Patterns in groundwater chemistry resulting from groundwater flow

Pieter J. Stuyfzand

Abstract Groundwater flow influences hydrochemical patterns because flow reduces mixing by diffusion, carries the chemical imprints of biological and anthropogenic changes in the recharge area, and leaches the aquifer system. Global patterns are mainly dictated by differences in the flux of meteoric water passing through the subsoil. Within individual hydrosomes (water bodies with a specific origin), the following prograde evolution lines (facies sequence) normally develop in the direction of groundwater flow: from strong to no fluctuations in water quality, from polluted to unpolluted, from acidic to basic, from oxic to anoxic–methanogenic, from no to significant base exchange, and from fresh to brackish. This is demonstrated for fresh coastal-dune groundwater in the Netherlands. In this hydrosome, the leaching of calcium carbonate as much as 15 m and of adsorbed marine cations (Na^+, K^+, and Mg^{2+}) as much as 2500 m in the flow direction is shown to correspond with about 5000 yr of flushing since the beach barrier with dunes developed. Recharge focus areas in the dunes are evidenced by groundwater displaying a lower prograde quality evolution than the surrounding dune groundwater. Artificially recharged Rhine River water in the dunes provides distinct hydrochemical patterns, which display groundwater flow, mixing, and groundwater ages.

Résumé Les écoulements souterrains influencent les différents types hydrochimiques, parce que l'écoulement réduit le mélange par diffusion, porte les marques chimiques de changements biologiques et anthropiques dans la zone d'alimentation et lessive le système aquifère. Ces types dans leur ensemble sont surtout déterminés par des différences dans le flux d'eau météorique traversant le sous-sol. Dans les "hydrosomes" (masses d'eau d'origine déterminée), les lignes marquant une évolution prograde (séquence de faciès) se développent normalement dans la direction de l'écoulement souterrain : depuis des fluctuations fortes de la qualité de l'eau vers une absence de fluctuations, de polluées vers non polluées, d'acides vers basiques, d'oxygénées vers anoxiques et méthanogènes, depuis des échanges de base inexistants vers des échanges significatifs, de l'eau douce vers l'eau saumâtre. Ceci est montré pour une nappe d'eau douce dans une dune côtière des Pays-Bas. Dans "l'hydrosome", on montre que la disparition du carbonate de calcium par lessivage à plus de 15 m et celle de cations adsorbés d'origine marine (Na^+, K^+ et Mg^{2+}) à plus de 2500 m vers l'aval-gradient correspond à environ 5000 ans d'écoulement, depuis que la barrière de la plage avec les dunes s'est mise en place. Les zones d'alimentation ponctuelle dans les dunes sont mises en évidence par l'eau souterraine montrant une plus faible évolution prograde de sa qualité que l'eau souterraine de la dune alentour. L'eau du Rhin utilisée pour la réalimentation artificielle dans les dunes a fourni des types hydrochimiques distincts, qui marquent l'écoulement, le mélange et les âges de l'eau souterraine.

Resumen El flujo subterráneo tiene una gran importancia sobre la hidroquímica de un sistema ya que reduce la mezcla por difusión, transporta las huellas químicas y biológicas de las acciones antrópicas en la zona de recarga y drena el sistema acuífero. Las tendencias globales vienen regidas por las diferencias en el flujo de agua meteórica que atraviesa el subsuelo. En un hidrosoma individual (cuerpo de agua de un origen específico), se suele desarrollar la siguiente línea de evolución (secuencia de facies) en la dirección del flujo: de gran a nula fluctuación en la calidad del agua, de agua contaminada a no contaminada, de ácida a básica, de óxica a anóxica-metanogénica, de nulo a importante cambio de base y de agua dulce a salobre. Esto puede verse, por ejemplo, en las aguas dulces presentes en las dunas costeras de Holanda. En este hidrosoma, el lixiviado de carbonato cálcico, hasta 15 m, y de cationes de adsorción marina (Na^+, K^+ and Mg^{2+}), hasta 2500 m en la dirección del flujo corresponde a unos 5000 años de lavado desde que se desarrolló la barrera de dunas. Áreas de recarga concentrada en las dunas se evidencian porque el agua subterránea

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Pieter J. Stuyfzand
Kiwa N.V. Research and Consultancy, Groningenhaven 7,
P.O. Box 1072, 3430 BB Nieuwegein, the Netherlands
Fax: +31-30-6061-165
e-mail: stuyfzan@kiwaoa.nl

muestra un bajo estado de evolución dentro de la línea de evolución antes presentada, si se compara con el agua circundante. La recarga artificial en las dunas con agua del Río Rin proporciona características hidroquímicas diferenciadas, lo que permite caracterizar el flujo subterráneo, la mezcla y las edades de las aguas.

Key words hydrochemistry · groundwater · the Netherlands · salt-water/fresh-water relations · paleohydrology

Introduction

Groundwaters typically have a large range in chemical composition (Hem 1970; Drever 1982; Matthess 1990; Appelo and Postma 1993). This large range is attributed to differences in: (1) origin (marine, meteoric, connate, metamorphic, magmatic, volcanic, plutonic, and juvenile; White 1957a, 1957b); (2) recharge rate; (3) interaction with the atmosphere (mainly evapotranspiration), biosphere (especially uptake and generation of CO_2 and organic acids), and lithosphere; (4) anthropogenic pollution; and (5) temperature and pressure.

Without groundwater flow as a carrier and a driving force, much less variety would exist, because diffusion would reduce the differences by mixing, if enough time were allowed for it (Volker 1961; Ranganathan and Hanor 1987). Groundwater flow thus protects the spatial and temporal quality variations against losses by diffusion, but it inevitably leads to some losses by dispersion.

On the other hand, groundwater flow, which is considered a major erosion agent (by dissolution), may also accentuate the differences or add to the diversity by sequential leaching of reactive phases from the aquifer matrix. For instance, when fast-reacting calcite becomes totally leached from a calcareous quartz sand in the recharge zone, an acidic hydrogeochemical environment is added to the calcareous groundwater system. In addition, high-flow zones are often much earlier depleted in the products of water–rock interaction than low-flow zones, mainly because: (1) there is less accumulation of weathering products; and (2) higher flow rates generally combine with an originally lower amount of reactive solids (less clay and organic matter in the more permeable strata).

The relationship between hydrochemistry and groundwater flow can be used in:

(1) prospecting for drinking water (Edmunds 1981), ores (Runnells et al. 1992), and oil and gas (Schoeller 1955; Tóth 1980); (2) reservoir engineering, such as estimating natural recharge rate, recharge focus areas, flow patterns, degree of mixing, and age of groundwater (Mazor and George 1992; Stuyfzand 1993); and (3) environmental research, for instance by estimating natural background concentrations (Edmunds et al. 1987).

The main focus of this study is directed to chemical patterns in coastal dune groundwater in the western Netherlands. These patterns provide a fairly complete set of evolutionary trends in the direction of groundwater flow. They offer a good example of facies shifts due to prolonged leaching and examples of how to determine in a chemical manner the recharge focus areas, flow patterns, degree of mixing, and age of water. Locations are shown in *Figure 1*.

Groundwater Flow Systems and Hydrochemical Systems

Groundwater Flow Systems

A groundwater flow system (GFS) is defined as a coherent, three-dimensional unit of groundwater flow with one recharge and one or more discharge areas (Tóth 1963; Engelen and Jones 1986). The terms supraregional, regional, subregional, and local are used to denote a GFS with decreasing dimensions in the landscape. The largest system normally has the following characteristics: exfiltration on the topographically lowest terrains; an overall smallest hydraulic gradient, longest transit times, and highest temperature; and the smallest fluctuations in flow velocity, volume, and chemical composition, at least when the stage of chemical maturity is reached (see below).

