet #3 (3-ALL), showing its 16 main sectors between cell A and IJ, the sections or chapters with further explanations, and cells that require input if the standard setting needs alteration (see text below). Cells in red and italics are in hidden columns.

Info	Data taken from sheet #2				Input Data Converted			from #2	Calculations based on converted data							
Address	Sample	Site	Date	Quantity	Gases	Main Compo-sition	Trace Ele-ments	Iso-topes	Check on Analysis	Base Exch + nonmar.	Chem Water-type	Min. Equi-libria	Ratio's	Hydro-chem. Facies	TDS Contri-butions	Various Calc. Param.
Start	A	D	I	K	M	Q	AV	DG	DO	DY	EH	FA	FU	GF	HL	HT
End	C	H	J	L	P	AU	DF	DN	DX	EY	EZ	FT	GE	HK	HS	IJ
Total No.	3	5	2	2	4	31	63	8	10	18	10	20	11	32	8	17
Hidden	0	0	0	0	0	0	0	0	0	0	*EH-EP*	*FJ-FT*	0	*GF-GH, GJ-GV*	0	0
Chapter					3.1 - 3.2				3.3	4	5	6	7	8	9	10
Cells for Input									DO8:DR8	DZ1:EB2			GB8:GC8	GI7:GI8	HS8	IE1:IE2
										EY8				HI8:HK8		IH8:II8

TABLE 2.5. Cells in worksheet #3 (3-ALL) where default setting may need to be changed.

Section of sheet #3 o #5	input cells	Contents	Default settings				section	Eq.#
Check on Analysis	DO8:DR8	Selection of EC, pH, SO4 and PO4 data to use	lab	lab	IC	total	3.3	
Base Exchange + nonmarine conc.	DZ1:EB2	Parameters for *SALI*: Ca,K,Cl salt / fresh end members		422/85	408/2	19805/30	4.4	4.11-4.12
	EY8	δ18O sea water, for correcting δ18O for a marine contribution				0	4.2	4.8
Ratio's	GB8:GC8	Yes or no correction of COD for inorganic contributions			+	-	7.4	7.1-7.3
Hydrochemical Facies	GI7:GI8	Constants a and c in (SO4)0 = aCl + b for type F			0.277	29.7	8.3	
	HI8:HJ8	0 if WAPI on A-F, 1 if WAPI on A-J			0	1	8.4	8.1-8.2
	HK8	0 if code WAPI / HYFA-simple, 1 if code WAPI / HYFA detailed			0	1		
Processes contributing to TDS	HS8	Cl of fresh end member				30	9.6	9.10
Various Calc. Param.	IE1:IE2	Minimum concentration of nonmarine Sr and Ca+Mg [meq/L]			0.616	2.390	10.4	10.16
	IH8:II8	0 if EC-Calculated, 1 if EC measured			0	1	10.7-10.8	10.20-10.21

Additional input

In top rows 1-8 additional input is required if the standard setting needs to be altered. The cells involved are indicated in Table 2.4 and specified in Table 2.5.

Conditional formatting

Conditional formatting is applied to the pH selected (column DP) when these values are default values in case pH was not determined: yellow if 5.001 (type = P), green if 6.001 (Type = M or T), turquoise if 7.001 (type = F or G).

Conditional formatting is also applied to the Ionic balance and delta EC, indicating when there is an unsatisfactory difference between the sum of cations and anions, and between the calculated and measured EC. For details see Table 3.2.

And parameter EPI in column IG is coloured turquoise, if N limitation is identified in the Eutrophication Potential Index.

Hiding and unhiding columns

Tailor your own worksheets by just hiding those columns you did not have data for or which you do not need anyhow. Hiding and unhiding is a standard function in Excel by just right-clicking on the 2 columns to the left and right of the column(s) you like to hide or unhide, and select 'Hide' or 'Unhide'.

2.4 Data output, corrections needed (sheets #4 and #5)

Only if Bird Dropping Corrections (BDC; type P only) or Filtration Bias Corrections (FBC; all types) are needed, then worksheets 4 (4-COR) and 5 (5-ALLcor) should be used. The bird dropping corrections are needed in rain water if PO_4 > 0.05-0.1 mg/L (see §3.6). The filtration bias corrections are needed in all watertypes on the following conditions: if type = T or M then if Al >200 ug/L and if pH>5.5; if type = F, G, O, P, S then if Al >20 ug/L and if pH>5.5 (see §3.7).

In sheet #4 all relevant analytical (converted) data from sheet #3 are corrected at the right hand side of the sheet (DQ:GT) and the corrected values are subsequently copied to the left hand side of the sheet. This side (A:DF) is nearly identical to sheet #3 qua layout. It contains the same parameters up to and including the trace elements, lacks the isotopes, but also contains checks on analysis (DG:DP). A blue-print of sheet #4 is provided in Table 2.6.

The data from sheet #4 are subsequently copied into sheet #5. The main difference between sheet #5 and #3, is that specific analytical data in sheet #5 (columns T:DF) have been corrected for bird droppings and/or filtration bias. This holds only for those parameters that are affected ànd can be corrected on the basis of a clear linear relation. The corrected analytical data are indicated on row #8 (BDC or FBC) of sheets 4 and 5. The formulae in columns DO-IJ of sheets #3 and #5 are identical, but the resulting values may be quite different!

→ You have to copy as many rows as needed, from the last row already present (Row # ≥11) or from row 9, in order to get all data from sheet #3 into #4, and from #4 into #5.

The correction factors on row 8 in sheet #4 can be changed if needed.

Conditional formatting of sheet #4

Conditional formatting (a tan colour) is applied to all data in columns DQ:EH if $PO4_{BDC}$ = 0.1 mg/L (indicating BDC), and in columns EI:GT if Al_{FBC} = 0 ug/L (indicating FBC).

In addition, conditional formatting is applied, as in sheets 3 and 5, to the pH selected (column DH) when these values are default values in case pH was not determined: yellow if 5.001 (type = P), green if 6.001 (Type = M or T), turquoise if 7.001 (type = F or G).

Conditional formatting is also applied to the Ionic balance and delta EC, indicating that there is an unsatisfactory difference between the sum of cations and anions, and between the calculated and measured EC. For details see Table 3.1.

TABLE 2.6. Blue print of worksheet #4 (4-COR), showing its 11 main sectors between cell A and GT, the sections of chapter 3 with further explanations, and cells that require input if the standard setting needs alteration (see text below).

Info	Data taken from sheet #3						Calculations based on corrected data				
Address	Sample	Site	Date	Quantity	Gases	Main Composition	Main Composition	Trace Elements	Check on Analysis	Bird Dropping Correction	Filtration Bias Correction
Start	A	D	I	K	M	Q	T	AV	DG	DQ	EI
End	C	H	J	L	P	S	AU	DF	DP	EH	GT
Total No.	3	5	2	2	4	3	28	63	10	18	64
Chapter							3.6 - 3.7		3.3-3.5	3.6	3.7
Input cells									DG8:DJ8	DR8:EH8	EI8:GT8

2.5 Auxiliary tools A (dependent)

There are 8 auxiliary tools which depend indirectly on worksheet #3 or #5, via #6 (Fig.2.1).

Worksheet #6 (6-Best)

Sheet #6 (6-Best) is created to get the data from either 3-ALL or 5-ALLcor, and change the units of the converted analytical data and part of the calculated parameters, from the standard units (see Table 3.1) into an alternative unit (see Table 3.1). The structure of #6 is equal to the one of 3-ALL and 5-ALLcor.

Cell A10 is used to choose the data you want in #6: by filling in 3 you automatically get the data from 3-ALL, and by filling in 5 (or any other number than 3) you automatically get the data from 5-ALLcor.

TABLE 2.7. The 5 units for all converted analytical data and part of the calculated parameters, in sheet #6.

Parameter	Standard	Unit code Output 6-Best				
	Unit	1	2	3	4	5
Dissolved gases	mg/L	mg/L	ug/L	mmol/L	ppm	mmol/kg
Eh	mV	mV	pe	-	-	-
Electrical Conductivity (EC)	uS/cm, 20oC	uS/cm, 20oC	mS/m, 20oC	uS/cm, 25oC	mS/m, 25oC	-
Main constituents , no nutrients	mg/L	mg/L	ug/L	mmol/L	ppm	mmol/kg
Total hardness	mmol/L	mmol/L	oD	-	-	-
NH4	mg/L	mg/L	mg N/L	mmol/L	ppm	mmol/kg
NO3	mg/L	mg/L	mg N/L	mmol/L	ppm	mmol/kg
NO2	mg/L	mg/L	mg N/L	mmol/L	ppm	mmol/kg
PO4	mg/L	mg/L	mg P/L	mmol/L	ppm	mmol/kg
SiO2	mg/L	mg/L	mg Si/L	mmol/L	ppm	mmol/kg
KMnO4 consumption	mg/L	mg/L	mg O2/L	mmol/L	-	-
NH4-albuminoid	mg/L	mg/L	mg N/L	mmol/L	ppm	mmol/kg
Trace elements	ug/L	mg/L	ug/L	mmol/L	ppb	umol/kg
Tritium	TU	TU	Bq/L	mBq/L	-	-
Ions corrected for marine contribution	mg/L or ug/L	mg/L or ug/L	u- or nmol/L	-	-	-
Ratios	mg/L	mg/L	mmol/L	-	-	-

Worksheet #7 (7-Spider + WAPI data)

A relatively small selection of samples (data rows) from sheet #6 is normally needed to construct a Spider plot or WAPI Radar plot. This selection is done in sheet #7 by filling in the row numbers of the samples desired, in yellow cells C11:C30. That way a maximum of 20 samples is automatically copied from sheet #6 to sheet #7.

Spider plot

For the Spider plot, also the desired elements and the desired normalization can be selected. A maximum of 30 elements can be choosen, by filling in their symbol in cells D2:AG2. The desired normalization should be indicated in cell A2 by an option number. The option number refers to the column number in sheet #18 (18-Period). Five options have been declared: Upper continental crust, SMOW, Rain water, MPC drinking water, and natural backgrounds of groundwater in the Netherlands.
A final step is needed to obtain a true Spider plot: Do copy data block D10:AG32, paste special as values on D38:AG60, then sort on row 60 (left-right,ascending).

WAPI-Radar

For the WAPI-Radar plot no further actions are needed. The data are copied in columns AI:AS.

Worksheet #8 (8-Spider Plot)

It is quite usual in geochemistry (White, 1995-2009) to normalize the contents of tracé elements, and more in particular those of the rare earth elements (REEs), by dividing them by the respective contents of one or other standard. Frequently a specific or average chondrite (silica rich meteorite without any signs of fusion nor differentiation) is chosen, or a specific rock type (for instance shale) or the average composition of the continental crust or upper soil.
A so-called ‘spiderplot’ arises when the logarithm of the normalized concentration of a number of trace elements (sometimes accompanied by a few main constituents) is plotted for the elements selected, after sorting them on the basis of increasing normalized concentration. An example is presented in Fig.2.2, which is based on data from sheet #2D (2D-Test-in).

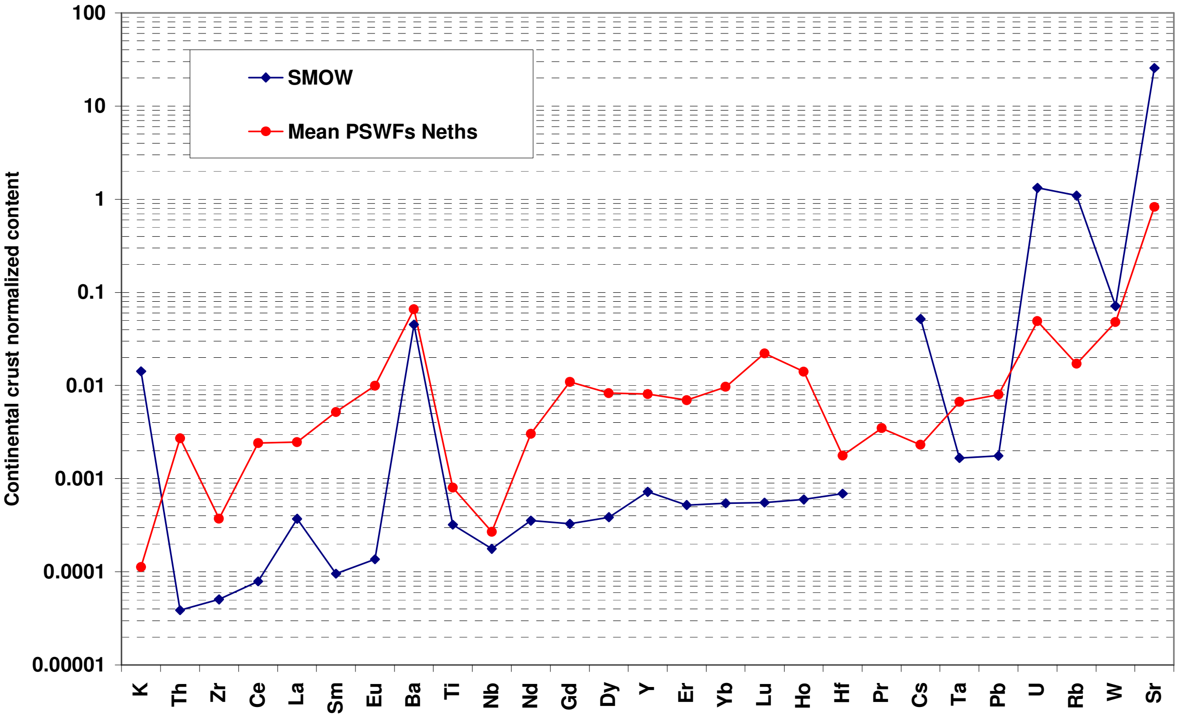


FIG. 2.2. Spider plot of SMOW and rain water in the Netherlands normalized to the mean earth's continental crust composition.

Worksheet #9 (9-WAPI-Radar plot)

The only actions needed to prepare a WAPI Radar plot are to step into this sheet #9, right click, choose Source data, select Name and select Values. The name should be chosen from columns AT:AU (by taking both not only the name but also the WAPI score is given), and the values from columns AI:AR.
Leave the X-axis labels $AI$8:$AR$9 as they are, and ignore any warning about negative or zero values by clicking OK.

Worksheet #10 (10-Norm exc)

Under Construction 2013.

Worksheet #11 (11-Complex-2)

Under Construction 2013.

Worksheet #12 (12-Stat+Rep)

Under Construction 2013.

Worksheet #13 (13-HyCA Export)

Under Construction 2013.

2.6 Auxiliary tools B (independent)

The independent auxiliary tools in worksheets 15-18 have been presented already in §1.2 (unit conversions) and §1.3 (periodic table of elements).

3 Data control

3.1 Conversion to standard units in HGC's database

Data from worksheet #2 (2-Raw) are automatically converted in Worksheet #3 (3-ALL) or #5 (5-ALLcor) to HGC's standard database units. These units and their conversion factors are given in Table 3.1.

TABLE 3.1. Standard units for chemical parameters in HGC's internal database, and the various input units for which conversions are automatically performed.

Parameter	Standard	Unit code			Conversion from unit X to Standard		
	Unit	1	2	3	1	2	3
Dissolved gases	mg/L	mg/L	ug/L	mmol/L	1	0.001	*GFW
Eh	mV	mV	pe	-	1	2300 RT / F	-
Electrical Conductivity (EC)	uS/cm, 20oC	uS/cm, 20oC	uS/cm, XoC	mS/m XoC	1	t	10 t
Main constituents , no nutrients	mg/L	mg/L	ug/L	mmol/L	1	0.001	*GFW
Total hardness	mmol/L	mmol/L	oD	-	1	5.6	-
NH4	mg/L	mg/L	mg N/L	mmol/L	1	1.29	*GFW
NO3	mg/L	mg/L	mg N/L	mmol/L	1	4.43	*GFW
NO2	mg/L	mg/L	mg N/L	mmol/L	1	3.29	*GFW
PO4	mg/L	mg/L	mg P/L	mmol/L	1	3.06	*GFW
SiO2	mg/L	mg/L	mg Si/L	mmol/L	1	2.14	*GFW
KMnO4 consumption	mg/L	mg/L	mg O2/L	mmol/L	1	3.95	*GFW
NH4-albuminoid	mg/L	mg/L	mg N/L	mmol/L	1	1.29	*GFW
Trace elements	ug/L	mg/L	ug/L	mmol/L	1000	1	*1000 GFW
Tritium	TU	TU	Bq/L	mBq/L	1	8.403	0.008403

t = 1 + 0.023 (20 - temp)

GFW = gram formula weight

2300RT/F = 59 at 25oC, 56.3 at 11oC

3.2 Conversion of - , <MDL and negative concentrations

Data from worksheet #2 (2-Raw) are automatically converted in Worksheet #3 (3-ALL) or #5 (5-ALLcor), if they contain either '-' (meaning no data available) or <X (where X is MDL = minimum detection limit) or negative concentrations. Cells with '-' are converted into empty cells (""). The conversion of <X is as follows: <X becomes 0.501 X. By not taking 0.5 X the converted data remain recognizable.
Negative input concentrations were frequently obtained from VU lab, indicating that the measured values minus the blanks were <0. They were converted as follows:

if X < 0 and if -X ≤ 2 MDL then: X = 0.502 MDL
if X < 0 and if -X > 2 MDL then: X = "" (empty cell).

NB: In case of highly mineralized waters, dilution for analysis will significantly raise the MDL. The above procedures may therefore lead to unrealistic, high concentration levels.

3.3 Selection of EC, pH, SO_4 and PO_4 data to use

EC and pH are frequently measured both in the lab and field, and SO_4 and PO_4 are frequently measured both by IC and ICP-OES. Normally we prefer the field data for EC and pH, but ill calibrated sensors or tough field circumstances may prevent these readings to be superior to the lab measurement. For further calculations in HGC it is essential to indicate which data are to be preferred. This should be done in cells DN8:DQ8 of worksheet #3 (3-ALL) and/or #5 (5-ALLcor).

3.4 Ionic balance (IB)

One of the methods to check the accuracy of chemical analyses is by calculating the ionic balance (IB) of the results of chemical analysis involving all or most major constituents. It is defined as follows with individual species in mg/L:

$$IB = 100\ (\Sigma C - \Sigma A) / (\Sigma C + \Sigma A) \qquad (3.1)$$

$$\Sigma C = Na/22.99 + K/39.01 + Ca/20.04 + Mg/12.15 + \qquad (3.2)$$

$$+ Fe/27.924 + Mn/27.47 + NH_4/18.04 + Al/9 + 10^{(3\text{-}pH)} / \gamma_1$$

$$\Sigma A = Cl/35.453 + SO_4/48.03 + HCO_3/61.02 + NO_3/62 + \qquad (3.3)$$

$$+ PO_4/\{94.97\ (1+10^{(pH-7.21)})\} + A_{ORG}$$

Where: ΣC = sum of cations (meq/L); ΣA = sum of anions (meq/L); HCO_3^- = alkalinity as HCO_3^-; PO_4^{3-} = orthophosphate [mg PO_4/L], of which only H_2PO_4 is considered as this species is not included in the alkalinity analysis (Stuyfzand, 1993); A_{ORG} = organic anions not included in the alkalinity analysis as HCO_3 [meq/L]; γ_1 = activity coefficient for species with charge ± 1 [kg H_2O/mole]. For calculation of γ_1 see Eq.6.10.

A_{ORG} [meq/L] is calculated following Oliver et al. (1983), with DOC in mg/L and HCO_3 in meq/L:

If $A_{ORG} > HCO_3$: $\quad A_{ORG} = K_{ORG}\ DOC / (100\ K_{ORG} + 10^{-(pH+1)}) - HCO_3 \qquad (3.4A)$

If $A_{ORG} \leq HCO_3$: $\quad A_{ORG} = 0 \qquad (3.4B)$

where:

$$K_{ORG} = 10\text{^}(0.039\ pH^2 - 0.9\ pH - 0.96) \qquad (3.5)$$

The calculation of ΣC and ΣA includes: the often neglected transformation of H^+ and OH^- activity as obtained by pH measurement, into its concentration; that part of orthophosphate, which is not included in the determination of alkalinity; and organic anions in so far not included in alkalinity, according to a procedure presented by Oliver et al. (1983).

The balance is judged square, if no colour appears according to the boundaries defined in Table 3.2, that is if: $|IB| < 4\%$, if $\Sigma C+\Sigma A > 8$ meq/l; $|IB| < 6\%$, if $\Sigma C+\Sigma A$ = 2-8 meq/l; and $|IB| < 10\%$, if $\Sigma C+\Sigma A < 2$ meq/l.

TABLE 3.2. Conditional colour formatting in HGC EXCEL sheets, to indicate undesired deviations from ionic balance (IB) and differences between measured and calculated EC (ΔEC-meas).

Cell colour	no colour	tan	orange	no colour	tan	orange
if:	**│IB│ (%)**			**ΔEC-meas (%)**		
ΣC+ΣA >8 meq/L	<4	<8	≥8	<4	<8	≥8
ΣC+ΣA = 2-8 meq/L	<6	<12	≥12	<6	<12	≥12
ΣC+ΣA <2 meq/L	<10	<20	≥20	<10	<20	≥20

IB (%) = 100 (ΣC-ΣA) / (ΣC+ΣA) **ΔEC-meas (%) = 100 (EC_{MEAS} - EC_{CALC}) / EC_{MEAS}**

3.5 Electrical conductivity (EC)

Backgrounds

The electrical conductivity (EC) of water at a standard reference temperature (here 20°C) indicates or mainly depends on the total amount of dissolved solids (TDS) or rather the total amount of charged ions in solution. Vice versa the sum of all analyzed major constituents of water can be used to calculate the EC. This calculated EC is useful when EC has not been measured, but is needed for instance to calculate the ionic strength or osmotic pressure of water, or to interprete geophysical resistance measurements, or to estimate missing values of major constituents in a water analysis (§3.9).

