

A new hydrochemical classification of water types

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ABSTRACT A water type is determined on the basis of subsequently the Cl-content, alkalinity, the most important cation and anion and a new parameter, [Na + K + Mg]-corrected for sea salt. The most important cation and anion are selected on preponderance in the ion balance, not by itself which is tradition, but including the support of geohydrochemical family members.

The new system results in easier identification of hydrogeochemical processes, like cation exchange, acidification and leaching of manure, in a universal applicability and in an easy handling, with options to further differentiate or associate. Two examples of application to The Netherlands are discussed and a listing of a computerprogram in FORTRAN-77 is included.

INTRODUCTION

The ten different hydrochemical classification systems quoted in a textbook by Matthes (1982), constitute only the top of an iceberg. Are there more inventors than adherents? Apparently, each system lacks a subdivision, which is subtle (diagnostic) and logical enough to satisfy a large group of users.

The method proposed here, exhibits many advantages and new criteria for subdivision. It evolved gradually from a system specific for groundwater in coastal, calcareous sand aquifers with cation exchange phenomena due to fresh or salt water intrusion (Stuyfzand, 1985), to a more or less universal system (Stuyfzand, 1986 a, b) with several options (Stuyfzand, in press) and minor improvements (this publication).

THE CLASSIFICATION SYSTEM

General aspects

The determination of a water type implies the successive determination of the main type, type, subtype and class of a water sample (Fig. 1).

Each of the four levels of subdivision contributes to the total code (and name) of the water type (Fig. 2). With 8 main types, 11 types, 27 subtypes (so far) and 3 classes, the theoretical maximum number of water types amounts to 7128. Of course, many water types do not exist in nature, which reduces the total number to a few hundred. Clearly, in complex situations the total number of water types

might still be confusingly and unnecessarily high. In that case several water types or even classification units have to form a so called association. Guidelines for sensible associations as well as for further differentiations are given. Instead of alkalinity on subdivision level II, also a new redox or pollution index or total hardness can be chosen (Stuyfzand, in prep.).

Main types

The chloride content determines the main type, as indicated in Table 1. The boundaries are based upon criteria discussed in Stuyfzand 1986a.

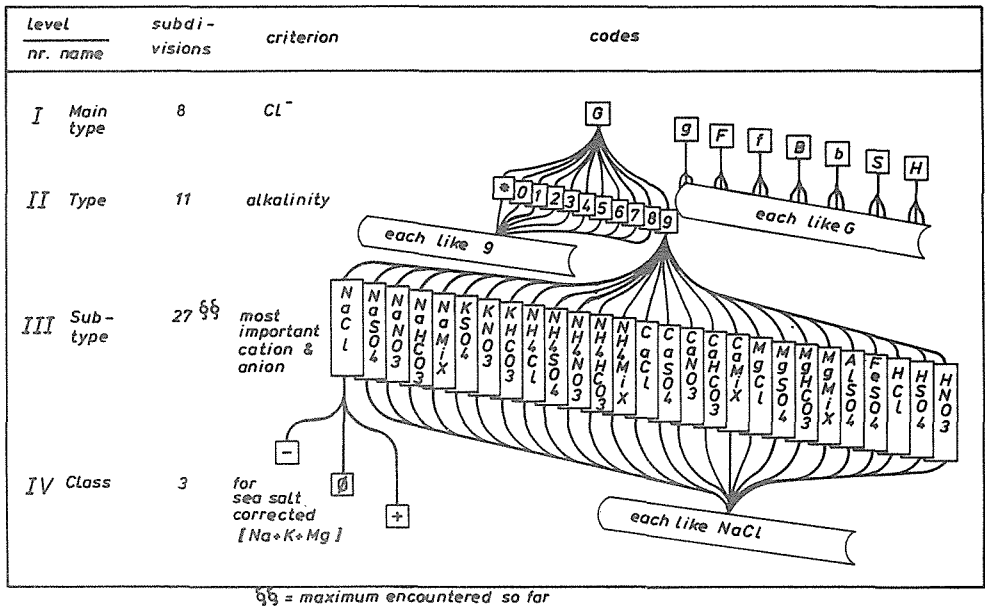


Fig. 1. The hierarchical structure of the classification system, with four levels of subdivision.