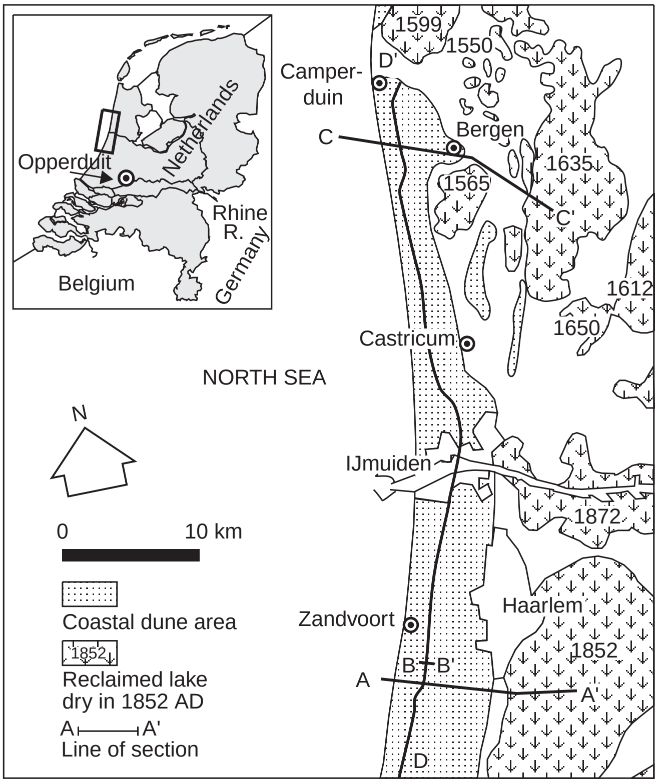


Figure 1 Location of the coastal dunes of the western Netherlands

During its initial stages, a GFS is always occupied by waters of different origins. The current recharge water has to displace all residual (relic) groundwaters. The flow system may be called hydrochemically mature when this process is completed, i.e., when it is occupied by one hydrosome (for definition, see below).

Hydrological maturity is attained when flow has reached steady state. Where density differences are negligible, steady groundwater flow is attained much earlier than complete displacement of all relic groundwaters. Thus, hydrological maturity precedes hydrochemical maturity. This situation is demonstrated in *Figure 2* for two relatively young GFSs in the coastal area of the western Netherlands: (1) the North Sea flow system, which was activated by reclamation of Lake Haarlemmermeer in 1853; and (2) the Rhine flow system, which originated in 1957 when artificial recharge of the dunes started. Both flow systems are more or less in steady state, as demonstrated by time series of potentiometric levels, whereas both North Sea and Rhine water occupy only part of their flow system, as evidenced by hydrochemical surveys.

Hydrochemical Systems: Hydrosomes and Hydrochemical Facies

A hydrochemical groundwater system, or hydrosome, is defined as a coherent, three-dimensional unit of groundwater with a specific origin. The term 'hydrosome' is analogous to the stratigraphical concept 'lithosome' (Krumbein and Sloss 1963). Examples in *Figure 2* are: (1) coastal dune groundwater recharged

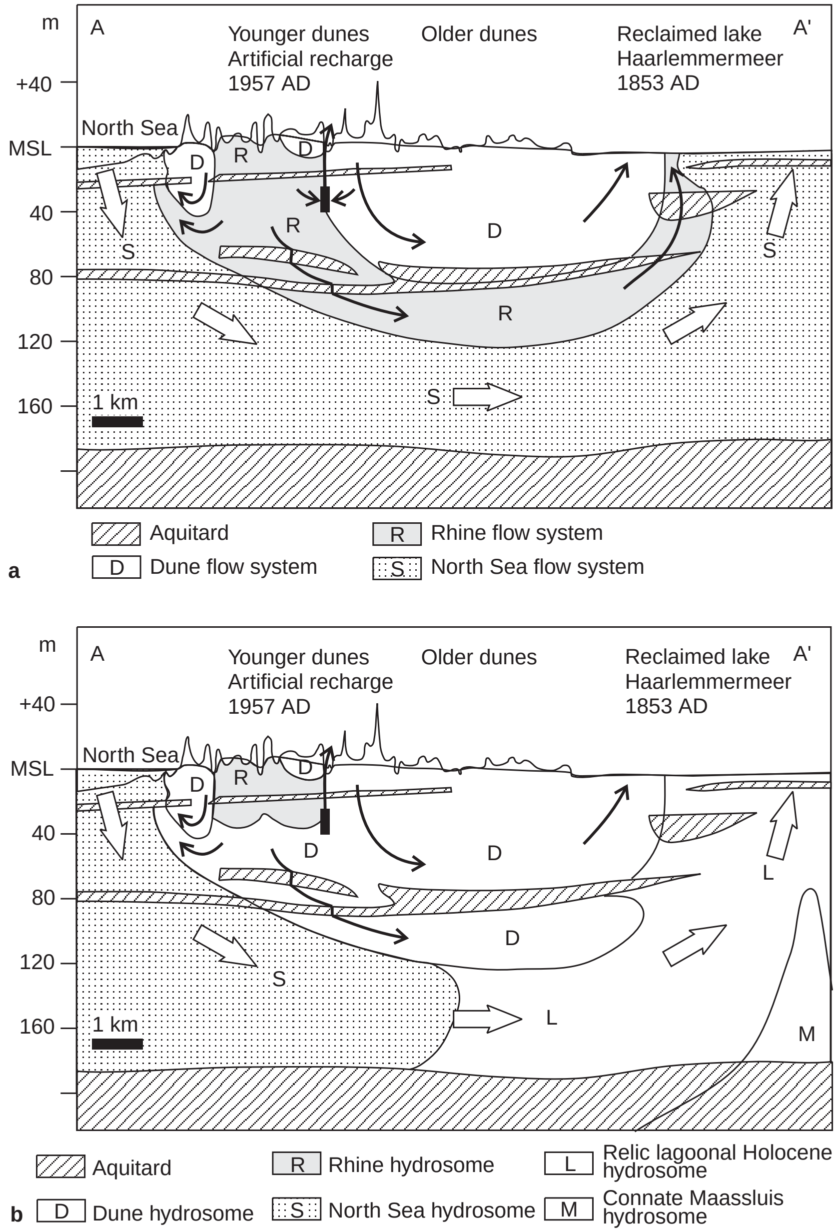


Figure 2a, b Section A–A' showing the current areal distribution of **a** groundwater flow systems and **b** hydrochemical systems, in the coastal dune area of the western Netherlands. The flow systems approximate steady state; the hydrochemical systems do not. Line of section shown in *Figure 1*. *Arrows* indicate present groundwater flow by local rain water; (2) intruded sea water; (3) recharged river water; and (4) 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 the water and the porous medium. Such variations in chemical character are used to subdivide a hydrosome into characteristic zones, or 'hydrochemical facies,' a term introduced by Back (1960).

A hydrosome is therefore composed of various hydrochemical facies units, which may constitute a facies complex or facies chain. On the other hand, the coexistence of several hydrosomes in a specific landscape may be considered a hydrochemical district or province. Examples of districts are coastal plains, inland fluvial plains, inland carbonate terrains, volcanic areas, intramontane depressions without discharge, and alpine crystalline areas. Definitions are shown in *Figure 3*.

Global and General Patterns

Patterns on a Global Scale

Shipovalov (1984) recognizes three types of hydrochemical zones on a global scale: (1) horizontal or latitudinal zonation, as a result of successive change of climatic belts; (2) vertical zonation, related to the depth below land surface and concomitant changes in water circulation; and (3) altitudinal zonation, related to the height of the land surface above sea level.

In general, a gradual increase of the mineralization of groundwater and shift from the dominant anion HCO_3^- via SO_4^{2-} to Cl^- are observed on moving from: (1) high to low latitudes, due to more evapotranspiration losses and more CO_2 production; (2) shallow to great depth, due to decreasing groundwater circulation and increasing water–rock interaction; and (3) high to low altitudes, due to reduced rainfall, more evapotranspiration losses, and more CO_2 production. The decreasing flushing rate of the aquifer system with meteoric water probably is the most dominant factor, because of its major impact on each of Shipovalov's zones.

The global patterns have many deviations, due, for instance, to a shallow occurrence of evaporites or to recent marine transgressions. The vertical zonations, as described by Chebotarev (1955) for large Australian basins, may have another explanation: they often relate to stratification of different hydrosomes. For instance, the deeper chloride brines may derive principally from ancient seawater, whereas the upper HCO_3^--waters stem from local rainfall.

