Base Exchange Indices as Indicators of Salinization or Freshening of (Coastal) Aquifers

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ABSTRACT

Base exchange indices are frequently used in regional hydrochemical surveys, for indicating whether an aquifer is salinizing or freshening, or has been freshened or salinized in the past. Seven different base exchange indices are compared and evaluated. The best index, for aquifer systems without dolomite, is BEX = Na + K + Mg – 1.0716 Cl (meq/L), because it not only indicates the right direction (fresh or salt water intrusion), but also the magnitude of the exchange reaction and side reaction with $CaCO_3$. For dolomitic aquifers BEX_D = Na + K – 0.8768 Cl (meq/L) is to be preferred.

Great care must be taken in interpreting base exchange indices, because of various sources of bias, like errors in ionic balance, and disturbing water-rock and water-biomass interactions. Memory effects of ancient shifts in the position of the fresh/salt water interface may mask actual freshening or salinization processes.

INTRODUCTION

High quality data, good maps and intelligent interpretation tools are needed for on-time identification of spatial and temporal changes in the position of the fresh-salt groundwater interface(s) and the underlying causes, in order to protect the aquifer system or well field from unexpected, severe salinization. A proper cation exchange index with the right interpretation algorithm may constitute such a tool.

Base exchange indices are normally translated into a salinized or freshened facies, or into a state of equilibrium. It is assumed that intruding sea water (with high concentrations of Cl, Na, K and Mg) is displacing fresh water with high Ca and HCO_3 concentrations or vice versa, and that at least Na is adsorbed during salinization, and Ca during freshening of the aquifer system. The classical exchange reaction is therefore schematized as follows:

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

with: EXCH = the base exchanger, like clay and peat; forward ($\rightarrow$) = salt water intrusion (salinization); backward ($\leftarrow$) = fresh water intrusion (freshening).

THE BASE EXCHANGE INDICES

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 1. Indices 1-4 in Table 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 1) that also quantifies the extent of the exchange reaction. Various problems with the above given indices are listed in Table 1. An index not suffering from most of the problems mentioned in Table 1, the Base

EXchange index (BEX) was proposed by Stuyfzand (1986), also as part of a chemical watertype classification.

Table 1. Overview of 5 base exchange indices from literature, with frequently encountered problems in their interpretation

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	Stuyfzand (1986) #	Na + K + Mg - 1.0716 Cl
7	This publication ##	Na + K - 0.8768 Cl

Problems:
1-7: other processes may influence values   1: CaCO3 dissolution influences ratio
1-5: bias due to analytical errors, no threshold   2: ocean water already positive
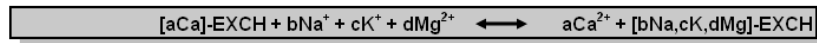1-4: do not quantify amount of cation exchange   5: ocean water already negative

\#: for aquifers without dolomite   ##: for aquifers containing dolomite

$$BEX = Na + K + Mg - 1.0716\ Cl \quad \text{(all in meq/L)}$$

with: 1.0716 = (Na+K+Mg)/Cl in mean ocean water

Class Code	BEX	INTERPRETATION		CONDITIONS
		If base exchange only process	if other process(es) relevant	for BEX, in meq/L
-	negative	Salinized	Marine cations deficit	<-(0.5+0.02Cl) and <1.5($\Sigma k - \Sigma a$)
•	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($\Sigma k - \Sigma a$)

\# and abs(BEX + {($\Sigma k - \Sigma a$)/abs($\Sigma k - \Sigma a$)} (0.5+0.02Cl)) > 1.5 abs($\Sigma k - \Sigma a$)

$$[aCa]\text{-EXCH} + bNa^+ + cK^+ + dMg^{2+} \longleftrightarrow aCa^{2+} + [bNa, cK, dMg]\text{-EXCH}$$

2a = b + c + 2d   Freshening $\longleftrightarrow$ Salinization

Figure 1. The Base Exchange index BEX as proposed by Stuyfzand (1986) with minor modifications according to Stuyfzand (1993).