Main type	code	Cl ⁻ mg/L	Main type	code	Cl ⁻ mg/L
very oligohaline	G	<5	brackish	B	300-10 ³
oligohaline	g	5-30	brackish-salt	b	10 ³ -10 ⁴
fresh	F	30-150	salt	S	10 ⁴ -2.10 ⁴
fresh-brackish	f	150-300	hyperhaline	H	>2.10 ⁴

Table 1. Division in main types on the basis of chloride concentration

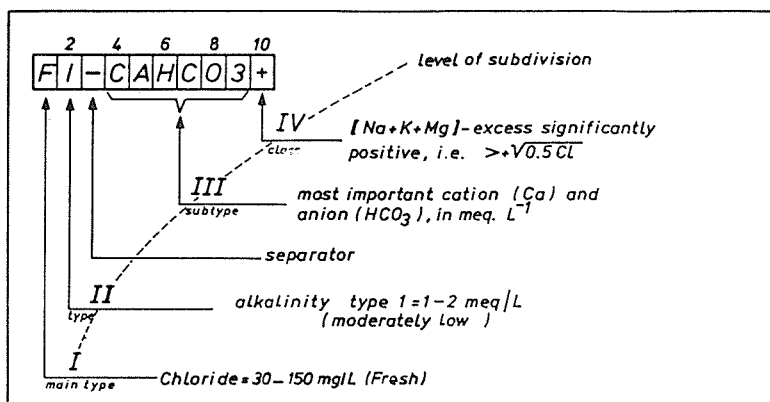


Fig. 2. Coding of a watertype in 10 positions. The example is called "a fresh, moderately low alkalinity, calciumbicarbonate water with a [Na + K + Mg]-surplus". This surplus is often due to a (former) fresh water intrusion. A shorter notation of F1-CAHCO₃ is F₁CaHCO₃.

Types

Each main type is further subdivided into a maximum of 11 types according to alkalinity (Table 2).

The upper boundary of each type except no. 9, is defined by:

$$\text{upper boundary type } x = 2^x$$

in meq/L, where x is an integer between -1 and 9.

Alkalinity (Alk) is defined as the quantity of strong acid per liter required to attain a pH close to 4.5.

For most natural waters with $4.5 \leq \text{pH} \leq 9.5$

$$\text{Alk} \approx \text{HCO}_3 + \text{CO}_3 \quad [\text{meq/L}]$$

Subtypes

Which cation and anion preponderate in the ion balance, determines more or less traditionally, through their combination the name of a water type (here "subtype"). However, in this classification the cation or anion with most meq/L does not necessarily determine the name of the subtype. First the dominating geohydrochemical family is determined both for cations and anions and then the dominating member of each family after a possible preselection of the strongest pair within a family. The procedure is clarified in the appendix.

Families with their members are positioned in Fig. 3 at the vertices of the two triangles, for instance the [Al + H + Fe + Mn] cation and the [SO₄ + NO₃ + NO₂] anion family. The relationship is of a hydrochemical and/or geochemical nature, wherein there are also direct family ties between the cation and anion families if they are positioned at the same vertex of the triangle (such as Ca + Mg and HCO₃ + CO₃). Couples are placed in brackets at the vertices of the triangles, e.g. [Al + H] and [NO₃ + NO₂]. Fields inside the triangles contain only the strongest family members which have been discovered thus far.

type	alkalinity	code	type	alkalinity	code
no. name	(meq/L)		no. name	(meq/L)	
-1 very low	< ½	*	5 very high	16 - 32	5
0 low	½ - 1	0	6 extremely high	32 - 64	6
1 moderately low	1 - 2	1	7 extremely high	64 - 128	7
2 moderate	2 - 4	2	8 extremely high	128 - 256	8
3 moderately high	4 - 8	3	9 extremely high	≥ 256	9
4 high	8 - 16	4			

Table 2. Subdivision of main types into types according to alkalinity

The grouping method used here, has the important advantage that otherwise very rare watertypes like $AlSO_4$, $FeSO_4$, KNO_3 , NH_4SO_4 , HCl and $MgHCO_3$ water are assigned much easier. This considerably increases the diagnostic value of the classification. The "Mix" anion family refers to all the water in which no anion family makes up more than 50% of the sum of the anions. The theoretical maximum number of subtypes is $9 \times 6 = 54$. Thus far, only the 27 indicated in Fig. 1 have been discovered.