Normal (Prograde) Evolution Along Flow Paths Within a Single Hydrosome

The normal hydrochemical evolution of a hydrosome in the direction of groundwater flow (back in time but forward in water–rock interactions) typically leads to the following prograde facies sequence or chain, as illustrated in *Figure 4.*

1. From strong quality fluctuations induced mainly by cyclic atmospheric and biological changes, to a very stable water quality, by longitudinal and transversal dispersion (Stuyfzand 1993).
2. From polluted with, for instance, SO_4^{2-}, NO_3^-, K^+, heavy metals, tritium, and persistent xenobiotics, to unpolluted, through: (a) elimination processes, such as filtration, acid buffering, sorption, breakdown, and decay; and (b) increasing age of the water, which results in a lower pollution load before the onset of industrialization (Edmunds et al. 1982; Stuyfzand 1984).
3. From acidic to basic water, by weathering reactions with the porous medium, which consume acids like

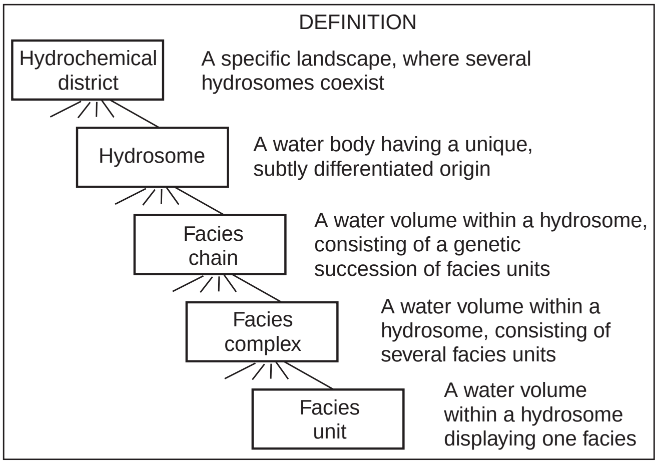


Figure 3 Hierarchical organization and definition of concepts used to denote hydrochemical systems. (After Stuyfzand 1993)

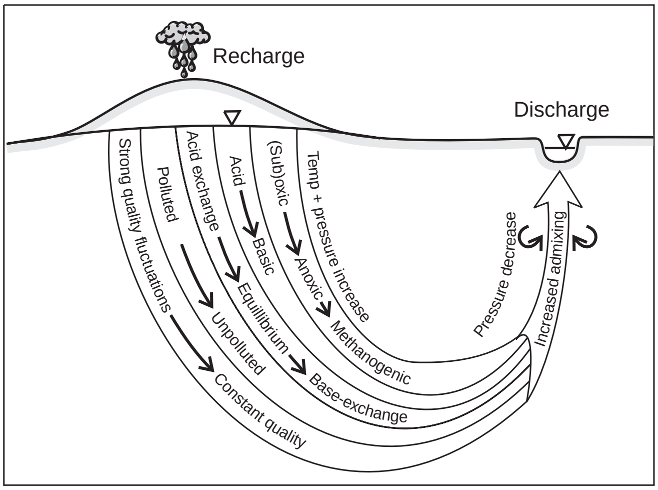


Figure 4 The normal, prograde water-quality evolution downgradient within a single hydrosome

H_2CO_3, H_2SO_4 and HNO_3 and produce alkalinity (Eriksson 1987).

4. From oxic to anoxic–methanogenic conditions, by continued oxidation of organic matter in a system closed from the atmosphere. This process results in a typical order of consumption of oxidants in water (Froelich et al. 1979; Champ et al. 1979; Edmunds et al. 1984) and an increase in alkalinity (Stuyfzand 1989).
5. From equilibrium between the exchange complex of the porous medium and its interstitial water to ion exchange and side reactions, during and after displacement by another hydrosome (Versluys 1931; Stuyfzand 1992), as happens when fresh dune water intrudes a coastal aquifer containing salt water.
6. From fresh to brackish or saline water, by hydrodynamic dispersion across the boundaries of adjacent hydrosomes or by continued evapotranspiration. The latter may lead to evolution lines described by Hardie and Eugster (1978) and Jankowski and Jacobson (1989).
7. From low to elevated pressure and temperatures, by way of downward migration of groundwater or by subsidence of the porous medium. The reverse may also occur, as happens when water is squeezed out of compacting clay; and a combination of both is observed where meteoric water first descends in a recharge area and subsequently ascends in a discharge zone. An increase of temperature and pressure may lead to K^+ and Mg^{2+} depletion by recrystallization of compacting clay (Muller 1967), to hyperfiltration (Freeze and Cherry 1979) and an increase of overall salinity by a reduction of the cation-exchange capacity (Schoeller 1955).

In most cases, the large differences in quality of groundwater with respect to recharge and discharge areas can be attributed to the above-mentioned evolution patterns 1–4 and 6. In clean background areas, this difference is accompanied by a higher degree of mineralization in the discharge areas. In polluted areas, the reverse situation may hold. In addition, discharge areas may become important mineral accretion zones, where either travertine is deposited (by CO_2-stripping), or iron hydrites (by oxygenation), or silica (by lowering of temperature or growth of diatoms), or any combination of these.

In a fixed position within the groundwater flow system, the normal evolution in the course of time is the reverse of the above-mentioned evolution lines 2, 3, 4, and 5. This reversal is caused by, respectively, a gradual breakthrough of less degradable pollutants, the leaching of acid neutralizing minerals, the leaching of reducing phases such as organic matter and pyrite, and the extinction of those cation-exchange reactions that relate to displacement of the former hydrosome.

Complications Within a Single Hydrosome

A retrograde facies evolution is defined, in analogy with the concept of retrograde metamorphism in petrology, as the return to a lower grade of evolution in the direction of groundwater flow. Examples are observed in flow-through lakes, where exfiltrating anoxic groundwater is re-aerated prior to back-infiltration on the other side of the lake, and in areas where groundwater flow is reversed (for instance by pumping).

Complicated evolution patterns arise where sanitation measures have a beneficial effect on groundwater, so that the pollution level first increases (abnormal) and subsequently decreases (normal) in the direction of groundwater flow. The abnormal part may be called an inversion. As shown in *Figure 5*, such an inversion has been observed in Rhine bank groundwater, due to immense quality improvements since the late 1970s. This groundwater was sampled in 1983 and 1995, along a flow path 700 m long using a row of monitoring wells with a well screen 1 m long (Stuyfzand, in press). The groundwater at 65 m distance was about 1 yr old, and the water at 700 m was about 8 yr, as deduced from tritium analyses. The results of phosphate, dichlorobenzene, and 1,3,3-trimethyloxindole (a waste product of dye manufacturing) showed an inversion in, respectively, 1995, 1983, and 1983 (*Figure 5*).The later inversion for phosphate is caused by a delayed phosphate reduction in the Rhine (compare insets in *Figure 5*) and by more sorption.

Other inversions relate to, for instance: (1) raised groundwater tables in the recharge area, which convert former (sub)oxic into anoxic conditions in the water-table domain; or (2) the deposition of clayey sediments on top of a decalcified oxygenated aquifer in its recharge area, thus restoring reducing and acid neutralizing phases that interact with young groundwater.

An important factor in the chemical evolution is the order of encounter of various minerals or rocks by the water as it moves through the flow system (Freeze and Cherry 1979; Palmer and Cherry 1985). If sulphate-depleted groundwaters contact gypsum in a later stage, the prograde redox sequence is disturbed.

The Netherlands' Coastal Dunes as an Example

General Hydrochemical Situation

The general hydrochemical situation of the coastal area of the western Netherlands is depicted by *Figure 6*, a cross section perpendicular to the North Sea coast line near Bergen. The section shows the areal distribution of hydrosomes and hydrochemical facies, applying the Hydrochemical Facies Analysis (HYFA) as proposed by Stuyfzand (1990, 1993). Five hydrosomes are recognized, in order of decreasing age:

1. Connate, marine water (M), which was codeposited with the Maassluis Formation at the beginning of the Pleistocene Epoch, about 2×10^6 yr ago.