Another beneficial use is to check the accuracy of chemical analyses by comparing the calculated (EC_C) with the measured EC (EC_M; either in lab or field).

The calculation of EC is not easy, as there are no simple relations in a natural mixed solution, between concentrations or activities and EC, due to interactions of electrical and ionic nature. The rule stated by Appelo & Postma (2005) that $EC = 50 (\Sigma k + \Sigma a)$, is practical but too simple for the purpose of checking the accurracy of a water analysis at higher concentration levels ($\Sigma k + \Sigma a > 6$ meq/L).

The most accurate way to calculate EC is based on all main dissolved constituents and was presented by Stuyfzand (1983), with updates in Stuyfzand (1987). A simpler, somewhat less accurate but still precise method was given by Stuyfzand (2001), using only all main anions. This method has been implemented in HGC, and is presented below. The more precise method will be added in a next version (column DW in sheet #3 and #5; column DO in sheet #4), while the anion-version will remain as an independent additional check.

Using the anion method, an analysis will earn the mark "good", if no colour appears according to the boundaries defined in Table 3.1, that is if the calculated EC (EC_C) approximates the accurately measured EC (EC_M) in such a way, that : $|\delta EC| < 4\%$, if $\Sigma C+\Sigma A > 8$ meq/l; $|\delta EC| < 6\%$, if $\Sigma C+\Sigma A = 2-8$ meq/l; and $|\delta EC| < 10\%$, if $\Sigma C+\Sigma A < 2$ meq/l, where :

$$\delta EC = 100 (EC_M - EC_C) / EC_M \qquad (3.6)$$

Calculation of EC via anions

Electrical conductivity at standard temperature of 20°C (EC_{20}) is calculated for fresh to slightly brackish waters ($\Sigma A = 3-30$ meq/L) as follows:

$$\begin{aligned} EC_{20} = 71.027 \{&0.94 + 1.38207 (Cl^-/35.453) + SO_4^{2-}/48.03 + NO_3^-/62 \\ &+ 0.95721 (HCO_3^-/61.02 + CO_3^{2-}/30.01)\} \end{aligned} \qquad (3.7)$$

with: concentrations in mg/L and EC_{20} in μS/cm.

This relation holds for solutions with EC_{20} in between about 300 and 2000 μS/cm (= 20-200 mS/m). For more dilute solutions (with $\Sigma A < 3$ meq/L, or $EC_{20} < 300$ μS/cm), like most rain waters, we take:

$$EC_{20} = 100\, \Sigma A \qquad (3.8)$$

And for more saline solutions ($\Sigma A > 30$ meq/L) we take:

$$EC_{20} = 133.605 (\Sigma A)^{0.9058} \qquad (3.9)$$

Differences in temperature (temp, °C) are corrected for by the following equation (TNO 1976; Thomas 1986; Hayashi, 2004):

$$EC_{20} = EC_t [1 + 0.023 (20 - temp)] \qquad (3.10)$$

3.6 Bird dropping corrections (rain water only)

Biogenic contributions to the composition of bulk precipitation may consist of bird-droppings, insect-droppings, plant and animal debris, marine plankton in sea spray, plant volatiles, micro-organisms, etc.
Rain gauges without a device to keep birds away, probably intercept more bird droppings than their surroundings. This justifies the application of preventive measures and, if not done, data correction procedures. It was concluded from the generally observed low orthophosphate levels in bulk precipitation obtained from gauges with an effective bird-scarer (Buijsman, 1989), that total PO_4-levels superior to about 0.10 mg/l or orthophosphate concentrations exceeding 0.05 mg/l, are highly suspect of interference with at least one bird-dropping on the equipment, and that PO_4 is the most reliable correction parameter for this type of bias.
The following correction procedure is optional but recommended.
The correction procedure, as based on data in Asman et al. (1982), Stuyfzand (1986d) and Stuyfzand & Arens (2011), therefore becomes for samples with PO_4-ortho > 0.05 mg/l or PO_4-total > 0.1 mg/L:

For X ≠ Na, K, Mg:

$$X_{BDC} = X - \beta_X (PO_4\text{-ortho} - 0.05) \tag{3.11A}$$

$$X_{BDC} = X - \beta_X (PO_4\text{-total} - 0.10) \tag{3.11B}$$

For X = Na, K, Mg:

$$X_{BDC} = X - \alpha_X \, Cl \tag{3.11C}$$

where X_{BDC}= concentration of constituent X after Bird Dropping Correction [mg/L]; X = measured concentration of X [mg/L]; PO_4 = measured phosphate concentration [mg/L]; β_X= correction factor depending on X (see Table 3.3); α_X= correction factor depending on X (see Table 4.3).

If X_{BDC} results <0 then the values indicated in Tabel 3.3 are to be taken. The β_X values are equal to the inclination of the linear regression line of parameter X (Y-axis) with PO_4 (X-axis). Values for β_{NH4} are to be lowered when raised NO_3 levels point at a partial nitrification.
Corrected data and data unaffected by bird droppings still contain about 1.4 mg/l organic carbon (TOC), 0.8 mg/l total organic NH_4 (deduced from data in Van Puffelen, 1986), as much PO_4-organic as PO_4-ortho (in between 0.02 and 0.05 mg/l, Van Puffelen, 1986; Buijsman, 1989).
→ The β_X values can be adjusted on row 8 of worksheet #4 (4-COR). PO_4 data with FBC are conditionally formatted in 3-ALL and 6-Best, yielding an orange cell.

TABLE 3.3. Correction factor (β_X) for selected parameters X, eliminating effects of bird droppings or other biogenic inputs in suspended form. In the example the measured and corrected contents are compared.

X	unit	β_X	Example		if corr
		α_X	meas	corr	<0
PO4-tot	mg/L	1.000	13.1	0.1	
pH		0.100	5.62	4.32	4.000
Cl	mg/L	0.217	10.8	7.98	0.109
SO4	mg/L	0.508	11.8	5.20	0.254
HCO3	mg/L	0.500	9	2.50	0.250
Na $	mg/L	0.556	6.4	4.44	0.278
K $	mg/L	0.021	7.5	0.16	0.010
Ca	mg/L	0.022	2.8	2.47	0.011
Mg $	mg/L	0.067	0.6	0.53	0.033
NH4	mg/L	0.186	3.5	1.08	0.093
SiO2	mg/L	0.003	0.14	0.10	0.001
TOC or DOC	mg/L	2.900	39.0	1.30	1.45

$ = to be corrected via Cl-corrected

3.7 Correction of dissolved trace elements for filtration bias

Suspended and colloidal particles cannot be easily and completely removed from solution, because their size spectrum may overlap with truly dissolved matter (Stumm & Morgan, 1981; Edmunds, 1981). For conveniency and more or less by convention, matter retained by a 0.45 µm filter paper is designated as suspended fines.

Checking and correcting dissolved trace element analyses of water for a contribution of suspended fines seems warranted, as acidification is an essential part of conservation for many trace elements, and filtration of water may have been neglected or may have suffered from bypasses during filtration. A check or correction can be performed only when typical indicators of suspended particles should be regarded as virtually insoluble under the hydrogeochemical conditions prevailing in the aquifer (Stuyfzand, 1987c). Aluminium is considered a good indicator of suspended clay in case of most water types with $5.5 < pH < 8.5$. Iron can be a good indicator of suspended iron hydroxide flocks, only if pH>5 and O_2 or NO_3 >1 mg/L.

The following correction procedure is optional but recommended.

For selected trace elements a Filtration Bias Correction (FBC) can be applied in HGC. The correction is as follows, assuming that the Al concentration in pH>5.5 water normally is <20 or <200 µg/L due to its extremely low solubility:

If water type = M, P or T:

$$X_{FBC} = X_{MEAS} - \theta_X (Al_{MEAS} - 200) \qquad (3.12A)$$

If water type = F, G, O or S:

$$X_{FBC} = X_{MEAS} - \theta_X (Al_{MEAS} - 20) \qquad (3.12B)$$

where: X_{FBC} = concentration of X corrected for filtration bias [µg/L]; X_{MEAS} = measured concentration of X [µg/L]; θ_X = correction factor for X, equal to the inclination of the linear relation between Al_{MEAS} and X_{MEAS} [-]; Al_{MEAS} = total aluminium in water sample [µg/L].

Fe was corrected only if pH>5, NO_3 or O_2 >1 mg/L and Al >20 ug/L.

Aluminum data with potential filtration bias are conditionally formatted in 3-ALL and 6-Best, yielding an orange cell.

TABLE 3.4. Correction factor (θ_X) for selected trace elements X as analyzed by either INAA (Neutron Activation) or ICP-OES, eliminating effects of filtration bias. R2 = squared correlation coefficient for the linear relation between X and Al, on which θ_X was based.
In the example the measured and corrected contents are compared.

X	unit	θ_X	R^2	θ_X	R^2	Example			If corr
		VU-ICP #		INAA ##		meas	corr ICP	corr INAA	<0
Al	ug/L					1310	20	20	
Ba	ug/L	0.0103	a			108	94.7		10.0
Be	ug/L	0.00024	0.90			0.50	0.19		0.02
Ce				0.00143	0.89	2.00		0.16	0.10
Cr	ug/L	0.0046	0.45	0.0016	0.82	3.0	0.5	0.9	0.5
Eu	ug/L	0.0004	a			0.60	0.08		0.05
Fe $	mg/L	0.0037	0.82			5.00	0.2		0.05
Hf				0.000063	0.7	0.122		0.04	0.02
La	ug/L	0.00266	0.83			5.00	1.6		0.10
Lu				0.000004	0.71	0.010		0.00	0.001
Pb	ug/L	0.01088	a	0.003	0.45	4.0	0.10	0.13	0.10
Sc	ug/L	0.00035	0.71	0.00024	0.98	2.00	1.5	1.7	0.5
Th				0.00025	0.93	0.35		0.03	0.02
Ti				0.064	0.98	95		12.4	0.5
V	ug/L	0.00903	0.70	0.0019	0.98	7.0	0.5	4.5	0.5
Yb	ug/L	0.0004	0.45			0.80	0.28		0.10
Zn	ug/L	0.0502	a	0.006	0.65	88.0	23.2	80.3	0.5

 # = data from dune sand aquifer (Stuyfzand & Arens, 2011)
= data from marine sands and silty sands (Stuyfzand, 1993)
a = R2 negative due to forcing regression line through X = Y = 0
$ = only in groundwater with pH>5 and NO3 > 1 mg/L

Not all trace elements show a significantly positive linear correlation with Al. The ones with a significant correlation (R^2 >0.45) are listed in Table 3.3, and are corrected in HGC (the others not). Different analytical techniques obviously result in different θ_X values, being on average >3 times higher for ICP-OES than for INAA. The θ_X values for INAA closely approximated their ratio in Dutch clay samples (Stuyfzand, 1993).
→ The θ_X values can be adjusted on row 8 of worksheet #4 (4-COR).

3.8 Conversion of old-fashioned parameters

In hydrochemical reports written around the beginning of this century, which may be extremely valuable in approximating natural backgrounds, old-fashioned expressions were used to denote the concentration of for instance Fe (Fe_2O_3), SO_4^{2-} (SO_3^{2-}) and HCO_3^- ($CaCO_3$ or $NaHCO_3$ or free + half-bound CO_2).
A general conversion formula for compound A_aB_b to A_cB_d, both expressed in mg/L, is :

$$A_c B_d = A_a B_b \frac{(\ MW\ of\ A_c B_d\ )}{(\ MW\ of\ A_a B_b\ )} \frac{a}{c} \tag{3.13}$$

where : MW = molecular weight (g/mol). For instance 5 mg Fe_2O_3/l = 3.5 mg Fe/l.

→ In worksheet '16 Element Converter' chemical units can be converted, using Eq.3.13.
→ Worksheet '17 Unit converter' presents more general unit conversions covering all kind of nonchemical units and some chemical units.

Conversions to alkalinity as HCO_3^- in mg/L are :

$$HCO_3^- = 2.77 (\ free + half\text{-}bound\ CO_2\ ) \tag{3.14}$$

$$HCO_3^- = 61.02 (\ \frac{Na_2CO_3}{106} + \frac{TotH}{2.8}\ ) \tag{3.15}$$

$$HCO_3^- = 61.02 (\ \frac{NaHCO_3}{84.01} + \frac{TotH}{2.8}\ ) \tag{3.16}$$

where : $NaHCO_3$ = excess alkalies as $NaHCO_3$, in mg/L; Na_2CO_3 = idem as Na_2CO_3, in mg/L; TotH = total hardness in german degrees = 5.6 (Ca^{2+}+Mg^{2+}) in mmol/L.

3.9 Estimating missing or erroneous values

It will undoubtedly occur that not all main constituents were analysed in some of the most critical samples. Sometimes it is possible to calculate the concentration of the missing or mistrusted ion(s), thereby heavily relying on a square ionic balance or correctly measured EC. This presupposes correctness of all other main components, and well established relations between two or more parameters, like between electrical conductivity and the sum of anions or between alkalinity and ammonium (Stuyfzand, 1988b).
Four cases of increasing complexity are discussed in order to illuminate the estimation of missing values.
→ In worksheet '3A Estimating missing values' the estimation has been automatized (3A still under construction)..

Case 1 : one major ion missing
Is only one major constituent (X in mg/l) lacking or mistrusted, then its concentration can be easily calculated using the ionic balance directly :

$$X = |\sum a - \sum k| \frac{MW_x}{Z_x} \qquad (3.17)$$

where MW_x = molecular weight of X (g/mol); and Z_x = charge of X. X may also stand for [Na^++K^+, expressed as Na^+], [Ca^{2+}+Mg^{2+}, expressed as Ca^{2+}] or [SO_4^{2-}+NO_3^-, expressed as SO_4^{2-}].

Case 2: one major cation and one major anion missing

Are there two missing or mistrusted values of major constituents, a cation and an anion, whereas EC has been correctly measured, then both values can be accurately calculated using an iterative procedure, which stops when the calculated EC approximates the measured EC within for instance one percent (Stuyfzand, 1983c).

During the successive approximations, starting with zero meq/l for both ions, the difference between the measured and calculated EC is divided by 100 each time, giving ΔEC/100. The first time this amount is added as meq/l to the lower of Σa and Σk, for instance Σk, whereas Σa is raised to the level of Σk + ΔEC/100. The next times ΔEC/100 is added to both. The whole procedure can be easily included in any computerprogram for the calculation of EC according to the method by Stuyfzand (1983c, 1987b).

Case 3: three major ions missing

Are there three missing values of major constituents, one cation and two anions or vice versa, whereas EC was not measured, then there still is a chance to complete the analysis, on the following conditions :

- one ion can be assumed zero, because it is the small partner of an internal consistency couple and its partner was analysed. *Internal chemical consistency couples* of groundwater samples are for instance O_2-Fe or NO_3-Fe (if pH > 4), NO_3-CH_4, Al - pH and ^3H - ^{14}C. For instance, when concentrations of O_2, NO_3 and tritium are high, with pH in between 5.5 and 9, then iron, methane and aluminium should normally be low, whereas carbon-14 cannot approach zero. An inconsistency may point at analytical errors, insufficient conservation, sampling errors or mixing, either by sampling or in the aquifer. An unbiased inconsistency using miniscreens points at mixing in the aquifer, whereas such an inconsistency obtained from a very long well screen of a pumping well, indicates the mixing of different water types in the well (mixing by sampling). So, if for instance Fe was >0.5 mg/L from a short observation welll, then NO_3 can be assumed zero; and
- one of the other missing ions can be reliably estimated by regression with a measured ion or parameter (like NH_4^+ or colour). Such regressions generally hold for a specific water type or group of water types only, so that the hydrochemical position of the sample must be assessed first. A missing ion can also be calculated by assuming equilibrium with a mineral phase (for instance Ca^{2+} from calcite or Al from gibbsite), for which thermodynamic data are well established.

The concentration of the remaining ion is subsequently calculated using Eq.3.17.

Case 4: EC measured, HCO_3 approximately known, no gypsum, no other data

The concentration of Cl can be estimated from EC measurements, provided HCO_3 can be estimated (or was measured), and the presence of gypsum in the system can be ignored. The estimate becomes linear at higher EC levels when the admixing of sea water becomes more prominent (Figs.3.1).

Fig. 3.1 shows that the simple linear regression equations strongly deviate at low EC values. At higher HCO_3 levels this deviation is stronger and continues to higher EC. Corrections of the simple Cl relations in Fig.3.1 for deviations at lower EC values and at higher HCO_3 concentrations, yielded Eqs. 3.18A – 3.18i given below. Their performance is excellent, at least when Cl >1000 mg/L or EC > 2500 uS/cm (Fig.3.2).

If HCO_3 <250 mg/L:
if EC < 30,000 uS/cm: $Cl = 0.4229*EC - 178 - 108.09*\ell n(EC)+695$ (3.18A)
if EC ≥ 30,000 uS/cm: $Cl = 0.4229*EC – 178$ (3.18B)
If HCO_3 = 250-500 mg/L:
if EC < 20,000 uS/cm: $Cl = 0.4215*EC - 238 - 136.37*\ell n(EC)+906$ (3.18C)
if EC ≥ 20,000 uS/cm: $Cl = 0.4215*EC – 238$ (3.18D)
If HCO3 = 500-1000 mg/L:
if EC < 20,000 uS/cm: $Cl = 0.4247*EC - 463 – 185.63*\ell n(EC)+1394$ (3.18E)
if EC ≥ 20,000 uS/cm: $Cl = 0.4247*EC – 463$ (3.18F)
If HCO3 =1000-2000
if EC < 6,500 uS/cm: $Cl = 0.3380*EC-459$ (3.18G)
if EC ≥ 6,500 uS/cm: $Cl = 0.4308*EC-832$ (3.18H)
If HCO3 >2000 mg/L
$Cl = 0.4218*EC-1054$ (3.18i)

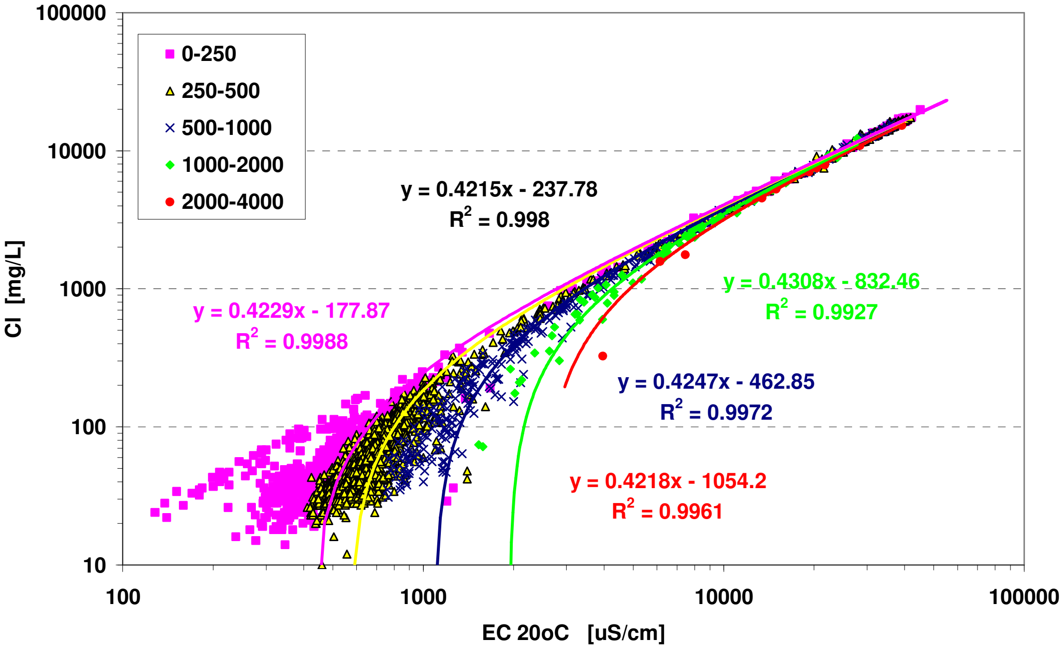


FIG. 3.1. Relation between EC and Cl concentration as depending on HCO_3 concentration classes [mg/L].

The importance of estimating Cl from EC readings is extremely high, because geophysical resistivity measurements are frequently used to map the fresh/brackish and brackish/salt interface. In addition, when the Cl concentration is known, further rough estimates can be given for other constituents, if a high correlation with Cl is warranted.

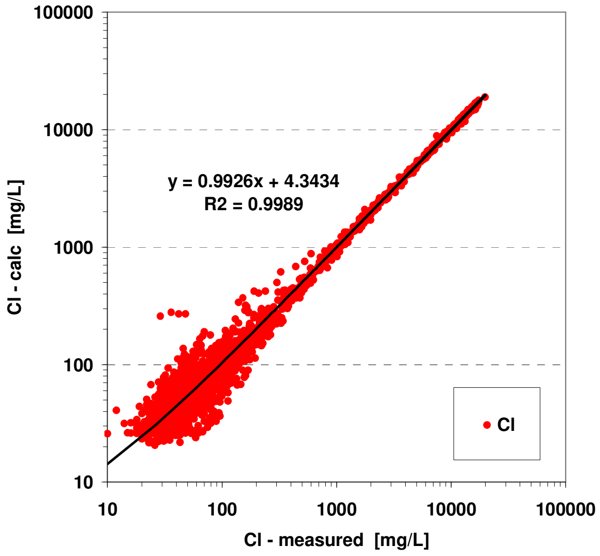


FIG. 3.2. Performance of Eqs. 3.18A – 3.18i to calculate Cl from EC measurements when HCO_3 concentration is known or approximately known (<250, 250-500, 500-1000, 1000-2000 or >2000 mg/L).