Classes

Finally, each subtype is subdivided into 3 classes (Table 3) according to a new parameter: the sum of Na, K and Mg in meq/L, corrected for a contribution of sea salt:

$$\{Na + K + Mg\} \text{ corr.} = [Na + K + Mg] \text{ measured} - 1.0716 Cl.$$

The factor 1.0716 is equal to $\{(Na + K + Mg)/Cl\}$ in meq/L for mean ocean water [Riley & Skirrow, 1965]. It is assu-

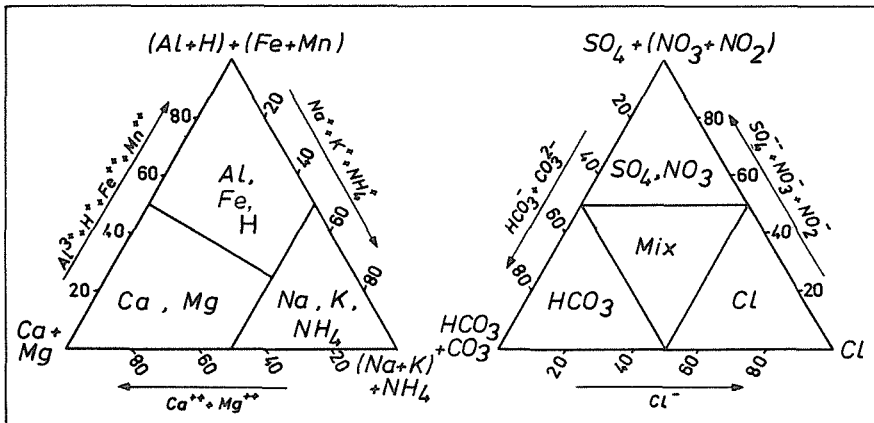


Fig. 3. Subdivision of types into subtypes on the basis of the proportional share of main constituents in the sum of the cations (left) and anions (right), both in meq/L.

Class	Code	Conditions for (Na + K + Mg) corrected (meq/L)
(Na + K + Mg) deficit ¹	-	< - $\sqrt{\frac{1}{2}}\text{Cl}$ and < $1.5(\Sigma\text{K} - \Sigma\text{A})$
(Na + K + Mg) equilibrium ²	.	\geq - $\sqrt{\frac{1}{2}}\text{Cl}$ and \leq $\sqrt{\frac{1}{2}}\text{Cl}$ and \$\$
(Na + K + Mg) surplus ³	+	> + $\sqrt{\frac{1}{2}}\text{Cl}$ and > $1.5(\Sigma\text{K} - \Sigma\text{A})$

¹ = often indicative of a salt water intrusion (anywhere, any time)
² = often indicative of adequate flushing with water of constant composition
³ = often indicative of a fresh water intrusion (anywhere, any time)

$$\text{\$ \$} = |(\text{Na} + \text{K} + \text{Mg})_{\text{corr.}} + \frac{(\Sigma\text{K} - \Sigma\text{A})}{|\Sigma\text{K} - \Sigma\text{A}|} \cdot \sqrt{\frac{1}{2}}\text{Cl}| > 1.5 |\Sigma\text{K} - \Sigma\text{A}|$$

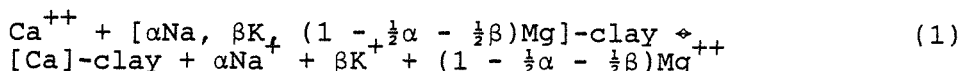
Table 3. Subdivision of subtypes into 3 classes based on (Na + K + Mg) corrected for sea salt. ΣK = sum of the cations; ΣA = sum of the anions.

med that all the Cl ions are of marine origin [Eriksson, 1952], that fractionation of the main constituents of sea water during spray formation can be ignored [Duce & Hoffman, 1976] and that Cl behaves conservatively.

The class boundaries at $\pm \sqrt{\frac{1}{2}}\text{Cl}$ form a compromise between the expected errors in chemical analyses, which adequately offset one another in the ion balance, and a rational, genetic differentiation of watertypes. If the ion balance of water is not sufficiently in equilibrium, it is pointless calculating {Na + K + Mg} corr. and nothing is printed at position 10 in Fig. 2. To check this, $1.5 (\Sigma\text{K} - \Sigma\text{A})$ is used in the manner indicated in Table 3.