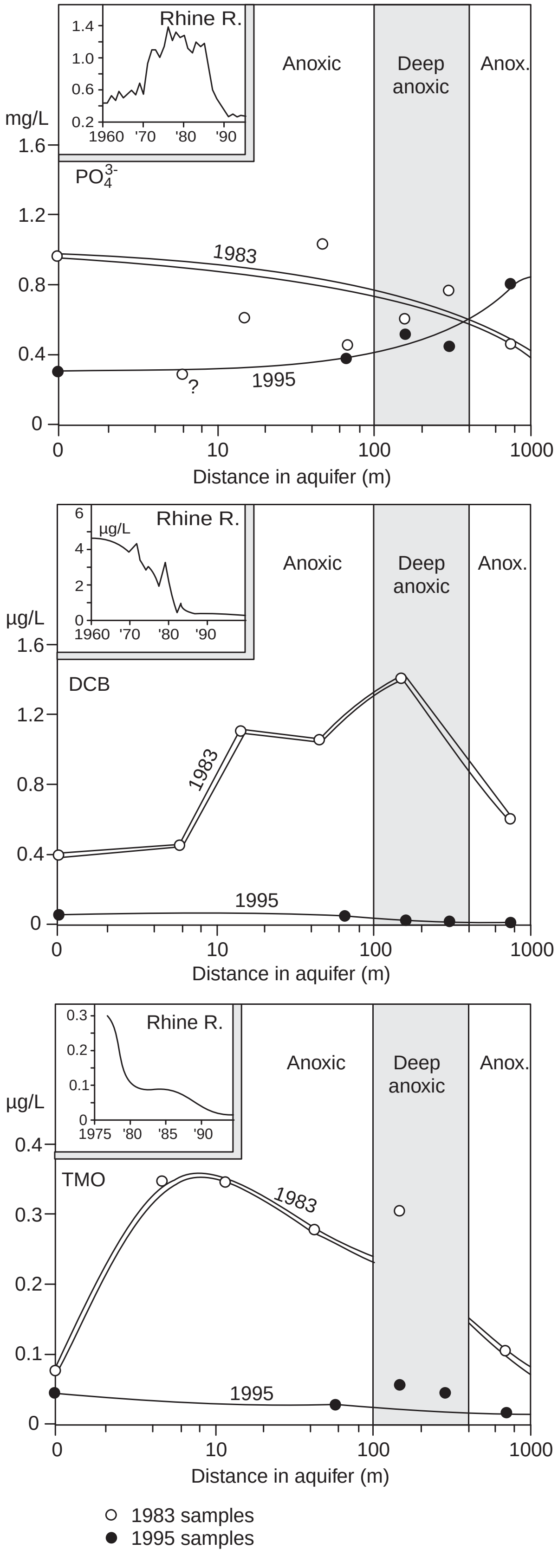


Figure 5 Inversions in the quality evolution of Rhine bank groundwater near Opperduit, the Netherlands, regarding specific pollutants whose loads were drastically reduced by sanitation measures during 1975–90. The *inset* shows concentration trends in the Rhine River near the German border. *DCB* = sum of all dichlorobenzenes; *TMO* = 1,3,3-trimethyloxindole. (After Stuyfzand 1998)

2. Relic, Holocene transgression waters (L), which were formed between 8000 and 300 yr ago during the various Holocene transgressions.
3. 'Actual' North Sea water (S), which infiltrated and still infiltrates through the actual sea floor, with a significant acceleration since the reclamation of lakes.
4. Fresh, coastal dune water (D), which started to form about 5000 yr ago when the first beach barriers were left behind an advancing shore line.
5. Polder water (P), which is mainly composed of Rhine River water (flushing and irrigating the polders) and autochthonous rainwater, less than 500 yr old.

These hydrosomes were mapped using the diagnostic natural tracers Cl^-, $\delta^{18}O$, and HCO_3^- (Stuyfzand 1993).

Within each hydrosome various facies are discerned by a combination of:

1. The redox level, as deduced from the concentrations of O_2, NO_3^-, SO_4^{2-}, Fe, Mn, and CH_4.
2. The most relevant mineral saturation index for the system (here, the calcite saturation index).
3. The pollution index POLIN, which is based on 6 equally weighted quality aspects (pH, the concentration of nitrate plus sulphate, the sum of 8 hazardous heavy metals, the concentration of organohalogens adsorbable to activated carbon, the amount of thermotolerant Coli bacteria, and tritium activity).
4. The Base EXchange index, BEX, defined as the sum of the cations Na^+, K^+, and Mg^{2+} (in meq/L), corrected for a contribution of sea salt. This index assumes no other sources and sinks for these ions, an assumption that generally holds in the western Netherlands (Stuyfzand 1993):

$$\mathrm{BEX} = (\mathrm{Na}^+ + \mathrm{K}^+ + \mathrm{Mg}^{2+})_{\mathrm{measured}} - 1.0716\ \mathrm{Cl}^-\ [\mathrm{meq/L}] \qquad (1)$$

In this definition, it is also assumed that the intrusion of fresh and salt groundwater leads to the following exchange process (with the meq balance: $2a = b + c + 2d$):

$$a\mathrm{Ca}^{2+} + [b\mathrm{Na}^+, c\mathrm{K}^+, d\mathrm{Mg}^{2+}]\text{–exchanger} \leftrightarrow [a\mathrm{Ca}^{2+}]\text{–exchanger} + b\mathrm{Na}^+ + c\mathrm{K}^+ + d\mathrm{Mg}^{2+} \qquad (2)$$

Although distinct deviations from Eq. (2) exist, the sign of BEX usually indicates the right direction of the displacement: a significantly positive value indicates freshening (reaction 2 proceeds to the right); a significantly negative value occurs at salinization; and a value