4 Base exchange and nonmarine concentrations

4.1 BEX: a Base Exchange index

4.1.1 Introduction

Traditionally cation exchange is represented by the following reaction during the intrusion of salt NaCl-water into fresh $CaHCO_3$ groundwater (reaction to right) or the intrusion of fresh $CaHCO_3$ water into salt NaCl groundwater (reaction to left):

$$Na^+ + \tfrac{1}{2}Ca\text{-}EXCH \leftarrow\rightarrow \tfrac{1}{2}Ca^{2+} + Na\text{-}EXCH \tag{4.1}$$

The first to recognize cation exchange in groundwater was not Renick (1924) as mentioned by several textbook writers, but Versluys (1916). Versluys (1916, 1931) used the ratio Na/(Na+Ca+Mg) as an index of base exchange. Schoeller followed in 1934 and 1956 with the 3 indices indicated in Table 4.1. Indices 1-4 and 6 in Table 4.1 are all expressed as a meq/L ratio, which makes them fit for the direction but unfit for quantifying the extent of the base exchange reaction. Delecourt (1941) was the first to introduce an index (see Table 4.1) that also quantifies the extent of the exchange reaction. Various problems with the above given indices are listed in Table 4.1. The most important objections to these older indices are: (1) being a ratio, they do not provide information on the amount of ions exchanged; (2) being without thresholds, an imbalance by other causes is too easily attained. Ocean water already exhibits a positive Schoeller-ratio, for instance; and (3) also Mg^{2+} is generally involved in the base exchange, often on the same side as Na^+ and K^+ (see below). An index not suffering from most of the problems mentioned in Table 4.1, the Base EXchange index (BEX) was proposed by Stuyfzand (1986), also as part of a chemical watertype classification.

TABLE 4.1. Overview of base exchange indices, with frequently encountered problems in their interpretation. Numbers 7-8 are BEX and BEX_D respectively, number 6 is discussed in §4.4..

No.	Author	Index [meq/L]
1	Versluys (1916, 1931)	Na / (Na + Ca + Mg)
2	Schoeller (1934)	[Cl - (Na + K)] / Cl
3	Schoeller (1956)	(Na + K) / Cl
4	Schoeller (1956)	(Ca + Mg) / (HCO3 + CO3 + SO4)
5	Delecourt (1941)	Na + K - Cl
6	Russak & Sivan (2010)	$[(Ca_M\text{-}Ca_{EXP}) / Ca_{EXP}] - [(K_M - K_{EXP}) / K_{EXP]} - 0.5$
7	Stuyfzand (1986) #	Na + K + Mg - 1.0716 Cl
8	Stuyfzand (2008) ##	Na + K - 0.8768 Cl

Problems:
1-8: other processes may influence values
1-5: bias due to analytical errors, no threshold
1-4: do not quantify amount of cation exchange

#: for aquifers without dolomite

1: CaCO3 dissolution influences ratio
2: ocean water already positive
5: ocean water already negative

##: for aquifers containing dolomite

Field data in the coastal area of the Western Netherlands, however, revealed that indeed also K^+ and Mg^{2+} are involved in these exchange processes (Stuyfzand, 1993), such that reaction 4.1 ‘grosso modo’ changes into reaction 4.2, with a+b+c = 0.5:

$$aNa^+ + bK^+ + cMg^{2+} + \tfrac{1}{2}Ca\text{-}EXCH \leftarrow\rightarrow \tfrac{1}{2}Ca^{2+} + [aNa,bK,cMg]\text{-}EXCH \tag{4.2}$$

4.1.2 Definition of BEX

BEX is the meq-sum of the typically marine cations Na^+, K^+ and Mg^{2+}, corrected for a contribution of sea salt (Stuyfzand, 1986, 1993):

$$BEX = Na^+ + K^+ + Mg^{2+} - 1.0716\ Cl^- \qquad [meq/L] \qquad (4.3)$$

The factor 1.0716 is equal to $\{[Na^+ + K^+ + Mg^{2+}]/Cl^-\}$ in meq/L for mean ocean water. It is hereby assumed that : (1) all the Cl- ions are of marine origin; (2) fractionation of the main constituents of sea water during spray formation can be ignored, so that the atmospheric Na^+, K^+ and Mg^{2+} contribution to fresh water exclusively depends on the Cl- concentration; (3) Cl- behaves conservatively; and (4) the 3 marine cations exchange together for Ca^{2+} according to Eq.4.2.

The boundary limits at ± (0.5 + 0.02 Cl) indicated in Fig.4.1, were introduced as a threshold against (a) the expected errors in chemical analyses, and (b) waters without base exchange, that derive from silica terrains where some Na^+, K^+ and Mg^{2+} ions dissolve by chemical breakdown of silicates. The term 1.5(Σk - Σa) is used as a measure of ionic imbalance (see Fig.4.1).

BEX does not apply to dolomitic aquifer systems, because significant amounts of Mg derive from the dissolution of dolomite. Therefore BEX was slightly modified into BEX_D for application to dolomitic systems (Stuyfzand, 2008). Its definition is given in Eq.4.4 and in Table 4.1, and its further characteristics are equal to those of BEX (Fig.4.1).

$$BEX_D = Na^+ + K^- - 0.8768\ Cl^- \qquad [meq/L] \qquad (4.4)$$

BEX = Na + K + Mg - 1.0716 Cl (all in meq/L) **if no dolomite**

with: 1.0716 = (Na+K+Mg)/Cl in SMOW

BEX = Na + K - 0.8768 Cl (all in meq/L) **if dolomite present**

with: 0.8768 = (Na+K)/Cl in SMOW

Code	BEX	INTERPRETATION	
		If only base exchange	if other process(es) relevant
-	negative	Salinized	Marine cations deficit
•	zero	no base exchange	Marine cations equilibrium
+	positive	Freshened	Marine cations surplus

$$[½Ca]\text{-EXCH} + aNa^+ + bK^+ + cMg^{2+} \longleftrightarrow [aNa,bK,cMg]\text{-EXCH} + ½Ca^{2+}$$

freshening ⟵ ⟶ salinization

Conditions for BEX to become +: >+(0.5+0.02Cl) and >1.5(Σk - Σa)
Conditions for BEX to become - : <-(0.5+0.02Cl) and <1.5(Σk - Σa)

FIG. 4.1. The Base Exchange index BEX as proposed by Stuyfzand (1986) with minor modifications according to Stuyfzand (1993, 2008).

4.1.3 Interpretation of BEX

Thus upon fresh water intrusion Ca^{2+} expels, grosso modo, the previously adsorbed, marine cations Na^+, K^+ and Mg^{2+} from the exchanger. Exchange reaction 4.2 proceeds from right to left then, leading to a significantly positive BEX (or $[Na^++K^++Mg^{2+}]$surplus). The reverse reaction occurs during salt water intrusion. This means that BEX constitutes an excellent base exchange index indeed, on the condition that other sources and sinks of Na^+, K^+, Mg^{2+} and Cl^- can be neglected.

Such ideal conditions prevail in the upper aquifer systems of The Netherlands, which are largely composed of quartz sands without evaporites and dolomites. A significantly positive BEX can then be translated into freshening (displacement of saltier groundwater), a significantly negative BEX into salinization (displacement of fresher groundwater), and a BEX = 0 into adequate flushing with water of constant composition.

Na^+, K^+ and Mg^{2+} do not always ad- or desorb simultaneously during salt or fresh water intrusion respectively (Stuyfzand, 1993; Appelo & Postma, 2005). This means that their individual concentrations corrected for a contribution of sea salt, do not always indicate the right direction of displacement. Deviations from reaction 4.2 are quantitatively insufficient, however, to influence the sign of BEX (Fig.4.2), which pleads for this classification parameter as an indicator of salinization or freshening.

4.1.4 Complications in interpretation

Any of the presented base exchange indices suffers from bias in the interpretation of its value, in addition to bias due to analytical errors. The most important ones are listed in Table 4.2, which more specifically holds for BEX and BEX_D.

False positive and negative BEX values relate to other sources and sinks of the cations and Cl. This does not mean that BEX is useless in those cases but needs to be interpreted in a different way (see also Fig.4.1).

Another problem is that actual and past shifts in the position of the fresh/salt water interface cannot be distinguished during a snapshot survey. The presence of a freshened watertype like $NaHCO_3$ groundwater with positive BEX may proof that the system has been freshened, which is important. If this does not relate to current shifts in the position of the fresh/salt water interface, then it constitutes significant palaeohydrological information.

If changes in Cl and BEX are monitored in wells, then some other interesting conclusions can be drawn e.g. about actual freshening or salinization (Table 4.2).

In the Netherlands, complication 1C can be encountered on a large scale in the upper tens of metres of groundwater in agricultural areas, whereas complications 1B and 2D are generally limited to the upper metres of groundwater in woodlands. Complication 6 is frequently observed in polder areas in the Netherlands.

TABLE 4.2. Problems with the interpretation of base exchange index BEX (Stuyfzand, 2008). Hypersaline and volcanic conditions excluded.

	Problems and Interpretation of BEX		Fresh	Salt
0	**Ad- and desorption of Na, K and Mg not simultaneous**		**CR**	**CR**
1	**False positive BEX:**			
	A	**Dissolution of minerals like dolomite (+Mg), albite (+Na), sodalite (+Na)**	**C**	**C**
	B	**Mineralization of fresh biomass (+K)**	**R**	**RR**
	C	**Leaching of fertilizers or manure (+K)**	**C**	**RR**
2	**False negative BEX:**			
	A	**Dissolution of halite (lack of K and Mg)**	**R**	**C**
	B	**Mineral transformations like dolomitization (-Mg)**	**R**	**CR**
	C	**New formation of minerals (-K, -Na, -Mg)**	**R**	**R**
	D	**Synthesis of biomass (rapid growing forest; -K)**	**R**	**RR**
	E	**Significant atmosferic inputs of Cl_2 gas (+Cl)**	**RR**	**RR**
3	**BEX (not false) indicates results of past shifts in fresh / salt interface**			
	A	**Positive BEX at specific point does not mean system is actually freshening**	**C**	**C**
	B	**Negative BEX at specific point does not mean system is actually salinizing**	**C**	**C**
4	**If chloride decreasing or constant and BEX trend:**			
	A	**from positive to 0, then Freshening**	**CC**	**RR**
	B	**from 0 to positive, then Salinization or False pos BEX**	**CR?**	**RR**
	C	**more negative, then False negat BEX**	**R**	**RR**
5	**If chloride increasing and BEX trend negative, then Salinization**		**CC**	**CC**
6	**If chloride increasing and BEX trend positive, then Salinization by special source water#**		**R**	**RR**

 # = for instance brackish surface water from a canal, with inputs from exfiltrating freshened groundwater or from agriculture

Dolomite = CaMg(CO3)2 Albite = NaAlSi3O8 Sodalite = Na8Cl2(AlSiO4)6

CC = very common; C = common; RC = uncommon, not rare; R = Rare; RR = very rare / nonexistent

4.2 Individual ions corrected for marine contributions

On many sites, especially coastal sites, chloride (pratically all watertypes) or sodium (rainwater only) can be assumed to derive exclusively from ocean water, through either the admixing of ocean water or the input via sea spray aerosols. This opens up an interesting way to correct the concentrations of various ions in water for the contribution of sea salt (via either sea water or sea spray), thus indicating their non-marine concentration. This helps to understand and quantify the hydrogeochemical genesis.
The calculation is simply as follows:

if watertype not rainwater: $X_C = X - \alpha_X \, Cl$ (4.5A)
if watertype rainwater: $X_C = X - \omega_X \, Na$ (4.5B)

$$\omega_X = 1.7972 \, \alpha_X \qquad (4.6)$$

where X_C = non-marine concentration of constituent X; X = concentration of X measured; Cl = measured Cl concentration; Na = measured sodium concentration; α_X = (X/Cl) in standard mean ocean water (SMOW), ω_X = (X/Na) in SMOW.

Appropriate values for α_X and ω_X are listed in Table 4.3, both on a mg/L and mol/L basis. In case of rain water and rain water fed groundwater bodies, it is assumed that the fractionation of the main constituents of sea water during spray formation can be properly ignored.
Further backgrounds are given by Stuyfzand (1993).
Chloride in rain water may show, however, a small excess compared to Na due to anthropogenic or volcanic Cl inputs, or small losses due to volatilization as HCl upon reaction with strong atmospheric acids. This can be demonstrated by using Eq.4.5B, correcting Cl for marine inputs via Na, because Na is generally accepted as being practically without bias in indicating the marine contribution (Ten Harkel, 1998).

For δ^2H and $\delta^{18}O$ the correction for a marine contribution is as follows:

$$\delta^2H_C = (\delta^2H_{MIX} - \delta^2H_{SEA} \, f_{SEA}) / (1 - f_{SEA}) \qquad (4.7)$$

$$\delta^{18}O_C = (\delta^{18}O_{MIX} - \delta^{18}O_{SEA} \, f_{SEA}) / (1 - f_{SEA}) \qquad (4.8)$$

where: the subscripts C, MIX and SEA stand for Corrected, Mixed sample and local Seawater, respectively; f_{SEA} = fraction of (intruded) sea water [-].

TABLE 4.3. Correction factor α_X and ω_X in Eq.4.5, in order to correct concentrations of various components for a contribution of sea salt, on either a mg/L or mol/L basis. TotH = total hardness.

Quality Parameter	SMOW		factor α_X		factor ω_X	
	mg/L	mmol/L	mg/L	mol/L	mg/L	mol/L
Major Constituents						
Cl^-	19805	558.63	1.0	1.0	1.7972	1.1654
Na^+	11020	479.34	0.5564	0.8581	1.0	1.0
K^+	408	10.44	0.0206	0.0187	0.0370	0.0218
Ca^{2+}	422	10.53	0.0213	0.0188	0.0383	0.0220
Mg^{2+}	1322	54.39	0.0668	0.0974	0.1200	0.1135
SO_4^{2-}	2775	28.89	0.1401	0.0517	0.2518	0.0603
TotH (Ca^{2+} + Mg^{2+})		64.92		0.1162		0.1354
BEX = Na_C+K_C+Mg_C		meq/L		1.0715		
BEX_D = Na_C+K_C		meq/L		0.8767		
Trace Elements						
B	4.6	0.4255	$2.323 \; 10^{-4}$	$7.617 \; 10^{-4}$	$4.174 \; 10^{-4}$	$8.8767 \; 10^{-4}$
Br^-	67.3	0.8423	$3.398 \; 10^{-3}$	$1.508 \; 10^{-3}$	$6.107 \; 10^{-3}$	$1.757 \; 10^{-3}$
F^-	1.3	0.0684	$6.564 \; 10^{-5}$	$1.225 \; 10^{-4}$	$1.180 \; 10^{-4}$	$1.428 \; 10^{-4}$
I	0.06	0.0005	$3.030 \; 10^{-6}$	$8.464 \; 10^{-7}$	$5.445 \; 10^{-6}$	$9.864 \; 10^{-7}$
Li^+	0.17	0.0245	$8.584 \; 10^{-6}$	$4.384 \; 10^{-5}$	$1.543 \; 10^{-5}$	$5.110 \; 10^{-5}$
Mo	0.01	0.0001	$5.049 \; 10^{-7}$	$1.865 \; 10^{-7}$	$9.074 \; 10^{-7}$	$2.174 \; 10^{-7}$
Rb^+	0.12	0.0014	$6.059 \; 10^{-6}$	$2.513 \; 10^{-6}$	$1.089 \; 10^{-5}$	$2.929 \; 10^{-6}$
Sr^{2+}	8.1	0.0924	$4.090 \; 10^{-4}$	$1.655 \; 10^{-4}$	$7.350 \; 10^{-4}$	$1.929 \; 10^{-4}$
Example			Na	Cl	Na	Cl
Unit = mg/L	$X_C = X - \alpha_X \, Cl^-$		50	100	50	100
X_C =			-5.6	mg/L	mg/L	10.1

4.3 BEX: the individual cations and side reactions

The individual cations Na^+, K^+ and Mg^{2+} do not always ad- or desorb simultaneously during salt or fresh water intrusion respectively, as can be seen for freshening groundwaters in Fig.4.2. It can be deduced that, in this study, Na* (=Na_C) indicates the right direction of displacement only when BEX >4, K* (=K_C) when BEX <10 and Mg* (=Mg_C) when BEX <8 meq/L.
Changes in Ca concentration are related to BEX as follows (Fig.4.2), provided other reactions like methanogenesis do not significantly contribute:

$$Ca_C = Ca_{C0} - f\ BEX \qquad (4.9)$$

With: Ca_C = calcium concentration corrected for sea salt (= Ca – 0.0376 Cl) after base exchange [meq/L]; Ca_{C0} = ditto before base exchange [meql/L]; f = reaction coefficient [<1].
Factor f was 0.5 during freshening in calcareous coastal dune aquifer systems in the Netherlands, and it was 1.0 during salinization (Stuyfzand, 1993). This indicates that the Ca losses are compensated for by dissolution of an amount of $CaCO_3$ equal to BEX/2 in case of freshening and equal to BEX in case of salinization.
Changes in TIC concentration were related to BEX, only during freshening, as follows (Fig.4.2):

$$TIC = TIC_0 + 2f\ BEX \qquad (4.10)$$

With: TIC, TIC_0 = Total Inorganic Carbon resp. after and before base exchange [mmol/L].

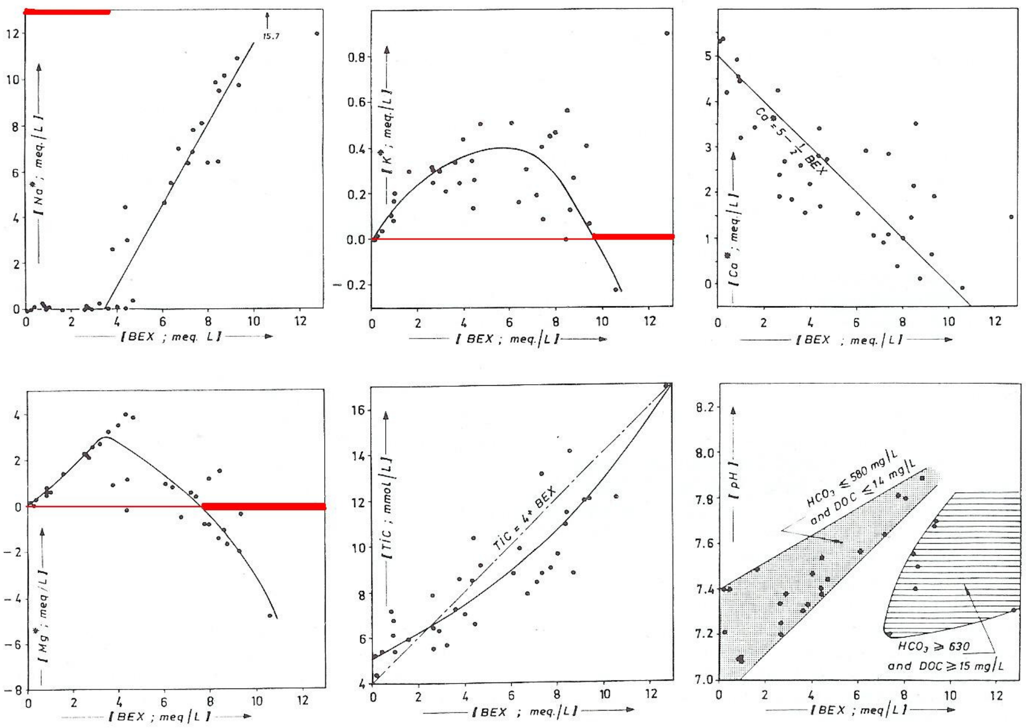


FIG. 4.2. Plot of sea salt corrected, main cations (X = X_C), total inorganic carbon (TIC) and pH in 36 deep anoxic groundwater samples, versus BEX for a sandy coastal dune aquifer system without dolomite in the Netherlands (slightly modified after Stuyfzand, 1993).*
Heavy red bars indicate samples where BEX correctly indicates freshening, while Na(= Na - 0.8581 Cl), K* (= K - 0.0187 Cl) and Mg*(= Mg - 0.1948 Cl) do not.*

4.4 When the saline end-member differs from SMOW

Russak & Sivan (2010) proposed a useful salinization index (SALI) for cases where cation exchange is the main process in the system, and where the chemical composition of the saline end-member deviates significantly from SMOW. The index is based on the opposite cation exchange characteristics of Ca^{2+} and K^{+} during salinization and freshening. This method enables distinguishing between salinization (SALI >0) and freshening (SALI <0) using only one sample, and considering the local saline end member and not average seawater composition.
SALI does not provide information on the extent of the exchange reaction. It is calculated as follows:

$$\mathrm{SALI} = [(Ca_M - Ca_{EXP}) / Ca_{EXP}] - [(K_M - K_{EXP}) / K_{EXP}] - 0.5 \qquad (4.11)$$

where the expected values of Ca (Ca_{EXP}) and K (K_{EXP}) are calculated and defined as:

$$X_{EXP} = X_S - (X_S - X_F)\,(Cl_S - Cl_M) / (Cl_S - Cl_F) \qquad (4.12)$$

where X denotes Ca or K [meq/L]; the subscripts F, M and S denote fresh water end-member, measured sample, and saline water end-member, respectively.

The empirical boundary line of the index between freshening and salinization is 0.5. For the sake of convenience, 0.5 is subtracted from the equation to set the boundary-line value at zero. In gypsum containing aquifers SALI should be calculated using only K and the factor 0.5 should be replaced by 0.15. SALI can be used in water whose salinity range is 10-80% of the saline end member.