Salt/fresh water intrusion and {Na + K + Mg}-corr.

The in- and extrusion of salt groundwater generally lead to the following empiric cation exchange reaction, not only in the Netherlands [Stuyfzand, 1986a], but also elsewhere in the world with comparable conditions, as can be deduced from data regarding the UK (e.g. Howard & Lloyd, 1983) and the USA (Chapelle & Knobel, 1983):



if clay forms the exchanger and with $0 \leq \alpha + \beta \leq 2$.

Upon fresh water intrusion, Ca expels the previously adsorbed Na, K and Mg ions from the exchanger. The above reaction then proceeds from left to right, leading to a significant {Na + K + Mg} surplus. The reverse reaction occurs during salt water intrusion.

Na, K and Mg do not always adsorb or desorb simultaneously during salt or fresh water intrusion respectively.

Deviations from reaction (1) are discussed by Stuyfzand (1988). They are quantitatively insufficient to influence

the sign of [Na + K + Mg]-corrected, which pleads for this classification parameter as an indicator of salinization or freshening.

Under ideal circumstances, which prevail in coastal aquifers in the North Sea basin, {Na + K + Mg} corr. thus determines the sign and in most cases quantifies the (total) cation exchange reaction, induced by a (former) change in the position of the fresh-salt interface.

Complications

In the following cases the parameter {Na + K + Mg} corr. demands a quite different interpretation:

1. dissolution of minerals which contain Na, K and/or Mg such as dolomite, albite, olivine and serpentinite;
2. mineralisation of biomass;
3. leaching, dissolution or drainage/infiltration of (artificial) fertilizers;
4. dolomitization and other transformations of minerals;
5. new formation (synthesis) of minerals comprising Na, K and/or Mg;
6. synthesis of biomass; and
7. significant atmospheric deposition of anthropogenic or volcanic Cl₂ gas.

Complications 1-3 can produce a {Na + K + Mg} surplus, complications 4-7 may cause a {Na + K + Mg} deficit.

However, these complications do not make the new parameter any less valuable because they can in themselves form subjects of study.

Flexibility: association and differentiation

In coastal districts with salt water intrusion in aquifers containing (some) lime, the association of the main types G + g + F + f in F, B + b in B or even the omission of all "subtypes" may be advantageous.

A further differentiation is useful when groundwaters within a single classification unit but of different origin occupy a single aquifer. For example, autochthonous, infiltrated atmospheric water and artificially recharged allochthonous surface water, such as Rhine water in the coastal dunes or along its river branches in The Netherlands. The latter can be coded with an "R" in position 1 of fig. 2, because the Cl content of these waters still falls within a single main type (within the association F + f in fact). Another possibility of differentiation is contained in the term "Mix" at subtype level. This could be replaced by MIF, MIC, MIS and MICL when F, ($\text{HCO}_3^- + \text{CO}_3^{2-}$), SO_4^{2-} , ($\text{NO}_3^- + \text{NO}_2^-$) and Cl respectively are to some degree predominant.

APPLICATION EXAMPLES IN THE NETHERLANDS

Fresh and salt water intrusion

In coastal dunes rich in lime with adjacent polders near

Castricum, 25 km NW of Amsterdam, a fresh water "lens" up to 100 m thick is floating on intruded North Sea water. The spatial distribution of water types according to the classification presented here, is shown in a cross section (Fig. 4). The association and differentiation used are indicated in Fig. 4.

In general, watertypes with a {Na + K + Mg} surplus, which points here exclusively at a fresh water encroachment, fringe the fresh water lens:

- at the bottom, because of a slow extension of the fresh water lens with depth as a reaction on the strong widening of the coastal dune belt between 950 and 650 years before present;
- on the inland side, because the eastward fresh water flow had been extended in consequence of the reclamation of marshland east of the dunes, particularly in the deep Schermer polder in 1635 (Fig. 4); and
- on the seaside, by a restoration of the westward fresh water flow since 1957. Artificial recharge reversed a strong lateral salt water intrusion due to excessive groundwater extraction for drinking water supply (1930-1956).