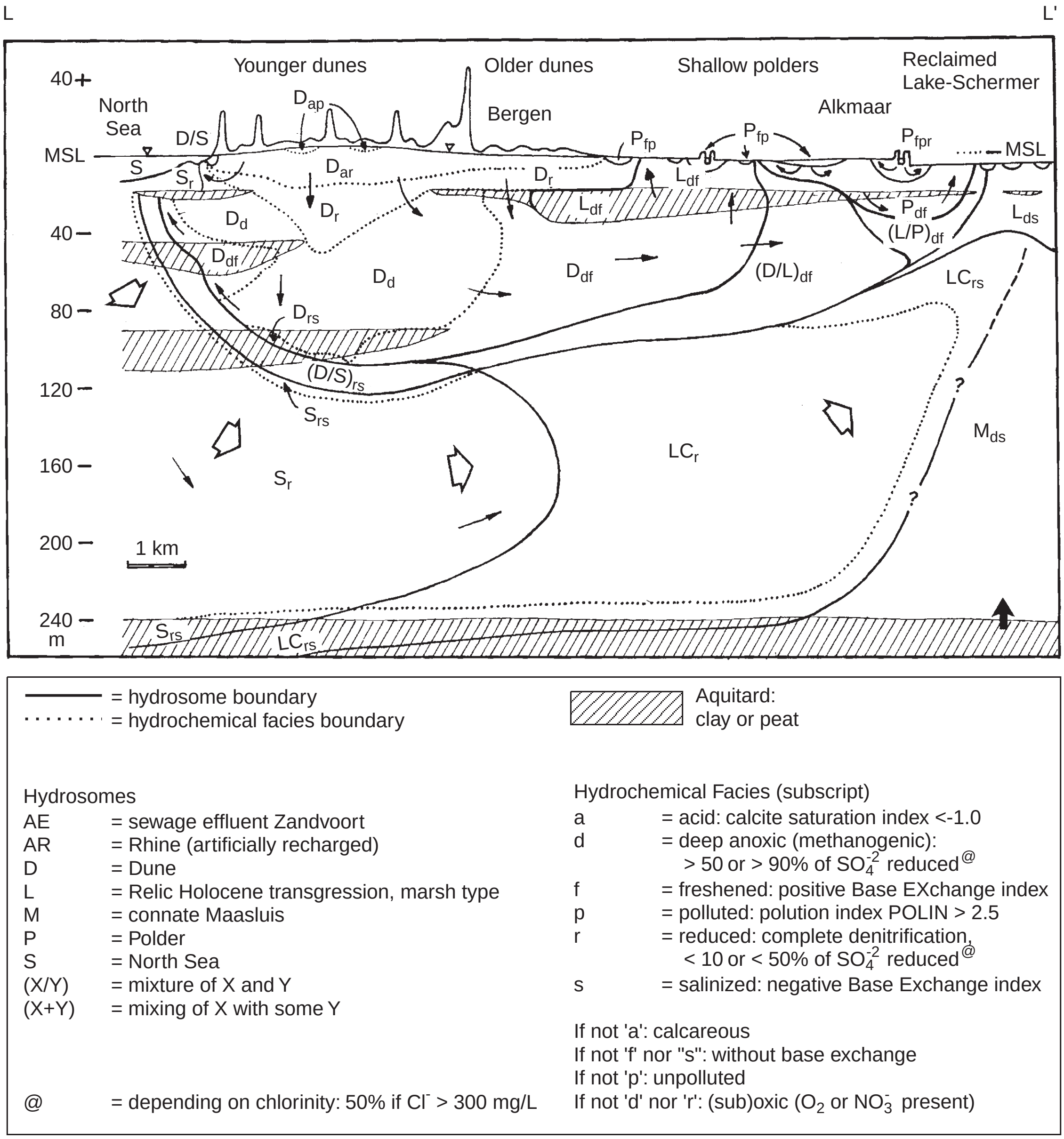


Figure 6 Section C–C' of the coastal area near Bergen, northwestern Netherlands, showing the areal distribution of hydrosomes with their hydrochemical facies. Line of section shown in *Figure 1*. *Arrows* indicate present groundwater flow. (After Stuyfzand 1993)

near zero occurs at equilibrium. For a further discussion, see Stuyfzand (1993).

Along the indicated very deep flow branch of the fresh dune hydrosome inland, the following facies are recognized in the flow direction *(Figure 6)*: ap = acid, polluted; ar = acid, reduced; r = reduced, calcite saturated; d = deep anoxic, calcite saturated; and df = deep anoxic, freshened, calcite saturated. This downgradient evolution is specified for selected components in *Figure 7* and corresponds well with the generalized prograde evolution depicted in *Figure 4*. The evolution is dictated by air pollution, the neutralization of acids by shell fragments, the consumption of oxidants in a closed system, and cation exchange due to displacement of relic saline water that transgressed the area during Holocene time. This displacement started since the formation of the beach barrier about 5000 yr ago, and it received a new impulse after reclamation of the shallow polders around 1550 AD and deep polders around 1630 AD.

The Environmental Pollution Record

Environmental pollution in the protected dune area consists exclusively of atmospheric pollution. The pollution record in dune groundwater, which is recharged by rainfall, is composed of: (1) decreasing levels downgradient (the first 5–30 m) for the mainly atmogenic trace elements Se, Cu, F^-, Pb, and Sb (in decreasing order of depth of penetration; not shown in

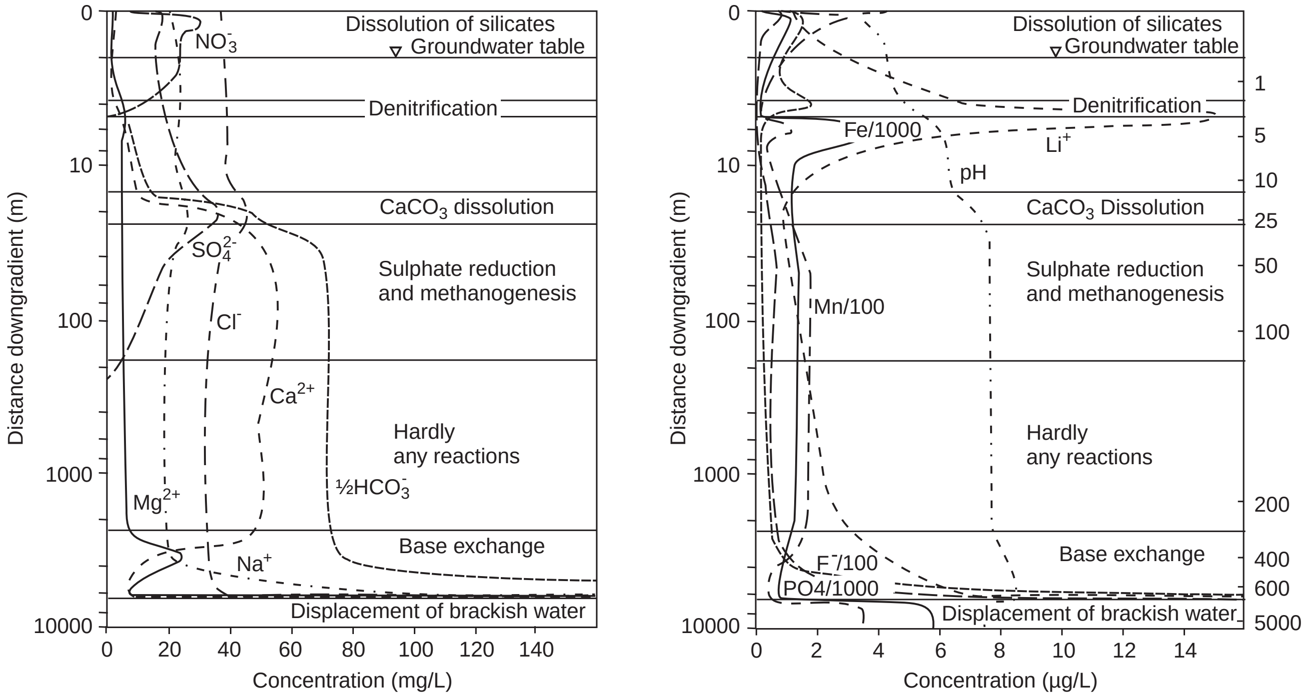


Figure 7 Prograde quality evolution of coastal dune groundwater in the flow direction in 1987–91. The water beyond 2500 m is situated in the polder area and exhibits base exchange due to previous displacement of brackish water. (Based on extensive data in Stuyfzand 1993)

Figure 7), and for organohalogens adsorbable to activated carbon (AOCl, not shown); and (2) a SO_4^{2-} peak between 10 and 20 m (*Figure 7*). The trace elements are retarded by sorption and precipitation, organohalogens (AOCl) are probably broken down by reductive dehalogenation, and the sulphate peak correlates with a peak in sulphate emissions during 1960–70.

The Leaching of Calcium Carbonate

The flow of fresh dune groundwater has led to decalcification of its recharge area to about 15 m below the dune surface, and to the development of an acidified zone (*Figures 6* and *7*). Based on calculations presented below, this leaching relates well to the age of the dune landscape and dune hydrosome, and higher $CaCO_3$ contents below 15 m prevent the decalcification front from affecting wells for drinking-water supply.

The rate of decalcification (V_{CaCO3}) is defined as the velocity with which the schematized sharp $CaCO_3$ boundary migrates downward. The rate is calculated using (Stuyfzand 1993):

$$v_{CaCO_3} = \frac{2.5\,Ca^{@}N}{(1-\varepsilon)\,\rho_s(CaCO_3)_{solid}} \tag{3}$$

with ε = porosity [fraction by volume]; ρ_s = density of solids [kg/dm^3]; $(CaCO_3)_{solid}$ = mean $CaCO_3$ content [mg/kg dry weight]; N = mean annual groundwater recharge [m/a]; $Ca^{@} = Ca^{2+}–0.021\ Cl^-–SiO_2/6$ = the mean Ca^{2+} concentration (mg/L) of the groundwater beneath the decalcification front, as derived exclusively from $CaCO_3$ dissolution; and 2.5 = conversion factor of Ca^{2+} to $CaCO_3$.

The mean $CaCO_3$ content of unleached dune sand near Bergen is about 2000 mg/kg (dry weight), $\varepsilon = 0.4$, $\rho_s = 2.65$ kg/L, N = 0.4 m/a (about 50% of gross precipitation) and $Ca^{@} = 40$ mg/L (Stuyfzand 1993). This yields a decalcification rate of 1.25×10^{-2} m/a. Below about 8 m of dune sand, beach sand overlies shallow marine sands; both units have a $CaCO_3$ content of about 10,000 mg/kg. The dune area was dated by De Mulder and Bosch (1982) to be at maximum 4850 years old; thus, decalcification may have proceeded to a depth of 8 + (48.5-8/1.25) × (1.25/5) = 19 m. This calculation approximates the observed decalcification depth of 15 m. Groundwater at >30 m below land surface, which is pumped for drinking-water supplies, is well protected against acidification, however, because the Eemian marine sands below 25 m contain 3–15% of $CaCO_3$.