5 Chemical watertype

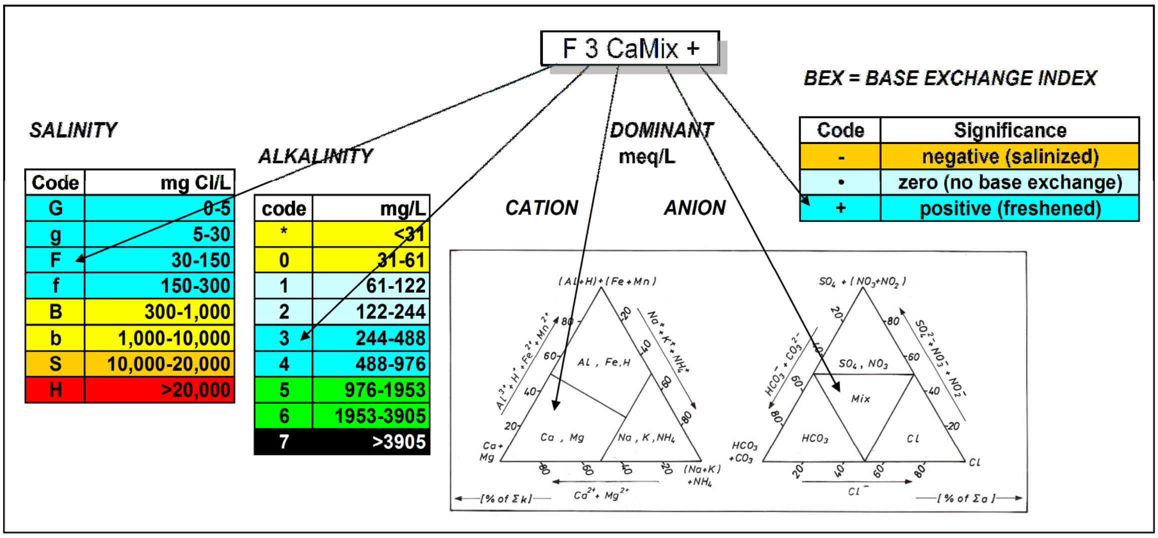
A water sample can be classified into a chemical watertype, when all its major dissolved constituents have been analyzed. This is useful for mapping purposes and communication. The more frequently used watertype classifications have been discussed by Matthess (1990).

In HGC Stuyfzand's chemical watertype classification is determined, because this classification offers many advantages over the others: (1) next to the normally addressed major constituents also frequently neglected ions are included (H, Al, Fe, K, NH_4, NO_2 and NO_3); (2) the assignment of the most important cation and anion is broader based, namely on support by geohydrochemical family members, which leads to an earlier assignment of relatively rare watertypes like $AlSO_4$, $FeSO_4$, NH_4SO_4, HCl, KNO_3 and $MgHCO_3$ water; (3) introduction of the term 'Mix' when no anion family dominates; (4) the addition of base exchange index BEX, which helps to identify cation exchange also in watertypes that otherwise would not be readily noticed as such, like $CaHCO_3$ and NaCl water; and (5) the resulting code in 9 positions yielding a more complete picture of water chemistry.

5.1 The classification system and its coding

The chemical watertype is calculated on the basis of the main constituents of water, according to the method of Stuyfzand (1986, 1989b; 1993). In one code (9 characters) the chlorinity, alkalinity, dominant cation and anion (including the support of geohydrochemical family members) and a base exchange index (BEX) are indicated (Fig.5.1).

For example the watertype 'F1CAHCO3+' indicates fresh water (30-150 mg Cl/L), with alkalinity class 1 (61-122 mg HCO_3/L) and calcium as the most important cation, HCO_3 as the most important anion, and a significantly positive base exchange index (+).



SALINITY

Code	mg Cl/L
G	0-5
g	5-30
F	30-150
f	150-300
B	300-1,000
b	1,000-10,000
S	10,000-20,000
H	>20,000

ALKALINITY

code	mg/L
*	<31
0	31-61
1	61-122
2	122-244
3	244-488
4	488-976
5	976-1953
6	1953-3905
7	>3905

DOMINANT meq/L

BEX = BASE EXCHANGE INDEX

Code	Significance
-	negative (salinized)
•	zero (no base exchange)
+	positive (freshened)

FIG. 5.1. Coding and significance of the chemical watertype according to Stuyfzand's method (modified after Stuyfzand, 1993).

5.2 Main types, by chloride

Chlorinity determines the main type, as indicated in Table 5.1, because of: (a) its paramount importance in the determination of the origin of waters, (b) its indicative value of the thalassogenic mineralization of water (by sea or rock salt), and (c) its relevancy to aquatic flora and fauna, and to the potential use of water to man. The 8 class boundaries are indicated in Table 5.1.

TABLE 5.1. . Division in main types on the basis of the chloride concentration.

Main Type	Main Type	Code	mg Cl/L	meq Cl/L	Boundary type [mg/L]
Fresh	**Oligohaline**	**G**	**0-5**	**<0.141**	
	Oligohaline-fresh	**g**	**5-30**	**0.141-0.846**	
	Fresh	**F**	**30-150**	**0.846-4.231**	**150 = MPC drinking water**
	Fresh-brackish	**f**	**150-300**	**4.231-8.462**	**300 = brackish taste noticeable**
Brackish	**Brackish**	**B**	**300-1,000**	**8.462-28.206**	**1,000 = geophys. maps, cattle**
	Brackish-salt	**b**	**1,000-10,000**	**28.206-282.064**	**10,000 = 50% mix ocean / fresh**
Salt	**Salt**	**S**	**10,000-20,000**	**282.064-564.127**	**20,000 = near ocean water#**
Hypersaline	**Hypersaline**	**H**	**>20,000**	**>564.127**	

 # = 19,805 mg/L

5.3 Types, by alkalinity

Each main type is subdivided into 9 types according to alkalinity (Table 5.2). Alkalinity is in many situations an excellent reaction progress variable, or in other words, a measure for the lithogenic mineralization of water. For most natural waters with 4.5 < pH < 9.5 alkalinity equals HCO_3^- + CO_3^{2-} in meq/l, of which CO_3^{2-} can be ignored if pH < 8.2.

TABLE 5.2. Subdivision of main types into 9 types according to alkalinity, on a ^{2}log-basis.

		Alkalinity as HCO3-	
Type	**code**	**mg/L**	**meq/L**
Very low	*****	**<31**	**<0.5**
Low	**0**	**31-61**	**0.5-1**
Moderately low	**1**	**61-122**	**1-2**
Moderate	**2**	**122-244**	**2-4**
Moderately high	**3**	**244-488**	**4-8**
High	**4**	**488-976**	**8-16**
Very high	**5**	**976-1953**	**16-32**
Extreme	**6**	**1953-3905**	**32-64**
Very extreme	**7**	**>3905**	**>64**

5.4 Subtypes, by the dominating cation and anion

The most important cation and anion determine the subtype in a way that bears a resemblance to the traditional assignment of a chemical water type. The direct preponderance in the ionic balance is decisive there, whereas here the support of geohydrochemical family members is included (Fig.5.2). Further details including a computer program, are given by Stuyfzand (1989g).
The deviating grouping method has the important advantage that otherwise very rare water types like $AlSO_4$, KNO_3, HCl, HNO_3, MgCl and $MgHCO_3$ water, are assigned much earlier than when a single ion is required to occupy >50% of the sum of cations or anions in meq/L for nomination. On the other hand the assignment is more substantial by the geohydrochemical family support, than when the dominant cation and anion (without family support) are chosen on the basis of the highest share in the sum of cations and anions in meq/L. Both aspects considerably increase the diagnostic value of the classification system.
The "Mix" anion family was also introduced, and refers to water in which no anion family makes up more than 50% of the sum of anions.

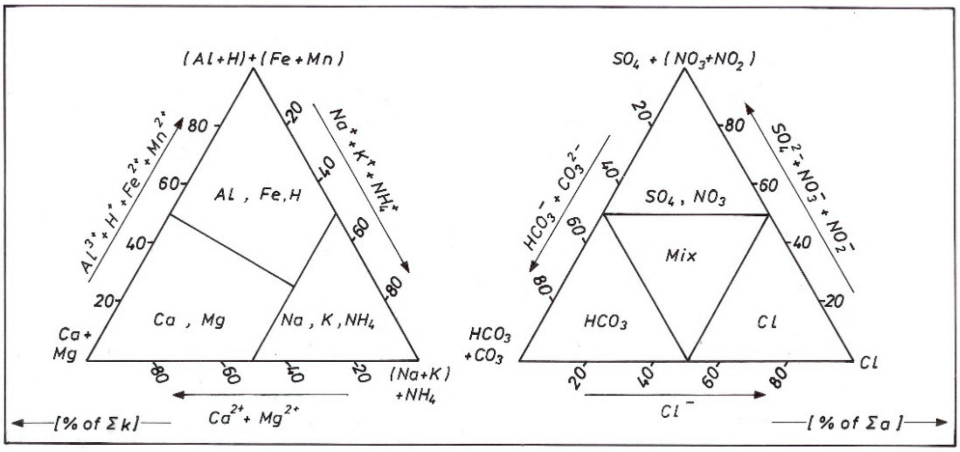


FIG. 5.2. Subdivision of types into subtypes on the basis of the proportional share of main constituents in the sum of the cations (left) and anions (right), both in meq/l (From: Stuyfzand, 1986). First of all, the dominating hydrochemical family at the vertices of each triangle is determined, for instance the [Al+H+Fe+Mn]- and [SO_4+NO_3+NO_2]-families. Then the strongest couple within a family (in brackets at the vertices) is selected, where present, for example [Al+H]. If now Al is superior to H^+, and SO_4^{2-} superior to [NO_3+NO_2] the subtype becomes "AlSO_4". The strongest family members discovered to date are placed in the appropriate fields inside the triangles.

5.5 Classes, by the base exchange index (BEX)

Finally, each subtype is subdivided into 3 classes (-, ● or +) according to the base exchange index BEX introduced by Stuyfzand (1986). This is the meq-sum of the typically marine cations Na^+, K^+ and Mg^{2+}, corrected for a contribution of sea salt. See §4.1 for further details.
The class boundaries of BEX at ± (0.5 + 0.02 Cl^-) form a threshold against (a) the expected errors in chemical analyses, which adequately offset one another in the ionic balance, and (b) waters without base exchange, that derive from silica terrains where more Na^+, K^+ and Mg^{2+} ions than Cl- ions dissolve by chemical breakdown of silicates.
If the ionic balance of water is not sufficiently in equilibrium, it is pointless calculating BEX and nothing is printed at the ultimate position of the watertype code in Fig.5.1. To check this, 1.5(Σk - Σa) is used as a measure of ionic imbalance in the manner indicated in Table 5.3.

TABLE 5.3. Subdivision of subtypes into 3 classes, based on the Base EXchange index BEX. Under ideal conditions (no other sources and sinks for Na^+, K^+ and Mg^{2+}), BEX constitutes an unambiguous cation exchange parameter. Where other sources or sinks of the typically marine cations are suspected, BEX requires another interpretation and can be neutrally called the marine cations surplus or deficit. Σk, Σa = sum of cations and anions, respectively

Class	BEX	INTERPRETATION		CONDITIONS
Code		If base exchange	if other process(es)	for BEX, in meq/L
		only process	relevant	
-	**negative**	**Salinized**	**Marine cations deficit**	**<-(0.5+0.02Cl) and <1.5(Σk-Σa)**
•	**zero**	**no base exchange**	**Marine cations equilibrium**	**>-(0.5+0.02Cl) and <+(0.5+0.02Cl) and #**
+	**positive**	**Freshened**	**Marine cations surplus**	**>+(0.5+0.02Cl) and >1.5(Σk-Σa)**

 # and abs(BEX + {(Σk-Σa)/abs(Σk-Σa)} (0.5+0.02Cl)) > 1.5 abs(Σk-Σa)

6 Mineral equilibria

Several excellent computer codes can be used to perform the tedious calculations needed to determine speciation of dissolved solutes and equilibrium of the solute with specific mineral phases. Just to mention a few: SOLMINEQ (Kharaka & Barnes, 1973), WATEQX (Van Gaans, 1988), and PHREEQC-2 (Parkhurst and Appelo, 1999).

These models are much more advanced than HGC but they need more data or more time/efforts to obtain results. HGC does not address so many minerals and is less accurate because of various simplications in its non-iterative calculations. Yet, comparison with for instance PHREEQC-2 indicates that HGC's results do not deviate substantially over a wide range of water qualities and temperatures.

Auxiliary tool #13 produces an export file to HyCA from where all selected samples are sluiced to the speciation and mineral equilibria calculations by PHREEQC-2.

The calculations in this chapter are valid up to an ionic strength of 2 (about 3 times ocean water). More saline waters need another approach (Van Gaans, 1988; Appelo and Postma, 2005).

6.1 Mineral equilibria calculations in general

The saturation index of water with a particular mineral M (SI_M) is generally defined as :

$$SI_M = \log (IAP / K_S) \tag{6.1}$$

where : IAP = Ion Activity Product of the mineral-water reaction in the sample [on a mol/kg water basis]; and K_S = the corresponding solubility product in pure water, adjusted to the temperature and pressure of the sample.

This means that water with an $SI_M = 0$, is in equilibrium with the mineral considered, with an $SI_M < 0$ it is undersaturated and will tend to dissolve the mineral when it is met, and with an $SI_M > 0$ it is oversaturated and may deposit the mineral.

Of course, the resulting SI's must be interpreted with great care, for at least four reasons : (a) analytical errors (especially pH and E_H) or sampling errors (introduction of O_2, escape of CO_2, H_2S and CH_4) may bias the calculation; (b) organic complexes are generally ignored or hard to incorporate; (c) minerals in nature are never pure whereas they are assumed so in the program (solid solutions can be dealt with, but require data that are frequently lacking); and (d) kinetics may be so slow that equilibrium will never be attained like in case of the chronic supersaturation of most groundwaters with respect to quartz.

Many groundwaters are close to equilibrium with calcite due to abundant calcitic and aragonitic shell fragments in most marine formations. Minor deviations (-0.3 to +0.3) occur due to errors in pH-measurement, and the cases of clear supersaturation (0.5-0.9) can be related to high concentrations of fulvic acids which complex Ca, and of Fe, PO_4 or Mg which inhibit crystallization. Waters with an SI_C in between -0.3 and -1.0 may reside in aquifers which still contain a large amount of carbonate rock. It was found empirically, that below -1.0 virtually no calcite traces are present any more (Edmunds & Kinniburgh, 1986; Stuyfzand et al., 1992b), with direct consequences for Ca^{2+}, alkalinity and pH in the water phase.

SI's for dolomite ($CaMg(CO_3)_2$) may attain significant supersaturation (1-2.5) without evidence of dolomite being actually present in the system. This is explained by a well known, extremely sluggish crystallization, in combination with dominant Mg sources from both ocean water and cation exchange processes.

Equilibrium and supersaturation with respect to siderite ($FeCO_3$) and rhodochrosite ($MnCO_3$) are also frequently observed but may likewise suffer from inaccuracies in pH measurement, unaccounted complexation of resp. Fe^{2+} and Mn^{2+} by fulvic acids, and from kinetic hindrances.

Barite ($BaSO_4$) frequently shows supersaturation (0.3-1.1) as well, indicating its relevance and the role of unaccounted complexation by fulvic acids and kinetic hindrances.
It can be concluded that mineral equilibria and especially mineral supersaturation should be interpreted with great care. Mineral supersaturation of water with respect to for instance calcite, dolomite, silicate, phosphate and iron minerals does by no means indicate that equilibrium will be attained by mineral deposition. This is of paramount importance, for instance in studying the risks on chemical clogging of membranes, injection wells and host aquifers (Stuyfzand & Raat, 2010).

6.2 The $Ca\text{-}CO_2\text{-}H_2O$ system

6.2.1 Calculation method, assumptions and TIC

HGC calculates the following parameters of the $Ca\text{-}CO_2\text{-}H_2O$ system, following the method presented by Stuyfzand (1987, 1989): Total Inorganic Carbon (TIC; mmol/L), Calcite Saturation Index (SI_C), pH (if needed), CO_2 and CO_3.
This method is less laborious and needs less data than PHREEQC-2, but is only slightly less accurate. For a comparison between both methods see Stuyfzand (1987,1989).
The pH is calculated only (pH_C) if lacking while the couple $CO_2\text{-}HCO_3$ or $HCO_3\text{-}CO_3$ has been analysed.
It is assumed that instead of HCO_3 the alkalinity is measured and expressed as HCO_3, and that instead of CO_2 the acidity ($=CO_2 + H^+ + Al^{3+} + Fe^{2+}$) is measured and expressed as CO_2. If CO_3 has been measured, then it derives from the fenolfthaleine alkalinity ($= 2CO_3^{2-} + OH^-$) and should be added to alkalinity as HCO3.
TIC is calculated as follows:

$$TIC = CO_2 + HCO_3^- + CO_3^{2-} \qquad [\text{mmol/L}] \qquad (6.2)$$

6.2.2 The calcite saturation index SI_C

The calcite saturation index is defined, conform Eq.6.1, as follows:

$$SI_C = \log \{ [Ca^{2+}] [CO_3^{2-}] / K_C \} \qquad (6.3)$$

Where: [X] = activity of ion X [mol/kg]; K_C = the solubility product of calcite in pure water, adjusted to the temperature and pressure of the sample.

Equilibrium of the $CO_2\text{-}H_2O$ system and saturation with respect to calcite are in general calculated in an iterative way (see e.g. PHREEQC-2; Parkhurst & Appelo, 1999). Here we use a simplified non-iterative way as described by Stuyfzand (1989c). The following equations are used:

$$(HCO_3^-)_T = Alk/\{1 + 2K_2/(\gamma_1^3\ 10^{-pH})\} \qquad (6.4)$$

$$(CO_3^{2-})_T = Alk\ K_2/(\gamma_1^3\ 10^{-pH} + 2K_2) \qquad (6.5)$$

$$(CO_2) = (\gamma_1\ (HCO_3^-)_T\ 10^{-pH}) / (10^{(i/10)}\ K_1) \qquad (6.6)$$

$$SI_c = 0.9865 \log \{[\gamma_1^8 (CO_3^{2-})_T\ (Ca_T^{2+} - CaSO_4^0)]/K_c\} - 3.4421\ 10^{-6}\ EC_{20} + 0.0012 \qquad (6.7)$$

where: $$CaSO_4^0 = \beta - \sqrt{(\beta^2 - \delta)} \qquad (6.8)$$

$$\beta = 0.5(Ca_T^{2+} + (SO_4^{2-})_T + [\gamma_1^8\ K_{CaSO4}]^{-1}) \qquad (6.9)$$
$$\delta = Ca_T^{2+}\ (SO_4^{2-})_T \qquad (6.10)$$

if $i \leq 0.5$ then: $$\log \gamma_1 = -0.5\ (\sqrt{i}/[1 + \sqrt{i}] - 0.3i) \qquad (6.11A)$$

if $0.5 < i \leq 2$ then: $\gamma_1 = 10^{-0.5\,(\sqrt{i}\,/\,[1\,+\,\sqrt{i}]\,-\,0.3i)} - 0.253\,i + 0.1233$ (6.11B)

$i = 0.5\,\Sigma\,\{\,m_C\,(z_C)^2\}$ [mol/kg H_2O] (6.12A)

If i is to be calculated from EC_{20} then:
if $EC_{20} \leq 700$ µS/cm: $i = 1.83\ 10^{-5}\ EC_{20}$ (6.12B)
else: $i = 1.42\ 10^{-5}\ EC_{20}$ (6.12C)

$$\log K_1 = -356.3094 - 0.06091964\,T + 21834.37/T + 126.8339\,\log T - 1684915/T^2 \qquad (6.13)$$

$$\log K_2 = -107.8871 - 0.03252849\,T + 5151.79/T + 38.92561\,\log T - 563713.9/T^2 \qquad (6.14)$$

$$\log K_C = -171.9065 - 0.077993\,T + 2839.319/T + 71.595\,\log T \qquad (6.15)$$

$$\log K_{CaSO4} = 0.998 + 0.0044\,T \qquad (6.16)$$

$$T = temp + 273.15 \qquad (6.17)$$

where: Alk = alkalinity as HCO_3^- [meq/L]; $(C)_T$ = measured total concentration of C [mmole/L]; K_1 = first dissociation constant of carbonic acid (H_2CO_3); K_2 = second dissociation constant of carbonic acid; K_c = solubility product of calcite; K_{CaSO4} = association constant of $CaSO_4^0$; Si_c = Saturation Index for calcite [-]; i = ionic strength [mol/kg H_2O]; γ_1 = activity coefficient for species with charge ± 1 [kg H_2O/mole]; EC_{20} = electrical conductivity at 20°C [µS/cm]; temp = temperature [°C]; T = temperature [K].

In case of aragonite instead of calcite, the calculated SI_C should be lowered by 0.2.
In case of a significant Mg-content of $CaCO_3$, however with Ca/Mg lower than in dolomite (where 1 on a molar basis), the calculated SI_C should be lowered by about 0.1 for each 0.1 molar fraction of Mg in $Ca_{(1-X)}Mg_XCO_3$ (Morse and Mackenzie, 1990).

6.3 The dolomite saturation index SI_D

The dolomite saturation index is defined, conform Eq.6.1, as follows:

$$SI_D = \log\{\,[Ca^{2+}]\,[Mg^{2+}]\,[CO_3^{2-}]^2\,/\,K_D\,\} \qquad (6.18)$$

where: K_D = the solubility product of dolomite in pure water, adjusted to the temperature and pressure of the sample.
Here we use again a simplified non-iterative way, using the following equations:

$$\log K_D = -17.09-9.436/(2.303*0.001987)*(1/298.15-1/T) \qquad (6.19)$$

$$SI_D = 0.9865\,\log\{[\gamma_1^{16}(CO_3^{2-})_T^2\,(Ca_T^{2+} - CaSO_4^0)\,(Mg_T^{2+} - MgSO_4^0)]/K_D\} - 3.4421\ 10^{-6}\ EC_{20} + 0.0012 \qquad (6.20)$$

where: $MgSO_4^0 = 1.175\,(Mg/Ca)\,CaSO_4^0$ (6.21)

In this approximation, only the complexes $CaSO_4^0$ and $MgSO_4^0$ are considered, in which the latter is calculated from the first by correcting for the slightly different formation constants via the factor 1.175 (= K_{MgSO40} / K_{CaSO40}).