The factor 1.0716 is equal to $\{[Na^+ + K^+ + Mg^{2+}]/Cl^-\}$ in meq/L for mean ocean water (Riley & Skirrow, 1975). The boundary limits at $\pm (0.5 + 0.02\ Cl)$ indicated in Fig.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. $1.5(\Sigma k - \Sigma a)$ is used as a measure of ionic imbalance (see Fig.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. Its definition is given in Table 1, and its further characteristics are equal to those of BEX (Fig.1).

PROBLEMS WITH THE INTERPRETATION OF BASE EXCHANGE INDICES

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 2, which more specifically holds for BEX and BEX_D.

Table 2.   Algorithm for interpreting base exchange index BEX.

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

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

BEX: THE INDIVIDUAL CATIONS AND SIDE REACTIONS

Na^+, K^+ and Mg^{2+} do not always ad- or desorb simultaneously during salt or fresh water intrusion respectively. This means that their individual concentrations corrected for a contribution of sea salt (X*), do not always indicate the right direction of displacement while BEX does (Fig.2).

Deviations from the reaction in Fig.1 are quantitatively insufficient, however, to influence the sign of BEX. This pleads for its use as an indicator of salinization or freshening.

Changes in Ca concentration are related to BEX as follows (Fig.2), provided other reactions like methanogenesis do not significantly contribute:

$$Ca* = Ca*_0 - f\,BEX \qquad (3)$$

With: Ca* = calcium concentration corrected for sea salt (= Ca – 0.0376 Cl) after base exchange [meq/L]; $Ca*_0$ = ditto before base exchange [meql/L];   f = reaction coefficient [<1].

Factor f is 0.5 during freshening in the calcareous coastal dune aquifer systems, which indicates that the Ca losses are compensated for by dissolution of an amount of $CaCO_3$ equal to BEX/2. During salinization f is 1.0 (Stuyfzand, 1993).

Changes in TIC concentration are related to BEX, only during freshening, as follows (Fig.2):

$$TIC = TIC_0 + 2f\,BEX \qquad (4)$$

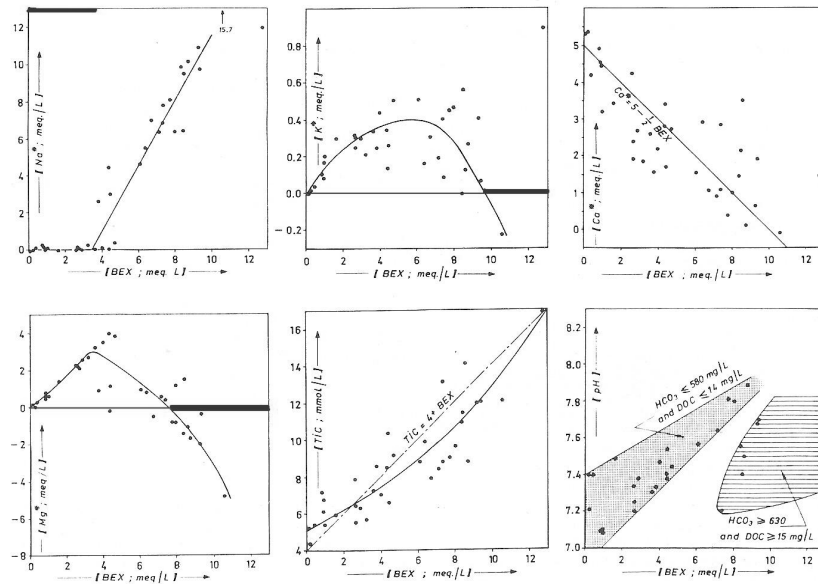With: TIC, TIC_0 = Total Inorganic Carbon resp. after and before base exchange [mmol/L].

Figure 2. Plot of sea salt corrected, main cations (X*), 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 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.

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