The Leaching of Adsorbed Marine Cations

The flow of fresh dune groundwater has also led to complete desorption of the marine cations Na^+, K^+, and Mg^{2+} (BEX = 0) up to a maximum distance of about 2500 m (*Figure 7*). The adsorption complex of the porous medium was saturated with salt water prior to the formation of the beach barrier.

The retardation factor R_{EQ} for breakthrough of dune water with BEX = 0, is:

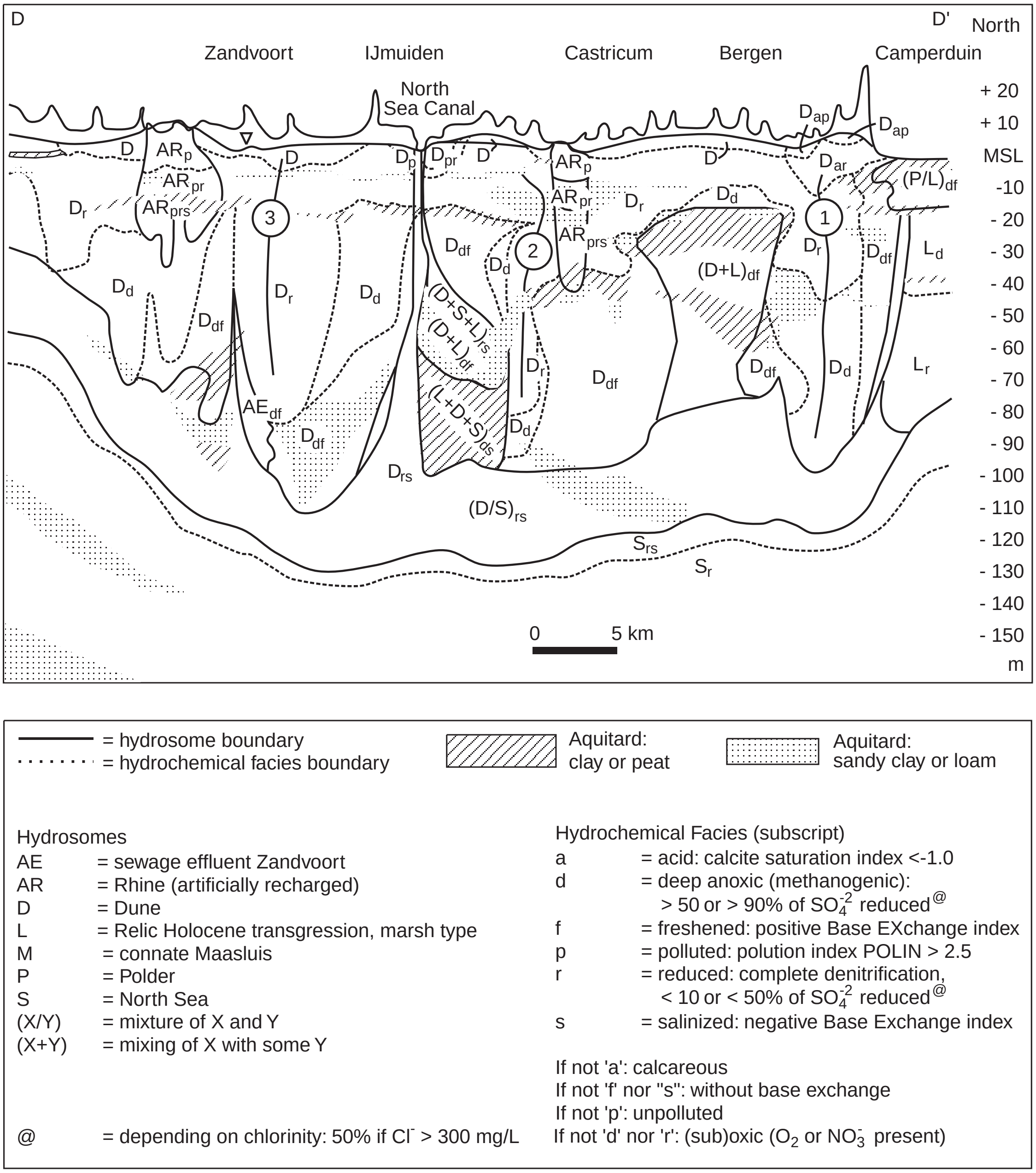
$$R_{EQ} = \frac{t_{EQ}}{t_{H_2O}} = 1 + \frac{\rho_s(1-\varepsilon)\,CEC}{\varepsilon\Sigma k} \tag{4}$$

with t_{EQ} = time for breakthrough of the displacing fluid with BEX = 0, since introduction in aquifer system [d]; t_{H2O} = transit time of the water phase in subsoil [d]; CEC = cation exchange capacity [meq/kg dry weight]; Σk = sum of cations in displacing fluid [meq/L].

This approach assumes one-dimensional, nondispersive flow in a homogeneous medium, and a simplification of the exchange process into a substitution of all ions sorbed during salt-water conditions, by the cations in the displacing fresh dune water.

The maximum age of water at the point of exit from the zone displaying BEX = 0 is calculated to be approximately 300 yr and was confirmed by radiocarbon analysis. Then, with $\Sigma k = 3.5$ meq/L, a mean CEC of 6 meq/kg for the coarse sandy deposits, $\rho_s = 2.65$ kg/L dry weight and $\varepsilon = 0.35$, the R_{EQ} is calculated at 9.3. This result means that the system up to this point must have been flushed with fresh dune water for about 2800 yr. This value corresponds well with the formation and accretion of the Bergen beach barrier during 4850–3000 bp (De Mulder and Bosch 1982) and a time of formation of the total fresh-water lens of 300–600 yr (Stuyfzand 1993).

Figure 8 Areal distribution of hydrosomes and their hydrochemical facies in longitudinal section D–D' in the coastal dunes from Zandvoort to Camperduin in the western Netherlands. Line of section shown in *Figure 1*. The recharge focus areas (*1–3*), which convey the bulk of dune water to the deep aquifers, are characterized below 20 m-Mean Sea Level by a relatively low redox index (reduced instead of deep anoxic) and the lack of a positive base exchange (indicating a freshened facies). (After Stuyfzand 1993)



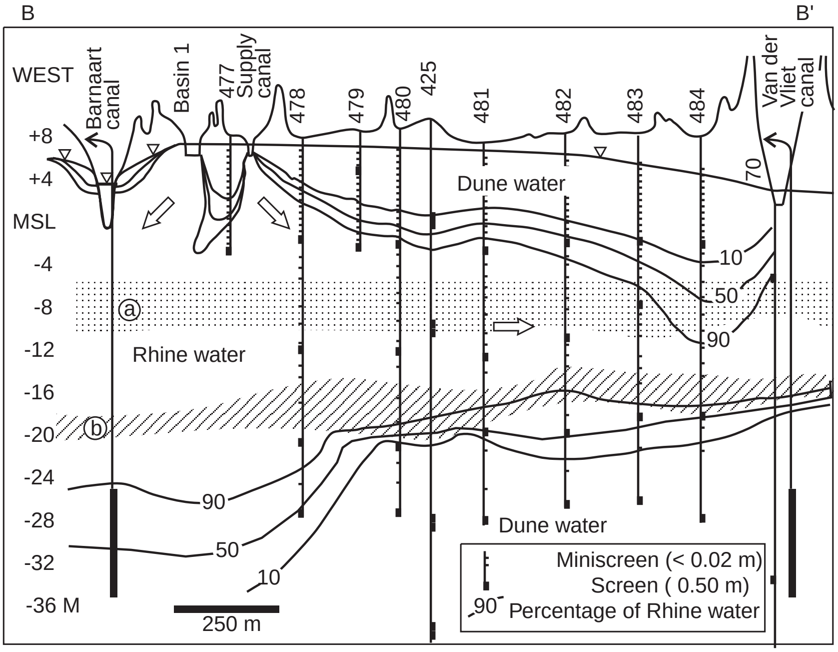


Figure 9 Section B–B' showing the areal distribution of recharged Rhine water in 1982, in the coastal dunes near Zandvoort, western Netherlands, amidst dune groundwater. Line of section shown in *Figure 1*. (After Stuyfzand 1993)

Recharge Focus Areas

Hydrochemical evidence of the main recharge areas in the coastal dunes consists of groundwater that displays a lower prograde quality evolution than the surrounding groundwater. This is the result of less water–sediment interaction and a higher leaching rate in recharge focus areas. Examples are shown in *Figure 8*, a longitudinal section of 50 km of coastal dunes in the western Netherlands. Three recharge focus areas can be discerned on the basis of a less reduced state (reduced instead of deep anoxic) and base equilibrium (BEX = 0) instead of a positive BEX (freshened facies). The recharge focus areas coincide with areas that lack important aquitards (*Figure 8*).