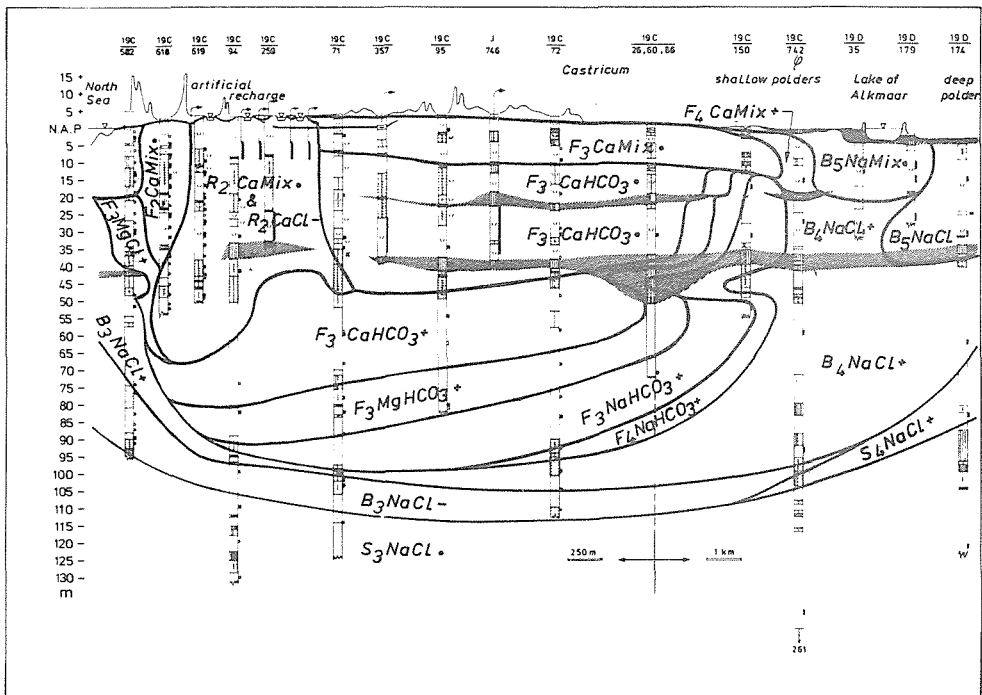


Fig. 4. Hydrochemical cross section over the coastal dunes and adjacent polders near Castricum, The Netherlands (modified after Stuyfzand, 1985). F = Cl < 300 mg/L; B = 300 < Cl < 10,000 mg/L; R = fresh, artificially recharged Rhine water.

It follows from Fig. 4, that during an actual fresh water intrusion, monitoring on one site would reveal ideally the successive passage of the watertypes S_3NaCl+ , B_3NaCl+ , B_5NaHCO_3+ (eventually), F_4NaHCO_3+ or F_3NaHCO_3+ , F_3MgHCO_3+ , F_3CaHCO_3+ and finally F_3CaHCO_3+ . In a snapshot these watertypes are found in that order in zones from the fresh water intrusion front towards the hinterland, long ago freed from salt. Salinizing brackish water (B_5NaCl-) in the deep Schermer polder probably reflects salt water intrusion during the Holocene transgression. B_3NaCl- water below B_3NaCl+ water under the fresh water lens indicates salt water intrusion upon excessive exploitation in the period 1930-1956. For more details reference is made to Stuyfzand (1988).

Excessive manuring and acidification

Excessive manuring and acid deposition deteriorate the quality of shallow groundwaters in many Pleistocene sandy recharge areas in The Netherlands. The catchment area of drinking water pumping station Vierlingsbeek in the SE-Netherlands is only an example.

There, the top 25 meters of groundwater with pH = 4-6.5 are influenced by excessive manuring (Fig. 5).

The order of influenced water types displaying increasing effects, is $F_0CaMix.$, $F^*CaSO_4.$, F^*CaSO_4+ and F^*CaNO_3+ .