6.4 The siderite saturation index SI_S

The siderite saturation index is defined, conform Eq.6.1, as follows:

$$SI_S = \log \{ [Fe^{2+}] [CO_3^{2-}] / K_S \} \qquad (6.22)$$

where: K_S = the solubility product of siderite in pure water, adjusted to the temperature and pressure of the sample.
Here we use again a simplified non-iterative way, using the following equations:

$$\log K_S = -10.89 - 2.48 / (2.3026 * 0.001987)\ (1/298.15 - 1/T) \qquad (6.23)$$

$$\begin{aligned} SI_S = {} & 0.9865 \log \{[\gamma_1^{8} (CO_3^{2-})_T\ (Fe_T^{2+} - FeSO_4^{0})]/K_S\} - \\ & 3.4421\ 10^{-6}\ EC_{20} + 0.0012 \end{aligned} \qquad (6.24)$$

where: $FeSO_4^0 = 0.891\ (Fe/Ca)\ CaSO_4^0$ (6.25)

In this approximation, only the complex $FeSO_4^0$ is considered, which is calculated from the $CaSO_4^0$ complex by correcting for the slightly different formation constants via the factor 0.891 (= K_{FeSO40} / K_{CaSO40}).

6.5 The rhodochrosite saturation index SI_R

The rhodochrosite saturation index is defined, conform Eq.6.1, as follows:

$$SI_R = \log \{ [Mn^{2+}] [CO_3^{2-}] / K_R \} \qquad (6.26)$$

where: K_R = the solubility product of rhodochrosite in pure water, adjusted to the temperature and pressure of the sample.
Here we use again a simplified non-iterative way, using the following equations:

$$\log K_R = -11.13 - 1.43 / (2.3026 * 0.001987)\ (1/298.15 - 1/T) \qquad (6.27)$$

$$\begin{aligned} SI_R = {} & 0.9865 \log \{[\gamma_1^{8} (CO_3^{2-})_T\ (Mn_T^{2+} - MnSO_4^{0})]/K_R\} - \\ & 3.4421\ 10^{-6}\ EC_{20} + 0.0012 \end{aligned} \qquad (6.28)$$

where: $MnSO_4^0 = 0.891\ (Mn/Ca)\ CaSO_4^0$ (6.29)

In this approximation, only the complex $MnSO_4^0$ is considered, which is calculated from the $CaSO_4^0$ complex by correcting for the slightly different formation constants via the factor 0.891 (= K_{MnSO40} / K_{CaSO40}).

6.6 The gypsum saturation index SI_G

The gypsum saturation index is defined, conform Eq.6.1, as follows:

$$SI_G = \log \{ [Ca^{2+}] [SO_4^{2-}] / K_G \} \qquad (6.30)$$

where: K_G = the solubility product of gypsum in pure water, adjusted to the temperature and pressure of the sample.
Here we use again a simplified non-iterative way, using the following equations:

$$\log K_G = 68.2401 - 3221.51/T - 25.0627 \log T \quad (6.31)$$

$$[Ca^{2+}] = \gamma_1{}^4(Ca_T - CaSO4^o) \quad (6.32)$$

$$[SO_4{}^{2-}] = \gamma_1{}^4(SO4_T - Ca_\Sigma SO4^o) \quad (6.33)$$

$$Ca_\Sigma SO4^o = \beta_\Sigma - \sqrt{}(\beta_\Sigma{}^2 - \delta_\Sigma) \quad (6.34)$$

$$\beta_\Sigma = 0.5(Ca_\Sigma{}^{2+} + (SO_4{}^{2-})_T + [\gamma_1{}^8\ K_{Ca\Sigma SO4o}]^{-1}) \quad (6.35)$$

$$\delta_\Sigma = Ca_\Sigma{}^{2+}\ (SO_4{}^{2-})_T \quad (6.36)$$

$$Ca_\Sigma{}^{2+} = Ca_T + Mg_T + Fe_T + Mn_T + Sr_T + 0.0226\ Na_T + 0.0404\ K_T \quad (6.37)$$

$$K_{Ca\Sigma SO4o} = 10^{2.31} \quad (6.38)$$

In this approach the only complexes which are taken into account, are those with SO_4. In addition, the association constants of $CaSO_4{}^o$ (logK = 2.30), $MgSO_4{}^o$ (logK = 2.37), $SrSO_4{}^o$ (logK = 2.29), $FeSO_4{}^o$ (logK = 2.25), $MnSO_4{}^o$ (logK = 2.25) are considered close enough to take an average value (Eq.6.33), and to add the individual cation concentrations forming the virtual Ca_Σ concentration (Eq.6.32). In the latter, the association constants of $NaSO_4{}^-$ (logK = 0.70) and $KSO_4{}^-$ (logK = 0.85) are scaled to logK of $CaSO4^o$, yielding resp. the factors 0.0226 and 0.0404.

6.7 The barite saturation index SI_B

The barite saturation index is defined, conform Eq.6.1, as follows:

$$SI_B = \log \{ [Ba^{2+}]\ [SO_4{}^{2-}] / K_B \} \quad (6.39)$$

where: K_B = the solubility product of barite in pure water, adjusted to the temperature and pressure of the sample.
Here we use again a simplified non-iterative way, using the following equations:

$$\log K_B = 136.035 - 7680.41/T - 48.595 \log T \quad (6.40)$$

$$[Ba^{2+}] = \gamma_1{}^4(Ba_T - BaSO4^o) \quad (6.41)$$

$$[SO_4{}^{2-}] = \gamma_1{}^4(SO4_T - Ca_\Sigma SO4^o) \quad (6.33)$$

where: $BaSO_4{}^0 = 2.512\ (Ba/Ca)\ CaSO_4{}^0$ (6.43)

In this approximation, the complex $BaSO_4{}^0$ is calculated from the $CaSO_4{}^0$ complex by correcting for the slightly different formation constants via the factor 2.512 (= K_{BaSO40} / K_{CaSO40}).

6.8 The fluorite saturation index SI_F

The fluorite saturation index is defined, conform Eq.6.1, as follows:

$$SI_F = \log \{ [Ca^{2+}]\ [F^-]^2 / K_F \} \quad (6.44)$$

where: K_F = the solubility product of fluorite in pure water, adjusted to the temperature and pressure of the sample.
Here we use again a simplified non-iterative way, using the following equations:

$$\log K_F = 66.348 - 4298.2/T - 25.271 \log T \tag{6.45}$$

$$[Ca^{2+}] = \gamma_1{}^4(Ca_T - CaSO4^o) \tag{6.32}$$

$$[F^-] = \gamma_1(F_T - MgF^+) \tag{6.46}$$

where: $$MgF^+ = \gamma_1{}^5(Mg_T\, F_T)\, K_{MgF} \tag{6.49}$$

$$\log K_{MgF} = 1.82 - 3.2\ / (2.3026 * 0.001987)\ (1/298.15 - 1/T) \tag{6.50}$$

By ignoring various complexes (like CaF^+ and NaF^0) and by ovrstimating MgF^+ a rather crude approximation is obtained.

7 Ratios

HGC calculates the following frequently used ratios: Cl/Br, Cl/Na, Ca/Mg, Ca/Sr, HCO3/Ca, HCO3/ΣA, Fe/Mn, COD_O/DOC, MONC (= 4–1.5 COD_O/DOC), SUVA (=UVA_{254}/DOC) and $^2H/^{18}O$.
Several of these ratio's can be calculated on either a mg/L or mol/L basis. The choice is to be indicated on row 8. COD can be with or without correction for contributions of inorganic species; also to be indicated on row 8 of 3-ALL or 5-ALLcor.

7.1 Chloride/bromide ratio: Cl/Br

The Cl/Br-ratio is frequently used to determine the origin of water or its salinity (Alcala & Custodio, 2005; Stuyfzand & Stuurman, 2008). HGC calculates the ratio on either a mg/L or mol/L basis. The conversion of mg/L into mol/L is by multiplication with 2.254.
Typical values of the Cl/Br-ratio, both on a mol/L and mg/L basis are given in Table 7.1. A better separation is obtained when plotting the Cl/Br-ratio against the Cl concentration (Fig.7.1).
Typical values of the Cl/Br-ratio on a mg/L basis, for the Netherlands are (Stuyfzand, 2007): Rhine River water and its infiltrates = 625-750, Meuse River water and its infiltrates = 410-570, coastal dune groundwater = 300, Rhine infiltrate with extreme HCO_3 concentrations (600-3000 mg/L) due to the passage of thick sludge deposits = 100-300, and polder water in greenhouse districts with inputs from methyl-bromide = 50-100.

TABLE 6.1. Typical values of the Cl/Br-ratio in various waters (deduced from data in Fig.8.3 which derives from Alcala & Custodio, 2005).

Cl / Br -ratio	**molar base**		**mg/L base**	
	min	**max**	**min**	**max**
ALCALA & CUSTODIO, 2005				
Agricultural plots with methyl-Br	200	500	89	222
High altitude/continental	220	550	98	244
Inland areas	300	650	133	288
Ocean water	651	659	289	292
Coastal groundwater	500	710	222	315
Leaching of garbage and solid waste	750	1000	333	444
Halides of volcanic origin	750	1100	333	488
Urban waste waters	900	1400	399	621
Coastal arid climate	700	1300	311	577
Leaching of gypsum + halite	1200	5400	532	2396
Leaching of halite	3500	6600	1553	2928

7.2 Ratio's: Cl/Na, Ca/Mg, Ca/Sr, Fe/Mn

The Cl/Na, Ca/Mg, Ca/Sr, Fe/Mn ratios are used to determine some of the hydrogeochemical processes acting on groundwater by water-rock interaction. HGC calculates these ratio's on either a mol/L or mg/L basis. The choice should be entered in the top yellow cells on row 8 of 3-ALL or 5-ALLcor.

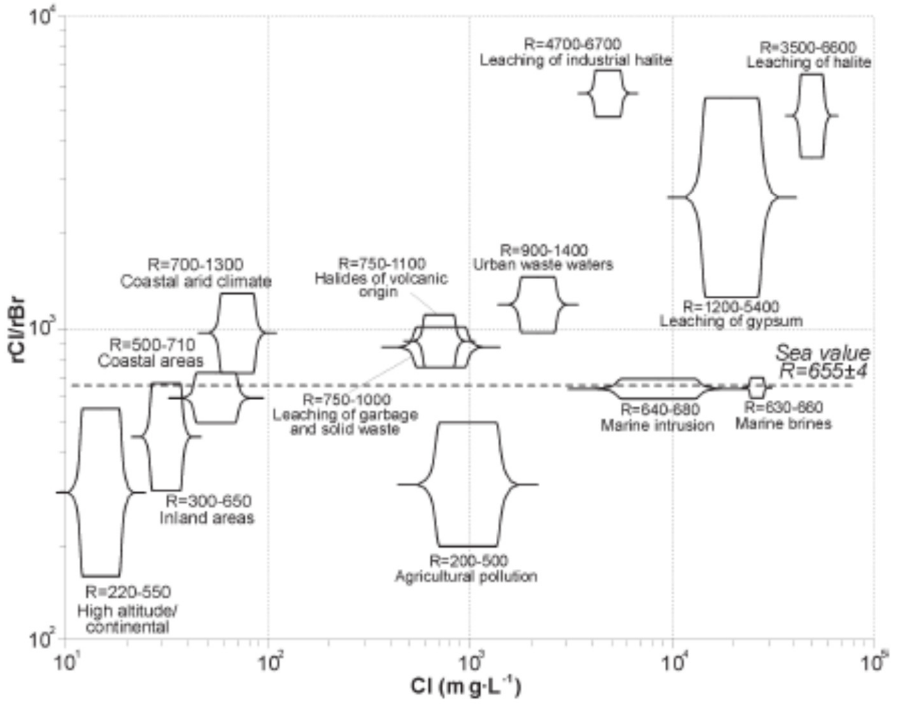


FIG. 7.1. Plot of the Cl/Br-ratio on a mol/L basis versus Cl (mg/L) for different types of salinity in various waters mainly in Spain and Canary Islands. After Alcala & Custodio, 2005.

7.3 The HCO_3/Ca, HCO3/(Ca+Mg) and HCO_3/ΣA ratio

The HCO_3/Ca ratio or HCO_3/(Ca+Mg) ratio (mol/L basis) is mainly used to determine some of the hydrogeochemical processes acting on groundwater by water-rock interaction. It may for instance indicate the main source of calcite dissolution: if 2 then by CO_2, if 1 then by strong acids from atmospheric inputs and/or pyrite oxidation. The choice between HCO_3/Ca or HCO_3/(Ca+Mg) ratio needs to be indicated on row 8 of 3-ALL or 5-ALLcor.
The HCO_3/ΣA ratio (meq/L basis) is mostly used to determine the origin of water or its source of salinization (Stuyfzand, 2010).

7.4 The COD_O/DOC ratio, MONC and SUVA

COD_O/DOC-ratio

The COD_O/DOC ratio is defined as the ratio of Chemical Oxygen Demand (COD) by dissolved organic substances over Dissolved Organic Carbon (DOC), on a mol/L basis. It therefore indicates the oxidizable fraction of dissolved total organic carbon. Usually COD is determined in the lab by the water's consumption of either $KMnO_4$ (in mg/L $KMnO_4$), or $K_2Cr_2O_7$ (in mg/L $K_2Cr_2O_7$). The determination of COD_O should be done on a 0.45 μm filtrated water sample, and be corrected for contributions of inorganic species, notably Fe^{2+} and NO_2^-

$$COD_O = COD - 0.143\ Fe^{2+} - 0.348\ NO_2^- \qquad (7.1)$$

where; COD_O = COD by organic substances [mg O_2/L]; COD = total COD including inorganic nonvolatile substances [mg O_2/L]; Fe^{2+} and NO_2 in mg/L.
Correction for NH_4, H_2S and CH_4 is not needed, because NH_4 is stable at low pH during determination, and H_2S and CH_4 volatilize during the analytical procedure.

Environmental water samples have been analyzed mostly, especially in the past, on $KMnO_4$-consumption. With 1 mg $KMnO_4$/L equivalent to 1/3.95 mg O_2/L and conversion into mol/L we obtain:

$$COD_O / DOC = (0.2531*KMnO_4/32) / (DOC/12) = 0.095\ KMnO_4 / DOC \qquad (7.2)$$

where: both $KMnO_4$ and DOC in mg/L.

In theory the maximum value of COD_O/DOC is 1, because 1 mmol DOC/L consumes not more than 1 mmol O_2/L ($O_2 + C \rightarrow CO_2$). DOC can be replaced by TOC provided also COD was measured in an unfiltrated water.

MONC

Vogel et al. (2000) defined the *Mean Oxidation Number of Carbon (MONC)* as follows:

$$MONC = 4 - 1.5\ COD_O / DOC \qquad (7.3)$$

where: COD in mg O_2/L; DOC in mg C/L.

The MONC value must always lie in the range [-4, +4]. Values outside this range are chemically impossible indicating a problem during COD or TOC analysis. MONC values may also be non-integer numbers, like phenol having a MOC value of -2/3. Aliphatic short-chain alcohols like methanol, ethanol, and propanol [all -2] are the most reduced organic species completely soluble in water. At the other end of the MONC scale, short-chain mono and dicarboxylic acids like formic [+2] and oxalic acid [+3] are found. Aqueous solutions usually exhibit values in the range [-2, +3]. Urea is an interesting compound as it is one of the few organic substances (if not the only one) having a MONC of +4.

SUVA

The *specific ultraviolet absorbance at 254 nm (SUVA)* is defined as follows:

$$SUVA = UVA_{254} / DOC \qquad (7.4)$$

where: UVA_{254} = ultraviolet extinction at 254 nm (E/m).

SUVA is both a measure of the aromaticity of dissolved organic compounds or humic content, and a control parameter for DOC data. Due to a higher stability of UVA_{254} measurements against analytical and coincidental failures compared to the DOC concentration, outliers of SUVA often indicate outliers of DOC. Normally SUVA increases downgradient, indicating a preferential removal of non-aromatic (non-humic), aliphatic components of DOC.

7.5 The $\delta^2H/\delta^{18}O$ ratio

This ratio of the most common stable isotopes of the water molecule indicates whether we are close to the global (GMWL) or local meteoric water line (LMWL), or whether evaporation has happened. In case of significant evaporation losses, the ratio will become higher (Fig.7.1).

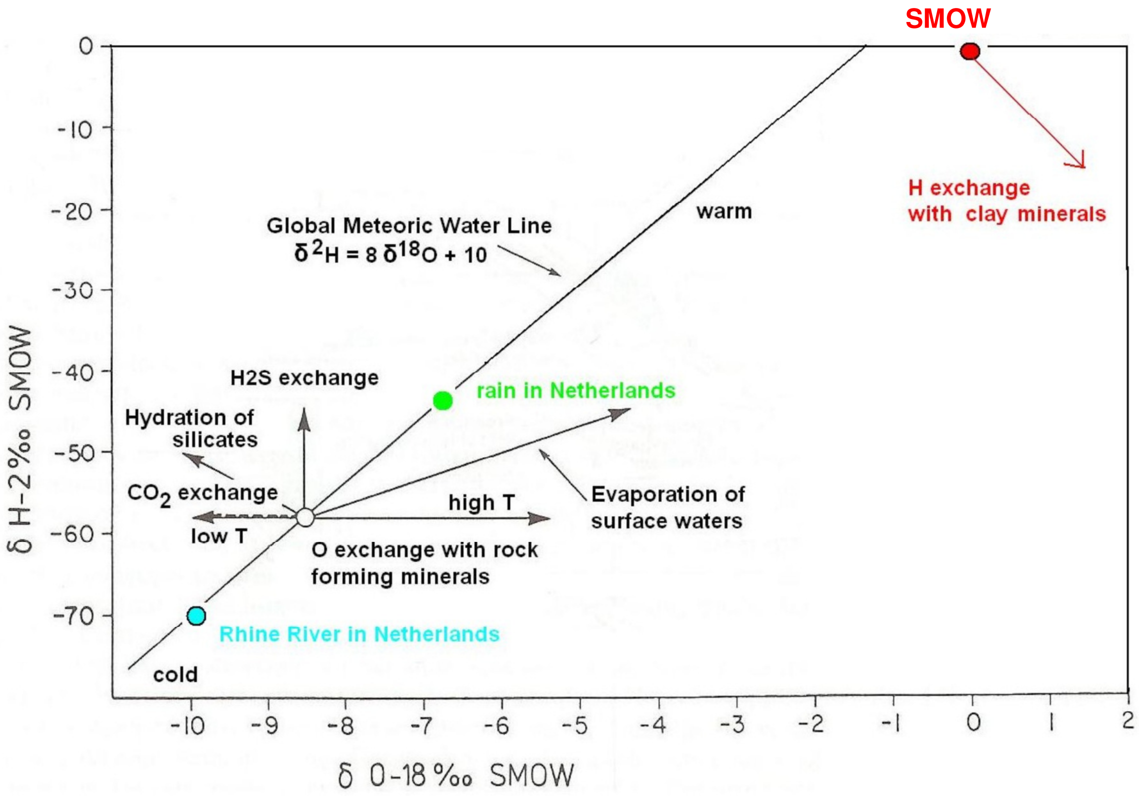


FIG. 7.1. Plot of deuterium versus ^{18}O for meteoric waters and SMOW, with indication of potential deviations from GMWL (Global Meteoric Water Line). The most frequent reason of deviation is evaporation of surface water.

8 Hydrochemical facies

8.1 Introduction

The Hydrochemical Systems Analysis (HSA) was introduced by Stuyfzand (1993, 1999) to provide tools for mapping groundwater quality in a way similar to mapping the geology, pedology or hydrological systems of an area (Table 8.1). The methodology presented here deviates slightly from the original HSA, in order to better address the mapping of man-made groundwater bodies in (semi)natural environments, in the larger variety of hydrogeochemical environments in the European Union today.
The methodology presented here results in the mapping of generic water types. For a further characterization of inorganic water quality a chemical classification of water types can be useful, like the one presented in Ch.5.