Flow Patterns and Degree of Mixing

Hydrochemistry provides further insight into the actual flow and mixing of groundwaters. An example is presented in *Figure 9*; pretreated Rhine River water has been pumped into basins since 1957 for artificial recharge of the coastal dunes near Zandvoort (see also *Figure 8*). On top of the laterally migrating Rhine water, over a distance of 1 km from the supply canal to the draining Van der Vliet canal, a dune-water lens developed as a consequence of natural recharge (about 0.4 m/a) by rainfall. Rhine water could be easily recognized by its anomalous Cl^- concentration (about 150 versus 25–60 mg/L) and $\delta^{18}O$ (about –9.4 versus –7.5‰ V-SMOW). The nearly stable interface between the dune-water lens and Rhine water parallels flow, whereas the downward moving interface between Rhine water and deep dune groundwater is approximately perpendicular to the flow direction. Groundwater flow between the strongly recharging supply canal and basin 1 contains a component perpendicular to the section. The mixing of the upper dune and Rhine water was accurately modeled with a transverse dispersivity of dune sand of 0.0025 m (Stuyfzand 1993).

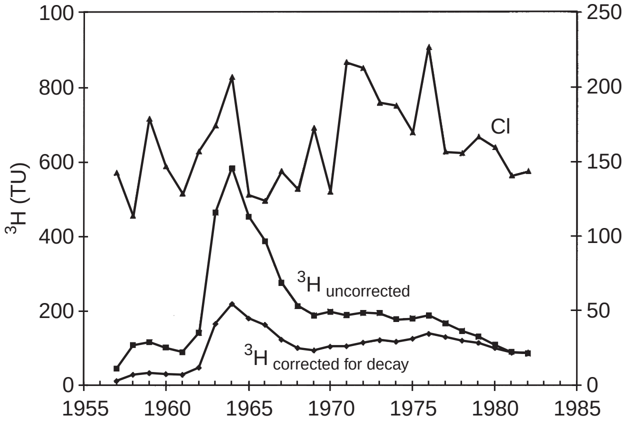


Figure 10 Input signal of tritium and chloride in pretreated Rhine water, recharged in dunes south of Zandvoort. Anomalous years are used for groundwater dating (see *Table 1*)

Age Determination

The same infiltrated Rhine water, as discussed above, was dated in detail using the technique of spatial history matching with the environmental tracers chloride and tritium.

Anomalous years in the input signal of these semi-natural labels, shown in *Figure 10*, were easily traced back in the areal distribution of Cl^- and tritium, shown in *Figure 11*. These years are listed with their character-

Figure 11 Section B–B' showing the areal distribution pattern of chloride and tritium, and the deduced age distribution of recharged Rhine water, in March 1981. 78^A, 78^S = autumn and summer 1978 respectively; *a*, *b* = Holocene aquitard a and b, respectively. Line of section shown in *Figure 1*. (After Stuyfzand 1993)

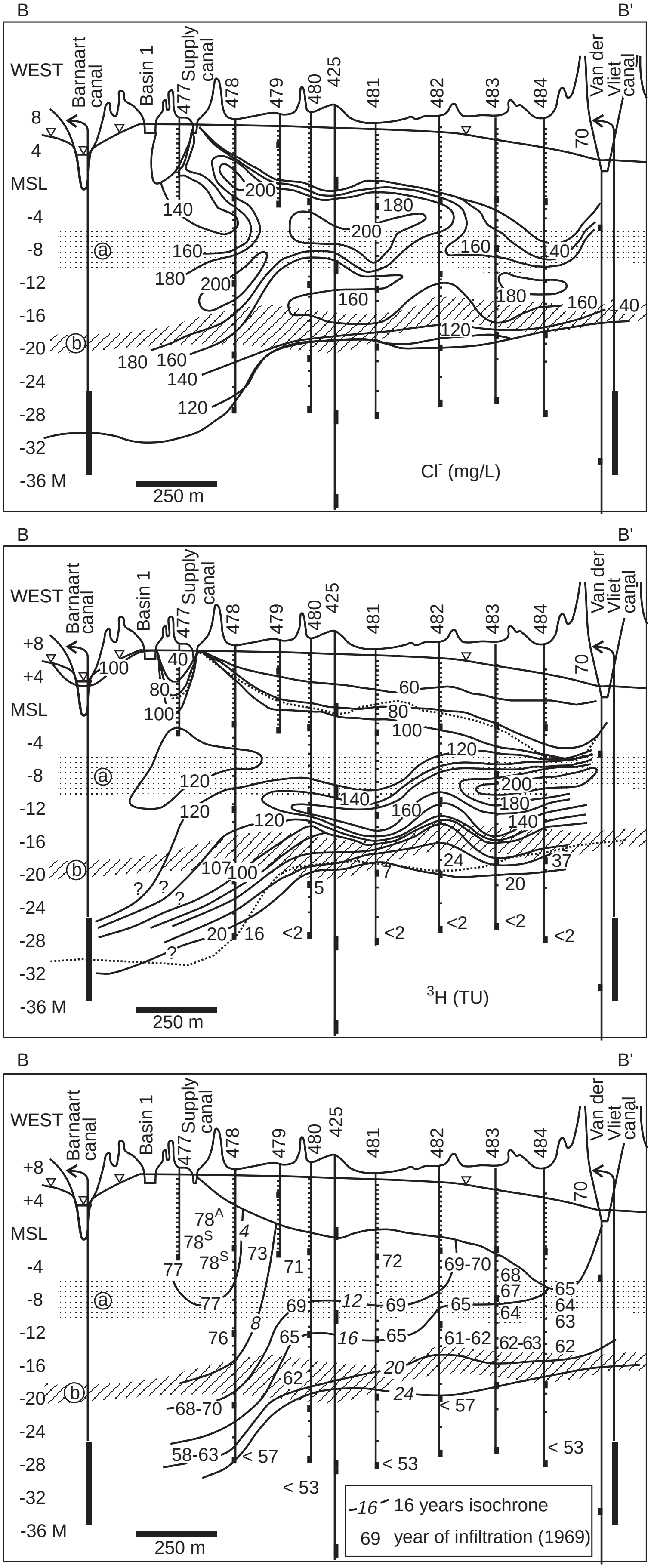


Table 1 Years with an anomalous chloride concentration and tritium activity in pretreated Rhine River water (used to recharge the coastal dunes south of Zandvoort). These years are used for dating Rhine groundwater

Years	Cl^- mg/L	^3H TU
1961–1962	145	60
1964	180	200
1968–1969	150	100
1971–1972	212	110
1976	200	128

istics in *Table 1*. Dune water that infiltrated before 1953 has $^3H < 1$ TU. With these key years, the 24-year interface between Rhine and displaced, deep dune water, and additional information in the input record, years of infiltration were determined for Rhine groundwater samples where possible. The results are shown with the derived isochrones in *Figure 11*. The age distribution reveals, as expected, high flow velocities in the upper aquifer and a strong delay in aquitards a and b. This pattern is distorted by vertical exaggeration and by a very close apparent hydrological position of the wells 480 through 482 (in reality, remote from each other). The apparent hydrological closeness of these wells is related to the oblique position of the cross section and complications in the groundwater flow pattern (Stuyfzand 1993).