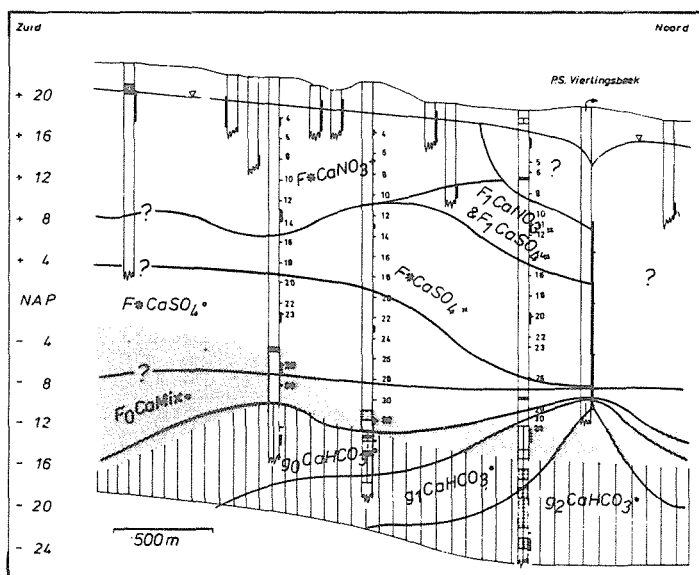


Fig. 5. Areal distribution of watertypes over pumping station Vierlingsbeek, SE-Netherlands, underlain by Pleistocene sediments poor in lime suffering from excessive manuring (simplified after Stuyfzand, 1986b).

NO₃ concentrations of 150-470 mg/L and K contents of 15-85 mg/L occur in fact in CaNO₃+ water. At a certain distance and depth NO₃ contents decrease due to oxidation of pyrite or organic sulfur and CaSO₄+ water is formed. The {Na + K + Mg} surplus in the most polluted water types is associated almost entirely with their high concentrations in manure and its leaching. Very low alkalinities are caused by acidification connected with prolonged leaching of the Pleistocene deposits, acid deposition and excessive manuring.

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APPENDIX: Computer program in FORTRAN-77 for the determination of a watertype.