Definitions

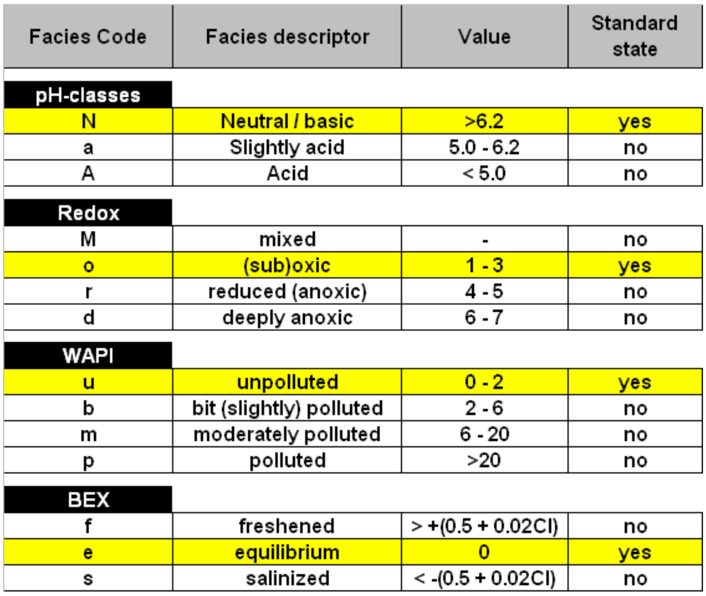
A *hydrochemical groundwater system*, or *hydrosome* (water body; ΰδωρ = water, σωμα = body), was defined by Stuyfzand (1993, 1999) as a coherent, 3-dimensional unit of groundwater with a specific origin. Examples are: coastal dune groundwater recharged by local rain water, intruded sea water, recharged river Rhine water and polder water. Within a given hydrosome the chemical composition of water varies in time and space, due to changes in recharge composition and in flow patterns, and due to chemical processes between water and its porous medium. Such variations in chemical character can be used to subdivide a hydrosome into characteristic zones or 'hydrochemical facies', a term introduced by Back (1960). A hydrosome is therefore composed of various facies units.
The *hydrochemical facies* is a mappable hydrochemical unit within a single water body, based on a broad spectrum of chemical analyses. It can be determined, for example, by the 4 indices in Table 8.2 that are individually calculated (Stuyfzand, 1993, 1999, 2006):

- the pH class or calcite saturation index SI_C (Stuyfzand, 1989a);
- redox index (based on the major redox sensitive species in water: O_2, NO_3, SO_4, Fe-total, Mn-total, NH_4 and CH_4);
- Base Exchange indeX (BEX); and
- a WAter Pollution Index (WAPI).

TABLE. 8.1. Comparison of the mapping of geological, pedological, hydrological and hydrochemical data, with a first grouping according to the genesis or origin, and subsequent subdivision on the basis of specific characteristics (modified after Stuyfzand, 1993).

	(SUB)SOIL		GROUNDWATER	
	GEOLOGY	**PEDOLOGY**	**HYDROLOGY**	**CHEMISTRY**
1. GENETICAL UNIT:	**Formation**	**Soil Type**	**Flow System**	**Water body (Hydrosome)**
Example	Westland Formation	Podzol	North Sea	Dune water
2. ZONES WITHIN:	**Sedimentary Facies**	**Horizon**	**Flow Branch**	**Hydrochemical Facies**
Examples	Younger dune sand	A0	1st order (local)	acid, polluted
	Older dune sand	A1	2nd order (subregional)	acid, (sub)oxic
	Beach sand	A2	3rd order (regional)	calcareous, anoxic
	Shallow marine sand	B	4th order (supraregional)	ditto, deep anoxic
	Lagoonal clay	B2		ditto, freshened
	Basal peat	C		

TABLE 8.2. The various hydrochemical facies descriptors and their code. If standard state, then the code is omitted for simplicity. After Stuyfzand (2006).



Facies Code	Facies descriptor	Value	Standard state
pH-classes			
N	Neutral / basic	>6.2	yes
a	Slightly acid	5.0 - 6.2	no
A	Acid	< 5.0	no
Redox			
M	mixed	-	no
o	(sub)oxic	1 - 3	yes
r	reduced (anoxic)	4 - 5	no
d	deeply anoxic	6 - 7	no
WAPI			
u	unpolluted	0 - 2	yes
b	bit (slightly) polluted	2 - 6	no
m	moderately polluted	6 - 20	no
p	polluted	>20	no
BEX			
f	freshened	> +(0.5 + 0.02Cl)	no
e	equilibrium	0	yes
s	salinized	< -(0.5 + 0.02Cl)	no

For mapping purposes each of these 4 chemical indices receives an appealing code. In order to reduce the number of codes on the map, those codes are not displayed which are considered ‘standard state’ of the hydrochemical system. The *standard state* is: neutral, (sub)oxic, unpolluted and without base exchange. So, a water sample with coding ‘df’ signifies that it is pH-neutral, deeply anoxic, unpolluted and freshened.

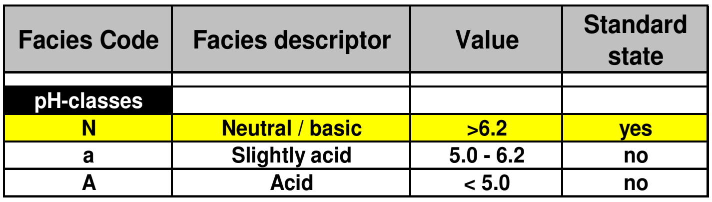
8.2 Acidity

One of the most important hydrochemical parameters is pH (Appelo & Postma, 2005). It determines a.o. the mobility of pollutants in infiltration water and the leaching rate of aquifer minerals. The classes discerned are listed in Table 8.3. They correspond with the general acid buffer sequence for multi-mineral soils (Ulrich et al., 1979).

TABLE 8.3. pH-classes as part of the hydrochemical facies determination. Top: the finest subdivision, with principal acid buffers and metal mobility. Below: the less differentiated subdivision.

pH-classes	Facies descriptor	Value	Principal acid buffer	Mobility metals
B	**Basic**	**>8.2**	**CaCO3, (H)CO3**	**Oxy-anions#**
N	**Neutral**	**6.2 - 8.2**	**CaCO3, HCO3**	**Oxy-anions#**
a	**Slightly acid**	**5.0 - 6.2**	**Al-silicates**	**Zn, Cd**
A	**Acid**	**4.2 - 5.0**	**Ca + Mg exchange**	**Cu, Ni**
H	**Strongly acid**	**<4.2**	**Al(OH)3, Fe(OH)3**	**Al, Cr, Fe, Pb**

 # like arsenate, molybdate, selenate, vanadate



Facies Code	Facies descriptor	Value	Standard state
pH-classes			
N	Neutral / basic	>6.2	yes
a	Slightly acid	5.0 - 6.2	no
A	Acid	< 5.0	no

8.3 Redox environment and redox index

The redox environment determines the mobility, dissolution, degradation and toxicity of inorganic and organic substances in or in contact with the water phase (Stumm & Morgan, 1981; Stuyfzand, 1998). The direct measurement of the redox potential E_H with electrodes runs into practical problems, however, and is handicapped by unreliable results (Lindberg & Runnells, 1984) or difficulties in quantitative thermodynamic interpretation (Peiffer et al., 1992). Unfortunately the same holds for its calculation from a single redox pair like Fe^{2+}/Fe^{3+} (Lindberg & Runnells, 1984; Barcelona et al.,1989).

Therefore Stuyfzand (1988, 1993) developed a semi-empirical redox index as based on all redox sensitive main components of water, i.e. O_2, NO_3^-, SO_4^{2-}, Fe, Mn, H_2S and CH_4. The system as followed by HGC is shown in Table 8.4.

Redox assessment systems similar to Table 8.4 were presented by a.o. McMahon & Chapelle (2008) and Chapelle et al. (2009). These use (somewhat) different and less practical criteria considering data availability and data precision, they do not deal with lacking data (which is frequently occurring), and do not define the ‘mixed’ redox classes shown in Table 8.4. Mixed redox classes are very common in water samples from pumping wells and even more from well fields, due to the inherent mixing of waters from different origins and redox environments, when long well screens are pumped (Mendizabal & Stuyfzand, 2011).

A mixed redox (M) results when antagonistic redox sensitive main components of water are present above a specific threshold concentration. For mapping purposes it can be useful to combine several redox levels into the redox clusters indicated in Table 8.4 (and 8.2).

Assessment of SO_4-reducing conditions

Water is classified as SO_4-reducing or methanogenic (redox level 6.7) if SO_4 = 0 or <MDL. With additional CH_4 data a distinction can be made between level 6 or 7 (Table 8.3). With higher SO_4 concentrations the assessment of SO_4-reducing conditions becomes difficult (Chapelle et al., 2009), however, especially when estimates of the original SO_4 concentrations $(SO_4)_0$ cannot be made (see below), or when information regarding H_2S smell during sampling, H_2S or H_2 data from laboratory measurements are lacking.

In case of watertypes M, O, P, T and S we assume by default that the measured SO_4 concentration equals $(SO_4)_0$. This excludes an SO_4-reducing environment for these watertypes. Only under particular conditions this assumption may be wrong, for instance in case of surface water in a swamp or close to the bottom where muds accumulated. A way to circumvent this, is to assign such waters (erroneously) watertype F but marking this for instance by giving F a red colour.

In case of groundwater the following approach is followed, with a different approximation for watertypes F and G.

In case of type F (infiltrated Fluvial water in the saturated zone) the concentration of $(SO_4)_0$ can normally be determined by using a known linear positive relation between SO_4 and Cl concentrations as observed in many Dutch surface waters (Stuyfzand, 1986):

For type F: $$(SO_4)_0 = a\,Cl + c \qquad (8.1)$$

Where: concentrations in mg/L; a, c = constants, for instance for Rhine River water a = 0.277 and c = 29.7 mg/L.

The values of a and b need to be entered in 3-Raw, cells GD7 and GD8 respectively.

In Eq.8.1 conservative behavior of Cl and SO_4 during and after infiltration is assumed for type F. Thereby, SO_4 mobilization by pyrite oxidation, SO_4 reduction and SO_4 mobilization by dissolution of gypsum are ignored. This conservative behavior of SO_4 is not always true, but in most cases it is so for type F. SO_4 reduction is normally manifested by a significant HCO_3 increase, and the presence of gypsum can be revealed by an SI_G approaching 0 or by anomalous values of ^{34}S or Sr. Gypsum may introduce an underestimate of the redox level, but can be ignored in many aquifers used for fresh water supply, as in the Netherlands.

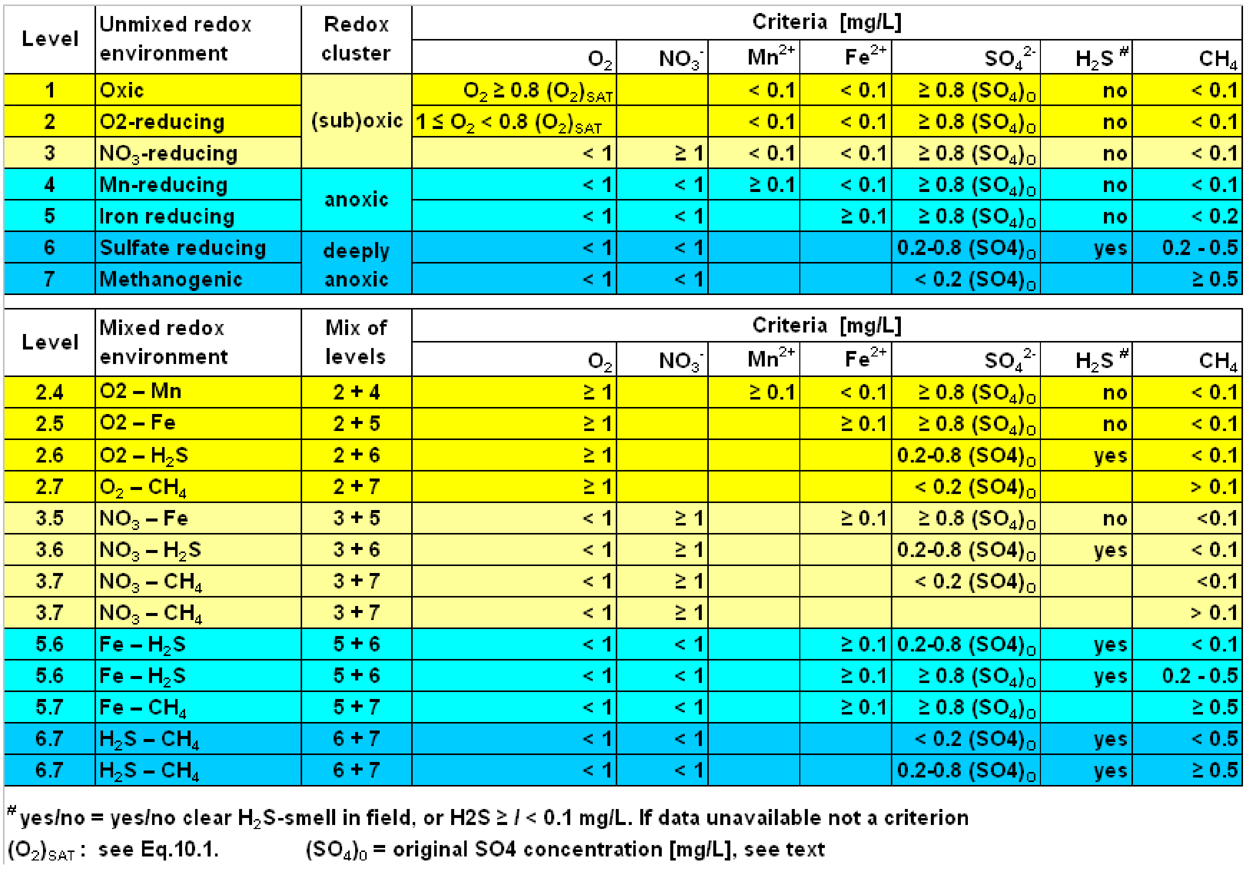
In case of type G (infiltrated local rain water in the saturated zone) the concentration of $(SO_4)_0$ can only be approximated, on the condition that SO_4 measured is < $SO4_C$ (sea salt corrected), by taking:

For type G, if $SO_4 < 0.14$ Cl: $$(SO_4)_0 = 0.14\ Cl + 30 \tag{8.2}$$

Where: 0.14 = SO_4/Cl ratio in SMOW [mg/L-basis]; all concentrations in mg/L.

The resulting estimate of $(SO_4)_0$ is in all cases on the conservative, i.e. low side, thus resulting in a bias yielding too few SO_4 reducing conditions. This applies in particular to groundwaters that show pyrite oxidation by either excessive fertilizer loads or declining water tables. In order to reduce this error, a second criterion was added for assigning SO_4 reduction, namely that methane should be 0.2–0.5 mg/L.

TABLE 8.3. Practical criteria for the determination of the redox index (slightly modified after Stuyfzand, 1988, 1993). Concentrations in mg/L.



Level	Unmixed redox environment	Redox cluster	Criteria [mg/L]						
			O_2	NO_3^-	Mn^{2+}	Fe^{2+}	SO_4^{2-}	H_2S #	CH_4
1	Oxic	(sub)oxic	$O_2 \geq 0.8\ (O_2)_{SAT}$		< 0.1	< 0.1	≥ 0.8 $(SO_4)_O$	no	< 0.1
2	O2-reducing		$1 \leq O_2 < 0.8\ (O_2)_{SAT}$		< 0.1	< 0.1	≥ 0.8 $(SO_4)_O$	no	< 0.1
3	NO_3-reducing		< 1	≥ 1	< 0.1	< 0.1	≥ 0.8 $(SO_4)_O$	no	< 0.1
4	Mn-reducing	anoxic	< 1	< 1	≥ 0.1	< 0.1	≥ 0.8 $(SO_4)_O$	no	< 0.1
5	Iron reducing		< 1	< 1		≥ 0.1	≥ 0.8 $(SO_4)_O$	no	< 0.2
6	Sulfate reducing	deeply anoxic	< 1	< 1			0.2-0.8 $(SO4)_O$	yes	0.2 - 0.5
7	Methanogenic		< 1	< 1			< 0.2 $(SO4)_O$		≥ 0.5

Level	Mixed redox environment	Mix of levels	Criteria [mg/L]						
			O_2	NO_3^-	Mn^{2+}	Fe^{2+}	SO_4^{2-}	H_2S #	CH_4
2.4	O2 – Mn	2 + 4	≥ 1		≥ 0.1	< 0.1	≥ 0.8 $(SO_4)_O$	no	< 0.1
2.5	O2 – Fe	2 + 5	≥ 1			≥ 0.1	≥ 0.8 $(SO_4)_O$	no	< 0.1
2.6	O2 – H_2S	2 + 6	≥ 1				0.2-0.8 $(SO4)_O$	yes	< 0.1
2.7	O_2 – CH_4	2 + 7	≥ 1				< 0.2 $(SO4)_O$		> 0.1
3.5	NO_3 – Fe	3 + 5	< 1	≥ 1		≥ 0.1	≥ 0.8 $(SO_4)_O$	no	<0.1
3.6	NO_3 – H_2S	3 + 6	< 1	≥ 1			0.2-0.8 $(SO4)_O$	yes	< 0.1
3.7	NO_3 – CH_4	3 + 7	< 1	≥ 1			< 0.2 $(SO4)_O$		<0.1
3.7	NO_3 – CH_4	3 + 7	< 1	≥ 1					> 0.1
5.6	Fe – H_2S	5 + 6	< 1	< 1		≥ 0.1	0.2-0.8 $(SO4)_O$	yes	< 0.1
5.6	Fe – H_2S	5 + 6	< 1	< 1		≥ 0.1	≥ 0.8 $(SO_4)_O$	yes	0.2 - 0.5
5.7	Fe – CH_4	5 + 7	< 1	< 1		≥ 0.1	≥ 0.8 $(SO_4)_O$		≥ 0.5
6.7	H_2S – CH_4	6 + 7	< 1	< 1			< 0.2 $(SO4)_O$	yes	< 0.5
6.7	H_2S – CH_4	6 + 7	< 1	< 1			0.2-0.8 $(SO4)_O$	yes	≥ 0.5

[#] yes/no = yes/no clear H_2S-smell in field, or H2S ≥ / < 0.1 mg/L. If data unavailable not a criterion

$(O_2)_{SAT}$: see Eq.10.1. $(SO_4)_0$ = original SO4 concentration [mg/L], see text

8.4 Water Pollution index WAPI

Aggregated quality parameters like pollution indices help to summarize a large amount of chemical and physical characteristics of water or soil, into a single number or figure which is understandable and informative to both layman and specialist. However, such a parameter or index normally addresses only one specific target (for instance the suitability of water for either consumption, irrigation or deep well injection) and very often it is valid for only one type of water (for instance either fresh surface water, groundwater or sea water). This explains why there are in fact so many indices in use (Stuyfzand, 1993; BKH, 1994).

8.4.1 Calculation and general aspects

The Water Pollution Index WAPI is determined on the basis of 10 water quality subindices, following the method developed by Stuyfzand & Lüers (2000) with minor modifications according to Stuyfzand (2006). The method is summarized in Table 8.4 and 8.5. The standard calculation is based on the simple average:

$$\text{WAPI} = (A + B + C + D + E + F + G + H + I + J) / 10 \tag{8.3}$$

In addition to WAPI, HGC also reports the individual score of each subindex (A-J). Most subindices consist of the unweighted mean of scores for related quality parameters, on the basis of the ratio of the measured value and the natural background (or target) value (NB) or maximum permissible concentration for drinking water (MPC). Their values are tabulated in Table 8.5.
In the Netherlands we use NBs according to LBB (1998), and MPCs according to WLB (2001), also valid in EU. The use of such ratio's is advantageous thanks to (a) their clear environmental significance, e.g. 3 meaning 3 times more polluted than natural background, and (b) the possibility to plot each subindex in a radar plot.
Subindices A-J cover the following water quality aspects: esthetics (A), acidity (B), oxidation or reduction capacity (C), nutrients (D), total salt content (E), inorganic micropollutants (F), organic micropollutants, pesticides excluded (G), pesticides (H), radioactivity (I) and microbiology (J).
WAPI can be easily adapted to embrace the available data on water quality and to relate to other (deviating) natural backgrounds.
The parameter B was squared, in order to obtain a range of scores comparable to the other 9 quality aspects. WAPI is based on total concentrations, because only these data are usually available. This means that there are no corrections of for instance heavy metals and PAHs for suspended solids or particulate organic carbon (POC).

TABLE 8.4. Determination of the Water Pollution Index WAPI by averaging quality aspects A – J (modified after Stuyfzand, 2002). Values >1 indicate that natural background levels are exceeded.
N.B.:If parameters are omitted, then the final division factor should decrease accordingly (C excluded). The natural background of each parameter equals its individual division factor.

WAPI = (A + B + C + D + E + F + G + H + I + J) / 10			Unit(s)
with:			
A =	Esthetics	(suspended solids + colour/20 + taste/2 + odour/2 + turbidity/4) / 5	#
B =	Acidity	$(\text{pH} - 7)^2$	-
C =	Oxidation or reduction capacity	| MOC | / 2.7 [me/L] with:	me/L
		MOC = $4O_2 + 5NO_3^- + 7SO_4^{2-} - 3NH_4^+ - Fe^{2+} - 2Mn^{2+} - 8CH_4$	mmol/L
D =	Nutrients (eutrophication potential)	(PO_4-P/0.02 + TIN/0.9) / 2	mg/L
E =	Total salt content	(Cl^-/12 + EC/350) / 2	##
F =	Inorg. micropollutants (Trace elements)	(As/5 + Ba/50 + Cd/0.05 + Cr/5 + Cu/3 + Hg/0.02 + Ni/9 + Pb/4 + Zn/9) / 9	ug/L
G =	Org. Micropollutants (excl. Pesticides)	(ΣBTEX + ΣLUMP + Σothers + ΣPAH + ΣVOCl)/5	ug/L
	ΣPAH =	(naf/0.1 + (ant+fen)/0.02 + (2fla+baa+chr+bkf+bap)/0.003 + (2bpe+ipy)/0.002) / 10	
	ΣLUMP =	(AOX/5 + EOX/0.5) / 2	
	ΣVOC =	(benz/0.2 + tolu/0.2 + chlo/0.01 + tri/0.01) / 4	
	Σothers =	(4-N-phenol + Tbfosf + Ibfura + Btzole) / 0.04	
H =	Pesticides	(atra + sima + diur + α-HCH + γHCH + HCB + bent) / 0.07	
I =	Radioactivity	(restβ/10 + ^{3}H/8) / 2	$
J =	Microbiology	([$Colc_{22}$]/10000 + [$Coli_{44}$]/10 + [Fs]/10) / 3	CFU/L

Units: # = resp. mg/L, mg/L Pt/Co, number of dilutions untill no taste, dito odour, FTE;
= resp. mg/L, uS/cm at 20oC $ = resp. mBq/L, TU

TABLE 8.5. Survey of parameters involved in the determination of the Water Pollution Index WAPI, with their natural backgrounds (division factor in WAPI), and various water quality standards applied in the Netherlands.