The 1964 peak of 218 TU is traced back to 610–790 m without significant smoothing (206 TU), whereas it is leveled off in other parts of the section. This pattern is explained by the low longitudinal dispersivity ($\alpha_L = 0.1$ m) of the homogeneous, well sorted dune, beach, and shallow marine sands, and a much higher dispersivity of the very heterogeneous aquitards a and b ($\alpha_L =$ several meters).

Conclusions

The mapping of water bodies with a specific origin (the *hydrosomes*, like North Sea, Rhine, polder, and dune water), and characteristic hydrochemical zones (the *facies*) within each hydrosome is very useful in areas with a high hydrochemical diversity and abundant data, such as the coastal dunes of the western Netherlands. The resulting maps are very helpful in water-resources allocation, the optimization of monitoring networks, water-pollution control, and the set-up of combined transport–reaction models. They also form a very effective communication tool for transfer of water-quality data in a geographical context, either from expert to expert or from expert to policy maker.

Groundwater monitoring programmes for drinking-water supplies, environmental protection, and nature conservation benefit from such maps in at least two ways: (1) by selecting the strategic positions for monitoring wells downgradient of expanding hydrosomes and downgradient of facies boundaries; and (2) by composing the right analytical programme, e.g., specific trace elements in acidified systems only, and specific organic microcontaminants exclusively in young, (sub)oxic waters or recharged fluvial water.

A deep position of less evolved groundwater amidst further evolved water may indicate the position of recharge focus areas of deeper aquifers. Recharge focus areas are also most susceptible to pollution, because little interaction occurs with aquitards rich in organic matter and other buffering phases, and they therefore require superprotection. The areal distributions of specific hydrosomes and hydrochemical patterns within them offer excellent possibilities of independent chemical verification of hydrological models.

References

Appelo CAJ, Postma D (1993) Geochemistry, groundwater and pollution. Balkema, Rotterdam

Back W (1960) Origin of hydrochemical facies of ground water in the Atlantic Coastal plain. 21st Int Geol Cong, Copenhagen 1960, Rept pt.1, pp 87–95

Champ DR, Gulens J, Jackson RE (1979) Oxidation reduction sequences in groundwater flow systems. Can J Earth Sci 16:12–23

Chebotarev II (1955) Metamorphism of natural waters on the crust of weathering. Geochim Cosmochim Acta 8:22–48, 137–170, 198–212

De Mulder EFJ, Bosch JHA (1982) Holocene stratigraphy, radiocarbon datings and paleogeography of central and northern North-Holland (The Netherlands). Meded Rijks Geol Dienst 36-3:111–160

Drever J (1982) The geochemistry of natural waters. Prentice-Hall, Englewood Cliffs NJ

Edmunds WM (1981) Hydrogeochemical investigations. In: Lloyd JW (ed) Case studies in groundwater resources evaluation. Clarendon Press, Oxford, pp 87–112

Edmunds WM, Bath AH, Miles DL (1982) Hydrochemical evolution of the East Midlands Triassic sandstone aquifer, England. Geochim Cosmochim Acta 46:407–424

Edmunds WM, Miles DL, Cook JM (1984) A comparative study of sequential redox processes in three British aquifers. IAHS Publ 150:55–70

Edmunds WM, Cook JM, Darling WG, Kinniburgh DG, Miles DL, Bath AH, Morgan-Jones M, Andrews JN (1987) Baseline geochemical conditions in the Chalk aquifer, Berkshire, U.K.: a basis for groundwater quality management. Appl Geochem 2:251–274

Engelen GB, Jones GP (1986) Developments in the analysis of ground water flow systems. IAHS Publ 163

Eriksson E (1987) Alkalinity production in soil and rock: a useful concept for understanding acidification of soil and fresh water. In: Norw Nat Comm for Hydrol (ed), Acidification and Water Pathways, Proc Int Symp Bolkesjo Norway 4–8 May 1987, vol 1, pp 29–35

Freeze RA, Cherry JA (1979) Chemical evolution of natural groundwater. In: Freeze RA, Cherry JA Groundwater. Prentice-Hall, Englewood Cliffs, NJ, pp 237–302

Froelich PN et al. (1979) Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. Geochim Cosmochim Acta 43:1075–1090

Hardie LA, Eugster HP (1978) The evolution of closed-basin brines. Min Soc Am Spec Publ 3:273–290

Hem JD (1970) Study and interpretation of the chemical characteristics of natural waters. Geol Surv Water-Supply Paper 1473

Jankowski J, Jacobson G (1989) Hydrochemical evolution of regional groundwaters to playa brines in Central Australia. J Hydrol 108:123–173

Krumbein WC, Sloss LL (1963) Stratigraphy and sedimentation, 2nd edn. Freeman, San Francisco

Matthess G (1990) Die Beschaffenheit des Grundwassers, Band 2, Zweite Auflage. Gebrüder Borntraeger, Berlin

Mazor E, George R (1992) Marine airborne salts applied to trace evapotranspiration, local recharge and lateral groundwater flow in Western Australia. J Hydrol 139:63–77

Muller G (1967) Diagenesis in argillaceous sediments. In: Larsen G, Chilingar GV (eds), Diagenesis in sediments, vol 8, Developments in sedimentology. Elsevier, Amsterdam, pp 127–177

Palmer CD, Cherry JA (1985) Geochemical evolution of groundwaters in sequences of sedimentary rocks. J Hydrol 75:27–65

Ranganathan V, Hanor JS (1987) A numerical model for the formation of saline waters due to diffusion of dissolved NaCl in subsiding sedimentary basins with evaporites. J Hydrol 92:97–120

Runnells DD, Sheperd TA, Angino EE (1992) Metals in water determining natural background concentrations in mineralized areas. Environ Sci Technol 26:2316–2323

Schoeller H (1955) Geochemie des eaux souterraines. Rev Inst Fr Pet 10:230–244

Shipovalov GV (1984) Altitudinal hydrochemical zonations of groundwaters. Water Resources:261–265

Stuyfzand PJ (1984) Groundwater quality evolution in the upper aquifer of the coastal dune area of the western Netherlands. IAHS Publ 150:87–98

Stuyfzand PJ (1989) Hydrochemical evidence of fresh and salt water intrusions in the coastal dunes aquifer system of the Western Netherlands. (Flemish) Natuurwetensch Tijdsch 70:9–29

Stuyfzand PJ (1990) Hydrochemical facies analysis of coastal dunes and adjacent low lands: The Netherlands as an example. In Bakker TWM, Jungerius PD, Klijn JA (eds) Dunes, European coasts, Catena Supplement 18, Catena Verlag, Cremlingen-Destedt, Germany, pp 121–132

Stuyfzand PJ (1992) Behaviour of major and trace constituents in fresh and salt intrusion waters, in the Western Netherlands. In: Custodio E (ed) Study and modelling of salt water intrusion into aquifers, Proc 12th Salt Water Intrusion Meeting, November 1992, Barcelona. CIHS–CIMNE, Barcelona, pp 143–160

Stuyfzand PJ (1993) Hydrochemistry and hydrology of the coastal dune area of the Western Netherlands. PhD, Free University of Amsterdam, published by Kiwa Ltd, Research and Consultancy, Nieuwegein, The Netherlands, IBSN 90-74741-01-0, 366p

Stuyfzand PJ (in press) Fate of pollutants during artificial recharge and bank infiltration in the Netherlands. In: Peters JH (ed) Proc 3rd Int Symp Artificial Recharge (TISAR), Amsterdam. Balkema, Rotterdam

Toth J (1963) A theoretical analysis of ground water flow in small drainage basins. J Geophys Res 68:4795–4812

Toth J (1980) Cross-formational gravity-flow of groundwater; a mechanism of the transport and accumulation of petroleum. In 'Problems of petroleum migration', AAPG Geol Studies 10:121–167

Versluys J (1931) Subterranean water conditions in the coastal regions of The Netherlands. Econ Geol 26:65–95

Volker A (1961) Source of brackish groundwater in Pleistocene formations beneath the Dutch polderland. Econ Geol 56:1045–1057

White DE (1957a) Thermal waters of volcanic origin. Geol Soc Am Bull 68:1637–1658

White DE (1957b) Magmatic, connate and metamorphic waters. Geol Soc Am Bull 68:1659–1682