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C
C      CONVERSION TO MEQ/L AND CALCULATION
C      ION BALANCE
C
C      1. CONVERSIONS (mg/L to meq/L ; pH
C      to H ; temp C (T) to K (TK)). INPUT
C      SPECIFICATION :HCO3 = total Alkali-
C      nity as HCO3 ,when pH<8.3 or unknown
C      CO3 ;CO3 = phenolphthalein Alkalinity
C      as CO3 (to pH = 8.3).
C      N.B.: PO4-conversion to mmol/L
C
C      IMPLICIT REAL (K,M,N)
C      CL = CL/35.453
C      SO4 = SO4/48.0288
C      HCO3 = HCO3/61.02
C      CO3 = CO3/30.01
C      NO3 = NO3/62
C      NO2 = NO2/46.006
C      F = F/19
C      PO4 = PO4/94.971
C      Na = Na/22.9898
C      K = K/39.0983
C      Ca = Ca/20.04
C      Mg = Mg/12.1525
C      NH4 = NH4/18.04
C      Fe = Fe/27.93
C      Mn = Mn/27.45
C      Al = Al/8.993
C      H = 10**(3.-pH)
C      TK = T + 273.15
C
C      2. CALCULATION PO4 NOT INCLUDED IN
C      ALKALINITY (H2PO4), IONIC STRENGTH
C      (MU) AND ACTIVITY COEFFICIENT
C      IONS CHARGED -/+1 (GAM1)
C
C      H2PO4 = PO4/(1.+10.0**(PH-7.21))
C      MU = 0.0005*( CL + HCO3 + NO3 +
C      * NO2 + F + H + NA + K +
C      * H2PO4 + 2.*[SO4 + CO3 + Ca
C      * + Mg + Fe + Mn] + 3.*AL)
C      GAM1 = 10.**(-0.5*(SQRT(MU)/(SQRT
C      (MU)+1.) - 3.*MU))
C
C      3. CALCULATION SUM CAT- AND ANIONS
C      (resp. SKAT and SAN)
C
C      SAN = CL + HCO3 + SO4 + NO3 + NO2
C      * + CO3 + F + H2PO4
C      * SKAT = H/GAM1 + Na + K + Ca + Mg +
C      * NH4 + Fe + Mn + AL
C
C      DETERMINATION WATERTYPE
C
C      COMP = "...-....."
C
C      A. MAIN TYPE
C
C      IF (CL.GT.564.127) THEN
C          COMP(1:1) = "H"
C      ELSE IF (CL.GT.282.064) THEN
C          COMP(1:1) = "S"
C      ELSE IF (CL.GT.28.206) THEN
C          COMP(1:1) = "b"
C      ELSE IF (CL.GT.8.462) THEN
C          COMP(1:1) = "B"
C      ELSE IF (CL.GT.4.231) THEN
C          COMP(1:1) = "f"
C      ELSE IF (CL.GT.0.846) THEN
C          COMP(1:1) = "F"
C      ELSE IF (CL.GT.0.141) THEN
C          COMP(1:1) = "g"
C      ELSE
C          COMP(1:1) = "G"
C      ENDIF
C
C      B. TYPE
C
C      ALK = HCO3 + CO3
C      ALKFI = INT(LOG(ALK)/LOG(2.) + 1.)
C      IF (ALK.LE.0.5) THEN
C          COMP(2:2) = "*"
C
C      ELSE IF (ALK.LE.1.) THEN
C          COMP(2:2) = "0"
C      ELSE IF (ALK.GT.256) THEN
C          COMP(2:2) = "9"
C      ELSE
C          WRITE(COMP(2:2),"(I1)")ALKFI
C      ENDIF
C
C      C. SUBTYPE
C
C      SNO3 = NO3 + NO2
C      HZ = H/GAM1
C      OHC = (10**(12.0875-0.01706*TK-
C      * 4470.99/TK))/(H*GAM1)
C      CO3F = CO3 - OHC
C      IF ((Na+K+NH4).GT.(SKAT/2.)) THEN
C          IF (NH4.GT.(Na+K)) THEN
C              COMP(4:6) = "NH4"
C          ELSE IF (Na.GT.K) THEN
C              COMP(4:5) = "Na"
C          ELSE
C              COMP(4:5) = "K"
C          ENDIF
C      ELSE IF ((Ca+Mg).GT.(HZ+Al+Fe+Mn)) THEN
C          IF (Mg.GE.Ca) THEN
C              COMP(4:5) = "Mg"
C          ELSE
C              COMP(4:5) = "Ca"
C          ENDIF
C      ELSE IF ((HZ+Al).GE.(Fe+Mn)) THEN
C          IF (Al.GT.HZ) THEN
C              COMP(4:5) = "Al"
C          ELSE
C              COMP(4:5) = "H"
C          ENDIF
C      ELSE IF (Fe.GT.Mn) THEN
C          COMP(4:5) = "Fe"
C      ELSE
C          COMP(4:5) = "Mn"
C      ENDIF
C
C      IF (CL.GT.(SAN/2.)) THEN
C          COMP(6:9) = "Cl"
C      ELSE IF (ALK.GT.(SAN/2.)) THEN
C          IF (HCO3.GT.CO3) THEN
C              COMP(6:9) = "HCO3"
C          ELSE IF (CO3F.GT.OHC) THEN
C              COMP(6:9) = "CO3"
C          ELSE
C              COMP(6:9) = "OH"
C          ENDIF
C      ELSE IF ((SO4+SNO3).GT.(SAN/2.)) THEN
C          IF (SO4.GT.SNO3) THEN
C              COMP(6:9) = "SO4"
C          ELSE
C              COMP(6:9) = "NO3"
C          ENDIF
C      ELSE
C          COMP(6:9) = "Mix"
C      ENDIF
C
C      D. CLASS
C
C      NaKMg = Na + K + Mg - 1.0716*Cl
C      IF ((NaKMg.GT.SQRT(.5*Cl)).AND.(NaKMg.
C      * GT.1.5*(SKAT-SAN))) THEN
C          COMP(10:10) = "+"
C      ELSE IF ((NaKMg.LT.-SQRT(.5*Cl)).AND.
C      * (NaKMg.LT.1.5*(SKAT-SAN))) THEN
C          COMP(10:10) = "-"
C      ELSE IF (SKAT.EQ.SAN) THEN
C          COMP(10:10) = "."
C      ELSE IF (ABS(NaKMg+SQRT(.5*Cl))*(SKAT-
C      * SAN)/ABS(SKAT-SAN)).GT.ABS(1.5*
C      * (SKAT-SAN))) THEN
C          COMP(10:10) = "."
C      ELSE
C          COMP(10:10) = " "
C      ENDIF

```