Quality Aspect	Quality Parameter	Unit	WAPI applied background	Target quality Groundwater LBB, 1998	Drinking Water Standard WLB, 2001	Artificial Recharge MACs Neths IB, 1993
A (esthetics)	Colour	mg/L Pt/Co	20		20	
	Odour	N*	2		2	
	Suspended solids	mg/L	0.5			0.5
	Taste	N*	2		2	
	Turbidity	FTE	1		1	
B (acidity)	pH	-	7		7-9.5	
C (ox/red cap)	CH4	mg/L	4.8			
	Fe(II)	mg/L	11		0.2 (tot)	
	Mn(II)	mg/L	1.1		0.05 (tot)	
	O2	mg/L	11		>2	
	SO4	mg/L	15	150	150	150
C + D	NH4	mg/L	0.4	2.6-12.9#	0.2	3.23
	NO2	mg/L	0.1		0.1	
	NO3	mg/L	2.5	24.8	50	24.8
D (nutrients)	total PO4	mg/L	0.06	1.22-9.2$	6.1 (tot)	1.22 (tot)
E (total salt)	Cl	mg/L	12	100	150	200
	Electr. Conductivity	uS/cm	350		1250	
F (IMPs)	As	µg/L	5	10	10	10
	Cd	µg/L	0.05	0.4	5	0.4
	Cr	µg/L	2	1	50	2
	Cu	µg/L	3	15	2 (plateau)	15
	Hg	µg/L	0.02	0.05	1	0.05
	Ni	µg/L	10	15	20	15
	Pb	µg/L	4	15	10	15
	Zn	µg/L	10	65	3	65
G (OMPs, BTEX)	benzene	µg/L	0.2	0.2	1 (sum BTEX)	
	toluene	µg/L	0.2	0.2	1 (sum BTEX)	
G (OMPs, Lump)	AOX	µg Cl/L	5			30
	EOX	µg Cl/L	0.5			
G (OMPs, others)	4-nitrofenol	µg/L	0.01			
	benzothiazole	µg/L	0.01			
	isobuthylfuranone	µg/L	0.01			
	tributylphosphate + -iso-	µg/L	0.01			
G (OMPs, PAHs)	anthracene	µg/L	0.02	0.02	0.05	0.02
	benzo(a)anthracene	µg/L	0.002	0.002	0.05	
	benzo(a)pyrene (Borneff)	µg/L	0.001	0.001	0.01	0.1(ΣB)
	benzo(ghi)perylene (Borneff)	µg/L	0.002	0.002	0.05	0.1(ΣB)
	benzo(k)fluoranthene (Borneff)	µg/L	0.001	0.001	0.05	0.1(ΣB)
	chrysene	µg/L	0.002	0.002	0.05	0.02
	fluoranthene (Borneff)	µg/L	0.005	0.005	0.05	0.1(ΣB)
	indeno(123cd)pyrene (Borneff)	µg/L	0.0004	0.0004	0.05	0.1(ΣB)
	naphtalene	µg/L	0.1	0.1		0.1
	phenanthrene	µg/L	0.02	0.02	0.05	0.02
G (OMPs, THMs)	chloroform	µg/L	0.1	0.01	25 (sum THM)	
G (OMPs, VOCs)	trichloroethene	µg/L	0.01	0.01	10 (+tetra)	0.5
H (Pesticides)	alpha-HCH	µg/L	0.01	0.01	0.1	0.05
	atrazine	µg/L	0.01	0.0075	0.1	0.1
	bentazone	µg/L	0.01		0.1	0.1
	gamma-HCH (lindane)	µg/L	0.01	0.00002	0.1	0.05
	hexachlorobenzene	µg/L	0.01	0.01	0.1	0.05
	simazine	µg/L	0.01		0.1	0.1
I (Radioactivity)	rest-beta	mBq/L	10		1	
	tritium	TU	8		840	
J (Microbiology)	colony counts 22`C	CFU/L	10000			
	faecal streptococs	CFU/L	10			
	thermotolerant coli counts	CFU/L	10			

WAPI-classes for mapping are suggested in Table 8.2. In HGC, parameters to calculate organic micropollutants, radioactivity and microbiology can be included or excluded, depending on data availability. There are 2 options to be indicated in cell HH8: option 1 is the full fledged version using all 10 subindices if available, and option 2 is the inorganic version based on subindices A-F. Therefore the simplified, inorganic WAPI ($WAPI_S$) becomes:

$$WAPI_S = (A + B + C + D + E + F) / 6 \qquad (8.4)$$

Lacking data are dealt with as indicated below.

8.4.2 WAPI-A: esthetics

Included are the content of suspended solids, turbidity, color, taste and odor, of which the latter 2 have not been included in HGC. The natural backgrounds of suspended solids (1 mg/L), turbidity (4 FTU), color (20 mg/L Pt/Co), taste (2 dilutions) and odor (2 dilutions) derive from MPCs for drinking water according to WLB (2001).

Missing parameters (empty cells) automatically reduce the division factor, which is max 5, in HGC max. 3 (data on taste and odour are lacking too frequently), and min. 1. If all 3 parameters are lacking, but the water type is either F, G or M then A is set at 0, because these waters are normally without suspended particles. If all 3 parameters are lacking, but the water type is not F, G or M, then A is set at not available (empty cell) resulting in not taking part in Eq.8.3 or 8.4.

8.4.3 WAPI-B: acidity

The pH is a measure for the degree of acidification on the one hand (pH <7) and alkalinization on the other (pH >7). pH-values of 6-8 are within the range of natural backgrounds (target values). A lower pH is regarded as undesirable in connection with the leaching of bases from the soil and the mobilization of heavy metals in soil and transport mains. A higher pH is undesirable as well because of (a) promoting the deposition of a.o. carbonates and phosphates, (b) its relation with algae blooms in surface water, and (c) enhancing the dissolution of silicate minerals and various metals.

8.4.4 WAPI-C: oxidation or reduction capacity

This capacity is calculated with MOC (Modified Oxidation Capacity) as indicated section 10.1.3 (see also Table 8.4). A positive value indicates oxidizing, a negative value reducing capacity.

A MOC-value in between +2.7 and -2.7 me/L is considered as the natural background because this agrees with respectively. (a) oxygen saturation at 11°C (11,3 mg O_2/L yielding 4*11,3/32 = 1,4 me/L) in absence of NO_3^- which is considered as largely anthropogenic, and with natural SO_4^{2-} ≤15 mg/L (dissolution of gypsum is thus considered as undesirable), and (b) modal concentration levels of natural NH_4^+, Fe^{2+}, Mn^{2+} and CH_4 in anoxic water which are easily removed by conventional water treatment systems.

Strongly positive MOC-values are associated with: (a) nitrate pollution for instance by agricultural activities, (b) sulfate pollution by for instance pyrite oxidation as a result of lowered water tables or nitrate pollution, (c) gypsum dissolution which is natural but quite problematic for drinking water supply, or (d) sea water admixing.

Strongly negative MOC-values normally result from deeply anoxic conditions by strong interaction of water with unstabilized organic matter and iron minerals. Deeply anoxic conditions can be purely natural and even advantageous for the (bio)degradation of various organic micropollutants and for immobilizing heavy metals (Schwarzenbach et al., 1993; Stuyfzand & Lüers, 1996; Appelo & Postma, 2005). The resulting, raised concentrations of NH_4^+, Fe^{2+}, Mn^{2+} and methane are, however, disadvantageous for (1) the air compartment (oxidation of CH_4, Fe^{2+} and Mn^{2+} leads to CO_2 emissions, and methane also contributes itself to the greenhouse effect), (2) the acidity of seepage water (oxidation of Fe^{2+} with precipitation of $Fe(OH)_3$ and oxidation of NH_4^+ ,both producing a lot of acidity), and (3) water supply companies (lots of purification sludges being produced).

8.4.5 WAPI-D: nutrients

Orthophosphate and TIN (= Total Inorganic Nitrogen = $NO_3^- + NO_2^- + NH_4^+$) are regarded as the most prominent and critical nutrients for plants and plankton, as other nutrients usually do not pose limits to growth (SiO_2 and K^+ sometimes excluded). The natural background for orthophosphate is set at 0.02 mg P/L, for TIN at 0.9 mg N/L. These values are close to the upper limits for mesotrafent environments (Vollenweider, 1976; Schindler, 1981). Higher values are undesirable due to increased risks on surface water eutrophication.

8.4.6 WAPI-E: total salt content

This parameter combines (a) the total amount of dissolved solids (TDS), for which Electrical Conductivity (EC) forms an excellent indicator, with (b) the share of sodium chloride in TDS, with Cl^- concentration as indicator. Natural backgrounds of resp. 350 µS/cm and 12 mg Cl^-/L are based on (i) natural backgrounds for Rhine River water and old groundwater in the Netherlands, and (ii) the adverse effects of higher levels. Higher levels may lead to (1) adverse effects on plants bound to fresh water ecosystems, sensitive crops, cattle and man, and (2) corrosion of water treatment plants and transport mains. Of course natural backgrounds can be both higher and lower, necessitating adjustments in the division factors if desirable.

8.4.7 WAPI-F: inorganic micropollutants

The heavy metals Cd, Cr, Cu, Hg, Ni, Pb and Zn as well as As belong to the environmentally hazardous inorganic micropollutants. Natural backgrounds of resp. 0.05, 5, 3, 0.02, 9, 4, 9 and 5 µg/L derive from those for surface water according to MILBOWA (1991). These values are, Cr excluded, considerably lower (more severe) than those for groundwater. The parameter F_{WAPI} can, if appropriate, be easily extended with for instance Al, B, Ba, F, Sb and Se (for which MPCs for drinking water are available).

8.4.8 WAPI-G: organic micropollutants, non-pesticide

Included are 4 groups of organic microcontaminants, which have been measured on a very frequent basis: 10 PAHs, 2 sum parameters (ΣLUMP; AOX and EOX), 4 VOlatile hydroCarbons (VOCs; benzene, toluene, chloroform and trichloroethene) and 4 other OMPs (4-nitro-fenol, benzothiazole, isobuthylfuranone and tributylphosfate). Natural backgrounds (0.001-3 µg/L; see division factor in Table 8.7) derive from those for surface water according to MILBOWA (1991) with several deviations when necessitated by MDLs of analysis and with few additions (AOX and Σothers).

G_{WAPI} can be assumed zero, when data on all OMPs are lacking, if water type = F, G or M, and if tritium <2 TU, because the soil or groundwater than normally infiltrated before 1954 (when the use of many OMPs still was rather limited). The parameter G_{WAPI} can be easily modified by regarding other OMPs, or be extended with more OMPs (within each of the 4 groups or with more groups).

8.4.9 WAPI-H: pesticides

This category includes 7 pesticides, amongst which 2 triazines (atrazine and simazine), 3 organochlorine pesticides (α-HCH, γHCH and HCB), a phenylureum-herbicide (diuron) and bentazone. The choice of these pesticides was determined by their availability in data records and their frequent presence.

Natural backgrounds (0.01 µg/L; see division factor in Table 8.7) derive from those for surface water according to MILBOWA (1991), with deviating higher values for atrazine, α- and γ-HCH due to their higher MDL of the current analysis.

For water of type F, G or M with tritium < 2 TU we can assume that H_{WAPI}, if measurements are lacking, equals zero, because the water in that case normally infiltrated prior to 1954 (when the use of pesticides mostly was at minimum). The parameter H_{WAPI} can be easily extended with other or more pesticides, pharmaceuticals, endocrine disruptors or personal care products.

8.4.10 WAPI-I: radioactivity

Rest-β and tritium have been taken together as a measure for radioactive contamination, because of their frequent measurement. Rest-β is equal to the total beta-radiation after subtracting a calculated contribution of natural ^{40}K (ca. 0.02 Bq/L per mg K^+/L) and after excluding tritium. Tritium (^3H) is a beta-radiating element as well and has a half life of 12.43 years. This heaviest isotope of hydrogen (part of the water molecule and therefore an excellent tracer) mainly originated from above ground nuclear tests (especially in the period 1954-1970), regular discharges by nuclear power plants, reactor incidents and cosmic radiation.

Natural backgrounds for Rest-β and tritium are estimated at respectively. 10 mBq/L and 8 TU, which are considerably lower than the target values posed by MILBOWA (1991). Tritium also constitutes, for groundwater, an indicator of potential contamination with modern, anthropogenic organic micropollutants. The parameter I_{WAPI} can be easily extended with for instance total alpha and gamma radiation.

8.4.11 WAPI-J: microbiology

The number of colony forming units (CFU) of cultivable cells on PCA at 22°C ($Colc_{22}$; also called colony counts), thermotolerant bacteria of the coli group ($Coli_{44}$) and faecal streptococci (Fs) have been taken together as a measure for bacteriological infection of water. One of the arguments to take these is the availability of their measurement. The natural backgrounds of respectively 10000, 10 and 10 CFU/L are based on data regarding surface water (RIWA, 1971-1996), dune infiltrate (Hoekstra, 1984) and Rhine bank filtrate (Van der Kooij, 1985). J_{WAPI} can be set standard at 0.3 in case of groundwater (type F or G), if there are no measurements at all, because groundwater does not contain any $Coli_{44}$ nor Fs, while showing a median $Colc_{22}$ of ca. 10^4 CFU/L (Hoekstra, 1984; Van der Kooij, 1985).

The parameter J_{WAPI} can be easily extended with sulfite reducing clostridia, aeromonas, giardia etc.

8.5 Radar plot of WAPI

The pollution index WAPI has the advantage that it (a) groups various quality parameters, and (b) relates analytical results to natural backgrounds or target values. This enables to directly plot each subindex into a radar plot, which is a standard plotting facility in spread sheets like Excel.

Such a radar plot is similar to the so-called 'AMOEBE'-approach (Ten Brink & Hosper, 1989; Baptist & Laane, 1996). AMOEBE is the acronym for 'Algemene Methode voor OEcosysteem BEoordeling' (General Method for Ecosystem Evaluation). It consists of a circular plot of many parameters with natural background or environmental target values forming the central circle. A kind of amoeba results when each parameter is plotted as a percentage of its natural background or environmental target value.

The principle of the WAPI radar plot is shown in Fig.8.1. It differs from the AMOEBE-approach by using a logarithmic scale, styling into radar instead of circles, and addressing other parameters.

→ In HGC go to worksheet #8 to define the samples to be shown on one Radar plot.

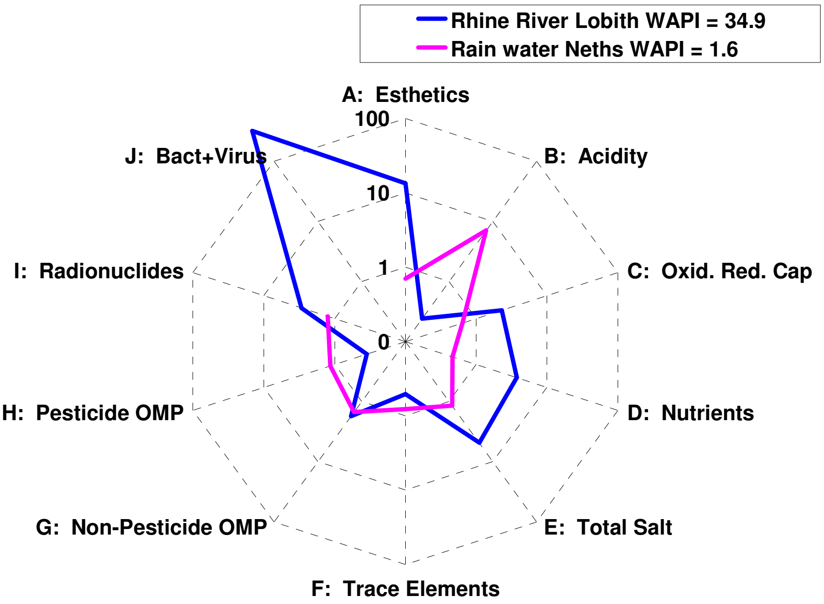


FIG. 8.1 Example of the WAPI radar plot (WAPI = WAter Pollution Index). 0, 1, 10, 100 = number of times the natural background value.

9 Quantification of processes contributing to TDS

9.1 Calculation of Total Dissolved Solids (TDS)

The concentration of total dissolved solids (TDS) in water is usually calculated by just summing up all the individual components excluding gases:

$$TDS = \Sigma \text{ major cations} + \Sigma \text{ major anions} + 10^{-(pH-3)} + \Sigma \text{ all trace elements (excl. gases)} + SiO_2 + 2.5\ DOC \quad [\text{mg/L}] \qquad (9.1)$$

Where: major cations = Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}, Al^{3+} [mg/L]
major anions = Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, NO_3^-, PO_4^{3-} [mg/L]

The factor 2.5 in Eq.9.1 is needed to convert organic C into organic material which is simplified as CH_2O. TDS can also be calculated from EC [uS/cm], if the concentrations of important ions are lacking, by taking:

$$TDS = 0.698\ EC \qquad (9.2A)$$

$$TDS = 4.059\ 10^{-21}\ EC^5 - 1.449\ 10^{-15}\ EC^4 + 1.832\ 10^{-10}\ EC^3 - 6.974\ 10^{-6}\ EC^2 + 0.8365\ EC - 0.5 \qquad (9.2B)$$

Eq.9.2A has normally been used when TDS is reported without analysis of all main constituents. Eq.9.1 is by far superior to Eqs.9.2A-B, and Eq.9.2B is superior to 9.2A. Eq.9.2A can be applied up to TDS 35,000 (SMOW), and 9.2B up to TDS 350,000 (brine).
→ Eq.9.1 is given in HGC in column HL, Eq.9.2B in column HX, in both sheet #3 and #5.
The residue on evaporation (RE) is about equal to TDS – 0.5 HCO_3 (all in mg/L).

9.2 Contribution of marine components (%TDS_M)

The total marine contribution to a water sample (%TDS_M) may derive from both atmospheric inputs and the admixing of standard mean ocean water (SMOW). Assuming no fractionation to take place during sea spray generation and Cl to be derived from ocean water only, yields the following quantification of %TDS_M:

All watertypes, P excluded:

$$\%TDS_M = 100\ (TDS / Cl)_{SMOW}\ (Cl / TDS)_W = 181.7\ (Cl / TDS)_W \qquad (9.3A)$$

if type = P and no BDC needed:

$$\%TDS_M = (TDS / Na)_{SMOW}\ (Na / TDS)_W = 326.5\ (Na / TDS)_W \qquad (9.3B)$$

where: TDS = Total Dissolved Solids [mg/L]; subscripts SMOW, W = in resp. standard mean ocean water and sampled water; Cl, Na = chloride, sodium [mg/L].

The factors 181.7 and 326.5 are based on TDS = 35984, Cl = 19805 and Na = 11020 mg/L for SMOW. In case a correction was needed for bird droppings or filtration bias, the information is found in sheet #5, otherwise in sheet #3. If TDS_W could not be determined using Eq.9.1 due to insufficient data, then it was calculated using Eq.9.2B.

9.3 Contribution of strong acids to TDS (%TDS_A)

Strong acids in natural waters mainly consist of H_2SO_4, HNO_3, HNO_2, HF and HCl. HCl is ignored in all waters except for rainwater, whereas organic acids are ignored in all waters. Thereby we obtain the following contribution of strong acids to TDS (%TDS_A):

All watertypes, P excluded:

$$\%TDS_A = 100\ (H + SO4_C + NO_3 + NO_2 + F)\ /\ TDS \qquad (9.4A)$$

if type = P and no BDC needed:

$$\%TDS_A = 100\ (H + SO4_C + NO_3 + NO_2 + F + Cl_C)\ /\ TDS \qquad (9.4B)$$

if type = P and BDC needed:

$$\%TDS_A = 100\ (H_{BDC} + SO4_{BDC,C} + NO3_{BDC} + NO2_{BDC} + F)\ /\ TDS_{BDC,FBC} \qquad (9.4C)$$

where: $H = 10^{3-pH}$ [mg/L]; X_{BDC} = Bird Dropping Corrected concentration of X [mg/L]; $SO4_{BDC,C} = SO4_{BDC} - 0.14\ Cl_{BDC}$ = SO_4 corrected for both bird droppings and a marine contribution [mg/L]; $Cl_C = Cl - Na / 0.5564$ = Cl corrected for a marine contribution, which is only possible to calculate when bird droppings do not play a role [mg/L]; $TDS_{BDC,FBC}$.= TDS corrected for bird droppings and filtration bias (sheet #5).
The values of Cl_C, $SO4_C$ and $SO4_{BDC,C}$ should be ≥0, otherwise their value is set at zero.

Note that rainwater composition is not corrected for bird droppings when PO_4-total ≤0.1 mg/L or PO4-ortho ≤0.05 mg/L (§ 3.4). The acids considered derive exclusively from atmospheric inputs in case of rainwater, and may have received additional inputs from oxidation reactions in case of the other types of water.

9.4 Contribution of bulk organic matter to TDS (%TDS_O)

The contribution of bulk organic matter to TDS is standard defined as follows:

if DOC measured:

$$\%TDS_O = 100\ (2.5\ DOC + NH_4 + NH4_{ALB} + PO_4)\ /\ TDS \qquad (9.5A)$$

Else if $KMnO_4$-consumption [mg/L] was measured:

$$\%TDS_O = 100\ (0.833\ KMnO_4 + NH_4 + NH4_{ALB} + PO_4)\ /\ TDS \qquad (9.5B)$$

In Eq.9.5B it is assumed that $KMnO_4$/DOC be 3 on average, which may need verification or alteration. Anyhow, the calculated organic matter contributions to TDS can be biased by other origins of NH_4 (especially industrial emissions contributing to rain water) and PO_4 (notably P-containing minerals contributing to groundwater).
In case a correction was needed for bird droppings or filtration bias, the information is found in sheet #5, otherwise in sheet #3.

9.5 Contribution of continental mineral dissolution to TDS (%TDS_C)

The remaining part of TDS is therefore mainly deriving from dissolution of continental minerals, like carbonates and silicates. Its contribution (%TDS_C) then becomes:

$$\%TDS_C = 100 - \%TDS_M - \%TDS_A - \%TDS_O \qquad (9.6)$$

In this calculation the dissolution of sulfate minerals like gypsum, the oxidation of sulfide minerals, the dissolution of phosphate and fluoride minerals are partly excluded, as the resulting concentrations of SO_4 and F are included in $\%TDS_A$, and the resulting concentration of PO_4 is included in $\%TDS_{BOM}$.
The dissolution of continental minerals can be subdivided into carbonates and silicates (quartz, opal, Al-silicates and gibbsite-like minerals). Their contribution ($\%TDS_{SIL}$ and $\%TDS_{CO3}$) can be roughly estimated by:

if $SI_C \geq -1$: $\%TDS_{SIL} = 100\ (SiO_2 + Al + \Sigma Litho_{TE})\ /\ TDS$ (9.7A)

if $SI_C < -1$: $\%TDS_{SIL} = 100\ (1.389\ SiO_2 + Al + \Sigma Litho_{TE})\ /\ TDS$ (9.7B)

$$\%TDS_{CO3} = \%TDS_C - \%TDS_{SIL} \qquad (9.8)$$

Where all concentrations in mg/L; $\Sigma Litho_{TE}$ = sum of all lithofile trace elements (see Eq.10.9).

In this approach we assume that in calcareous environments ($SI_C \geq -1$) silicate minerals other than quartz (SiO_2) or opal ($SiO_2.nH_2O$) hardly dissolve and therefore do not contribute. In decalcified environments ($SI_C < -1$) the dissolution of silicate minerals other than quartz or opal is accounted for by taking an average amount of Na+K+Ca+Mg (proportional to SiO_2; 1.389) as released by albite, orthoclase, anorthite and hornblende/augite respectively.
In case a correction was needed for bird droppings or filtration bias, the information is found in sheet #5, otherwise in sheet #3.

9.6 Contribution of SMOW to mixed sample (SMOW%)

If we know the Cl concentration of the fresh end-member in a sampled mixture (Cl_F) and if the saline end-member consists of SMOW, i.e. standard mean ocean water (Cl = 19805 mg/L), then the percentual contribution of SMOW (SMOW%) becomes:

$$SMOW\% = 100\ (Cl_{MIX} - Cl_F)\ /\ (19805 - Cl_F) \qquad (9.9)$$

where Cl_{MIX} = Cl concentration of sampled mixture [mg/L].

In case a correction was needed for bird droppings, the information is found in sheet #5, otherwise in sheet #3.

10 Various calculated parameters

10.1 Oxygen saturation and Oxidation Capacity

10.1.1 Oxygen saturation

The O2-saturation of water mainly depends on temperature and ionic strength. The latter can be represented by Cl-concentration, yielding the following expression (Peters, 1984):

$$(O_2)_{SAT} = 100\ O_2 / (14.594 - 0.4\ t + 0.0085\ t^2 - 97\ 10^{-6}\ t^3 - 10^{-5}\ (16.35 + 0.008\ t^2 - 5.32 / t)*Cl \qquad (10.1)$$

where: O_2 = oxygen concentration [mg/L]; t = temperature [oC]; Cl = chloride concentration [mg/L].

10.1.2 Oxidation capacity OXC

Postma et al. (1991) defined the oxidation capacity OXC [me/L] as follows:

$$OXC = 5\ NO_3 / 62 + 7\ SO_4 / 96.06 \qquad (10.2)$$

where: NO_3 and SO_4 in mmol/L.

10.1.3 Modified Oxidation Capacity (MOC)

The Modified Oxidation Capacity (MOC) is a new water quality parameter indicating the capacity of water to oxidize or reduce its environment. It was introduced by Stuyfzand & Lüers (2000), and appeared earlier (Stuyfzand, 1998b) in a more operational form. It is defined in its most elaborate form as:

$$MOC = 4\ O_2 + 5\ NO_3^- + 7\ SO_4^{2-} - 3\ NH_4^+ - Fe^{2+} - 2\ Mn^{2+} - 8\ CH_4 - 4\ DOC_{OX} \qquad (10.3A)$$

with: MOC in milli-electrons/L [me/L]; DOC_{OX} = oxidizable DOC; all concentrations in mmol/L.

In fact the total electron transfer is added up, resulting from the reduction of O_2 to H_2O, NO_3^- to N_2 and SO_4^{2-} to H_2S, and from the oxidation of NH_4^+ to NO_3^-, Fe^{2+} to $Fe(OH)_3$, Mn^{2+} to MnO_2 and CH_4 to CO_2.
A positive value indicates oxidation capacity, and a negative value reduction capacity. The factor -3 for ammonium is based on the fact that NH_4^+ oxidation to NO_3^- (-8 me/L) leads to NO_3^- which is capable of reducing other substances (+5 me/L). The oxidation by O_2, of 1 mmole of pyrite (FeS_2 to $Fe(OH)_3$) and 1 mmole of organic matter (CH_2O to CO_2) lowers MOC by resp. 1 and 4 me/L. See also section ??

Most problematic of all parameters is DOC_{OX} which is rarely known. Therefore a variant of Eq.9.3A is defined as follows:

$$MOC- = 4\ O_2 + 5\ NO_3^- + 7\ SO_4^{2-} - 3\ NH_4^+ - Fe^{2+} - 2\ Mn^{2+} - 8\ CH_4 \qquad (10.3B)$$

10.2 Sum parameters RE, TIN, Total hardness, TE groups

The following sum parameters are calculated: Residue on Evaporation at 180°C (RE; mg/kg), Total Inorganic Nitrogen ions (TIN; umol/L), Total hardness of water ($TotH_C$; mmol/L), and various trace element (TE) classes.

$$RE = 0.69778\ EC \qquad (10.4A)$$

$$RE = 1.805\ Cl \qquad (10.4B)$$

$$RE = TDS - HCO_3/2 \qquad (10.4C)$$

where: EC in uS/cm at 20°C, and Cl and HCO_3 in mg/kg.

$$TIN = NO_3^- + NO_2^- + NH_4^+ \quad [umol/L] \qquad (10.5)$$

$$TotH_C = Ca^{2+} + Mg^{2+} + Sr^{2+} \quad [mmol/L] \qquad (10.6)$$

Trace elements have been grouped according to Goldschmidt (see for instance White, 1998; Wedepohl, 1978), with a modification by Stuyfzand (1993) by introducing hydrophilic elements (see also Table 1.2), as follows:

$$\Sigma\ Chalco_{TE} = (Ag + As + Bi + Cd + Cu + Ga + Ge + Hg + In + Pb + Po + Sb + Se + Sn + Te + Tl + Zn) \qquad (10.7)$$

$$\Sigma\ Hydro_{TE} = (B + Br + I) \qquad (10.8)$$

$$\Sigma\ Litho_{TE} = (B + Ba + Be + Cr + Cs + Hf + Li + Nb + Rb + Sr + Ta + Th + U + V + W + Zr) + \Sigma\ REE \qquad (10.9)$$

$$\Sigma\ REE = \Sigma\ Lanth + Sc + Y \qquad (10.10)$$

$$\Sigma\ Lanth = (La + Ce + Pr + Nd + Pm + Sm + Eu + Gd + Tb + Dy + Ho + Er + Tm + Yb + Lu) \qquad (10.11)$$

$$\Sigma\ Sidero_{TE} = (Au + Co + Ir + Mo + Ni + Os + Pd + Pt + Re + Rh + Ru) \qquad (10.12)$$

In HGC the total concentrations are given of the chalcophilic (Eq.10.7), lithophilic (Eq.10.9), Rare Earth Elements (REE; Eq.10.10) and siderophilic elements (Eq.10.12).

10.3 Sodium Adsorption Ratio (SAR)

The Sodium Adsorption Ratio (SAR) is a frequently used parameter to predict the degree to which irrigation water tends to provoke cation exchange reactions in the soil, notably the exchange of Ca^{2+} and Mg^{2+} for Na^+. In the same way this also holds for artificial recharge or river bank infiltration during their initial phase, during and directly after displacement of the native groundwater. SAR is defined as follows:

$$SAR = Na^+/\sqrt{(Ca^{2+} + Mg^{2+})} \qquad (10.13)$$

with: concentrations in mmol/L (originally in meq/L but then dividing both Ca^{2+} and Mg^{2+} by 2; turns out to be the same).

Most critical is, in general, not the SAR-value of the influent but the SAR-value of the native groundwater (Olsthoorn, 1982). The SAR-values of the influent normally are low enough to be on the safe side (SAR < 6 with EC20 of 400-1000 μS/cm). The SAR-values of the native groundwater are more critical, especially when this is brackish. In case of waters with EC20 of 2000-5000 μS/cm SAR should be < 3 to be on the safe side.
With higher SAR-values there is danger of clay swelling and dispersion, which may clog the aquifer and result in a poor soil structure.
It is useful to plot SAR against Electrical Conductivity. See also Scheuerman & Bergersen (1990).

Appelo & Postma (2005) define the Exchangeable Sodium Ratio (ESR) as follows:

$$ESR = \beta_{Na} /(1 - \beta_{Na}) \approx K^{G}_{Na\backslash Ca} [Na^{+}] / \sqrt{([Ca^{2+}] + [Mg^{2+}])} \qquad (10.14)$$

Where:
β_{Na} = fraction of exchangeable Na in the cation exchange complex, on a meq/kg basis; $K^{G}_{Na\backslash Ca}$ = Gapon exchange constant; [X] = activity of X [mol/L]
The following relation between ESR and SAR is obtained when we assume $K^{G}_{Na\backslash Ca} = 0.5$, $K^{G}_{Na\backslash Ca} = K^{G}_{Na\backslash Mg}$, Na+Ca+Mg = the cation exchange complex, and activities equal concentrations, and when we combine Eq.8 with Eq. 8. while taking care of the different units (ESR mol/L, SAR mmol/L):

$$ESR = 0.0158\ SAR \qquad (10.15)$$

The critical ESR = 0.15, is reached when SAR = 10 for fresh water (ionic strength <0.015). Higher values raise the risk on clay swelling. This may lead to a poor soil structure and reduction of soil permeability, or to the mobilization of clay minerals that may clog the aquifer at some distance downgradient.

10.4 Strontium maturity index (SMI)

An indicator of downgradient evolutionary trends is the strontium maturity index (SMI). This index is defined as follows:

$$SMI = (Sr\#_M – Sr\#_0)/Sr\#_0] / [(Ca\#_M + Mg\#_M – Ca\#_0 – Mg\#_0)/(Ca\#_0+Mg\#_0)] \qquad (10.16)$$

where: $X\#_M$ = measured concentration of X corrected for sea water contribution [meq/L]; $X\#_0$ = minimum concentration of X in hydrosome, corrected for sea water contribution [meq/L].

SMI normally increases in a downgradient direction because strontium (Sr^{2+}) in carbonate rocks forms with initial formation and not from consecutive precipitation processes occurring later, i.e it does not form in re-precipitated calcite. Therefore, a comparison of Sr^{2+} to (Ca^{2+}+Mg^{2+}) contents can be a useful tool to groundwater maturity from which relative dating (or residence time) can be inferred (Tulipano et al. 1990; Emblanch et al. 2005).

10.5 Wirdum Ion Ratio (WIR)

Van Wirdum (1980) defined the Wirdum Ion Ratio (WIR) as follows:

$$WIR = 100^{*}Ca^{2+}/(Ca^{2+} + Cl^{-}) \qquad [\%] \qquad (10.17)$$

With: Ca^{2+} and Cl^{-} in mmol/L.

A high value is often characteristic for lithotrophic water (for instance fresh groundwater that dissolved much calcite), and a low value for thalassocline water (for instance ocean water). WIR is a frequently used parameter in ecohydrological research in the Netherlands, especially in combination with EC in a binary plot.
Detailed backgrounds are given by Van Wirdum (1980).
k

10.6 Eutrophication Potential Index (EPI)

A Water Quality Index (WQI) for hydro-ecological purposes may be exclusively based on the concentration of orthophosphate, which is considered as one of the most critical eutrophying nutrients for moist or wet ecosystems (Vollenweider, 1976; Schindler, 1981). Nitrogen ions (mainly NO_3^- and NH_4^+) are considered less critical, as a deficit can be made up through N_2-fixation by blue-green algae, cyano-bacteria or symbiotic bacteria. Hence, a simple division into 8 mappable phosphate classes may be employed as an index to denote eutrophication hazards (Table 10.??).
It should be realized, however, that low PO_4 levels do not necessarily indicate a low trophic status of the system, either because this means that all dissolved phosphate had been taken up by algae during a bloom period, or because high flow velocities may still result in a high nutrient load (Vollenweider, 1976; Van Dijk, 1984).
On the other hand high phosphate concentrations may not be synonymous to hypertrophic conditions, for instance when groundwater remains beyond the reach of the rooting system, or when other environmental conditions like temperature, pH or E_H are unfavourable to growth.
An important complication, accounted for in the Eutrophication Potential Index (EPI) given below, is that when the N/P ratio on a molar basis sinks below 30 (Lit), growth becomes limited by nitrogen:

$$\text{If } TIN / (PO_4 / 94.97) < 30 \quad \text{then:} \quad EPI = 4.5 + 0.721\ LN(94.97\ TIN / 30) \qquad (10.18)$$

$$\text{else:} \quad EPI = 4.5 + 0.721\ LN(PO_4)$$

where: TIN = Total Ionic Nitrogen, see Eq.10.5 [mmol/L], PO_4 [mg/L].
The term 94.97 TIN / 30 is the amount of PO_4 [mmol/L] matching a 30 times higher TIN content. When the condition TIN / (PO_4 / 94.97) < 30 is fulfilled, then the cell with the resulting EPI is automatically coloured in turquoise, indicating that N is growth limiting.

TABLE 10.1 Phosphate as a water quality index denoting eutrophication hazards (modified after Stuyfzand, 1993). EPI = Eutrophication Potential Index

class			PO_4^{3-} as:		
no	**EPI**	**name**	**mg PO_4^{3-}/l**	**mg PO_4–P/l**	**µmol P/l**
0	0 - 0.5	atrophic	< 0.004	< 0.001	< 0.04
1	0.5 - 1.5	oligotrophic	0.004 – 0.016	0.001 – 0.005	0.04 – 0.16
2	1.5 - 2.5	mesotrophic	0.016 – 0.064	0.005 – 0.020	0.16 – 0.66
3	2.5 - 3.5	slightly eutrophic	0.064 – 0.25	0.020 – 0.082	0.66 – 2.63
4	3.5 - 4.5	eutrophic	0.25 – 1.0	0.082 – 0.33	2.63 – 10.5
5	4.5 - 5.5	strongly eutrophic	1.0 – 4	0.33 – 1.31	10.5 – 42.1
6	5.5 - 6.5	hypertrophic	4 – 16	1.31 – 5.23	42.1 – 168
7	6.5 - 7.5	strongly hypertrophic	16 – 64	5.23 – 20.9	168 – 674
8	>7.5	extremely hypertrophic	> 64	> 20.9	> 674

10.7 Water density

Water density mainly depends on temperature and total dissolved solids or EC. There is also a strong pressure dependency, but that is of far less importance in hydrological research as long as the pressure increase with depth follows the hydrostatic pressure gradient. The following equations relate density (ρ in kg/L) to EC [μS/cm at 20°C] and temperature t [°C] at 1 atmosphere pressure:

$$\rho_{EC20,t} = \rho_{EC20,\,t=20}\ \rho_{EC20=0,t=t}\ /\ \rho_{EC20=0,t=20} \qquad [kg/L] \qquad (10.19)$$

It is hereby assumed that the salinity (represented by EC as derived from observations at 20°C) has the largest effect and that the temperature effect remains equal over the whole salinity range (0-225,000 uS/cm).

If EC ≤ 100,000 uS/cm and temperature t = 0-100 °C: (10.20A)

$$\rho = 0.99853767273053*EXP(5.26\ 10^{-7}*EC) * \{1.2899013\ 10^{-12}\ t^5 - 4.4880937\ 10^{-10}\ t^4 + 6.8770939\ 10^{-8}\ t^3 - 8.4536052\ 10^{-6}\ t^2 + 6.2537546\ 10^{-5}\ t + 0.99987881\}/0.99854$$

If EC > 100,000 uS/cm and temperature t = 0-100 °C: (10.20B)

$$\rho = [0.99853767273053*EXP(5.26*10^{-7}*EC) + 0.0001399*EXP(0.000028*EC)] * \{1.2899013\ 10^{-12}\ t^5 - 4.4880937\ 10^{-10}\ t^4 + 6.8770939\ 10^{-8}\ t^3 - 8.4536052\ 10^{-6}\ t^2 + 6.2537546\ 10^{-5}\ t + 0.99987881\}/0.99854$$

where: $EXP(X) = e^X$

The temperature effect is fitted to data in Handbook of Chemistry and Physics, and the EC effect is fitted to data supplied by Vincent Post (see Post, 2011) and to data in the above mentioned handbook as well.
The mean error, defined as the average of 100 abs($\rho_{CALC} - \rho_{MEAS}$)/ ρ_{MEAS} was for 157 samples only 0.03%, comparable to the much more complicated and data hungry method proposed by Post (2011).

→ In HGC one may choose either the preferred, measured EC or the calculated EC. If temperature was not measured/entered, then a temperature of 11°C is assumed.

10.8 Water viscosity

The dynamic viscosity of water (μ in Pa s = kg m^{-1} s^{-1}) is related to the kinematic viscosity of water (v) as follows:

$$\mu = v\ \rho \qquad (10.21)$$

The dynamic viscosity ($\mu_{EC20,t}$) as a function of EC (EC20 in uS/cm at reference temp = 20°C) and temperature (t in °C) is calculated as follows by fitting data in Handbook of Chemistry and Physics:

$$\mu_{EC20,t} = \mu_{EC20=0,\,t}\ \mu_{EC20,t=20}\ /\ \mu_{EC20=0,t=20} \qquad [Pa\ s] \qquad (10.22)$$

where: $\mu_{EC20=0,t}$ = dynamic viscosity [Pa s = kg m^{-1} s^{-1}] as a function of t, at EC = 0 μS/cm;
$\mu_{EC20,t=20}$ = dynamic viscosity [Pa s] as a function of EC, at 20°C;

$\mu_{EC20=0,t=20}$ = 1.002 = dynamic viscosity [Pa s] at EC = 0 and t = 20°C.

It is hereby assumed that the temperature has the largest effect and that the salinity effect (salinity represented by EC) as derived from observations at 20°C remains equal over the whole temperature range (0-100°C).

if EC ≤ 60000:

$$\mu_{EC20,t} = 0.001\ [-1.095\ 10^{-7}\ t^4 + 2.536\ 10^{-5}\ t^3 - 1.788\ 10^{-3}\ t^2 + 0.0141\ t + 43.902]\ (510\ /\ (t+43.1))^{1.5}\ (1.003 + 1.16735\ 10^{-6}\ EC)/1.003 \qquad (10.23A)$$

if EC > 60000:

$$\mu_{EC20,t} = 0.001\ [-1.095\ 10^{-7}\ t^4 + 2.536\ 10^{-5}\ t^3 - 1.788\ 10^{-3}\ t^2 + 0.0141\ t + 43.902)](510\ /\ (t+43.1))^{1.5}\ \{1.003 + 1.16735\ 10^{-6}\ EC + 6.26881\ 10^{-27}\ EC^{4.859571}\}/1.003 \qquad (10.23B$$

where: $\mu_{EC20=0,t}$ = dynamic viscosity [Pa s = kg m^{-1} s^{-1}] as a function of t, at EC = 0 μS/cm;
μ_{EC} = dynamic viscosity [Pa s] as a function of EC, at 20°C;
t = temperature [°C];
EC = Electrical Conductivity [μS/cm at 20°C).
1.003 = dynamic viscosity [Pa s] at 20°C and EC = 100 μS/cm (calculated using Eq.6)

10.9 Salinity correction of $\delta^{18}O$ analytical data

The conventional analytical procedure for ^{18}O in aqueous solutions (via CO_2 equilibration) yields $\delta^{18}O$ values on an activity scale rather than a value for the isotope concentration (Sofer & Gat, 1972). This is not the case for ^2H, so that a conversion of high salinity $\delta^{18}O$ values is needed. Sofer & Gat (1972) recommend the following conversion between the two scales in natural chloridic solutions containing Mg, Ca and K:

$$\delta^{18}O_C = 1.11\ Mg + 0.47\ Ca - 0.16\ K)\ (10^3 + \delta^{18}O_M)\ 10^3 + \delta^{18}O_M \qquad (10.24)$$

Where: $\delta^{18}O_C$, $\delta^{18}O_M$ = corrected and measured $\delta^{18}O$ values, respectively (‰ SMOW); concentrations of Mg, Ca and K in mol/kg H_2O.

11 Normalization of analytical data

Principles
Under construction.

Norm exceedance
Under construction.

Spider plot
See §2.5, Fig.2.2

WAPI Radar plot
See §8.5, Fig.8.1

12 Complexation of Ba, Cd, Co, Cu, Ni, Pb and Zn in fresh water

See: Stuyfzand, P.J. & F. Lüers 1997

Under construction.

13 References

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