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CHAPTER 5.2

Groundwater Quality Background Levels

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5.2.1 Introduction

Groundwater forms complex, three-dimensional bodies in which recharge, flow conditions and interaction with the solid matrix are point dependent. This means that, in a given groundwater body, the chemical, radiochemical and biochemical characteristics of water vary both in space (horizontally and vertically) and slowly with time. When anthropogenic effects are added, variations may be intensified with respect to pristine conditions. Thus, the water quality of a given groundwater body cannot be represented by any set of single analytical values, and the degree of human influence cannot be established by a simple comparison to a reference list.

The terms background, threshold and baseline quality values have been classically used in many scientific disciplines to try to identify anomalous concentrations with respect to what are considered as "typical" values. These values are critical to define water quality for a given use, and have to be defined for groundwater as a guide for protection and remediation programmes.

The baseline chemical composition or baseline quality of a groundwater body may be defined, quite instinctively, as the physicochemical conditions due only to natural processes during recharge, flow and water–rock interaction. Should this be possible, any impact on groundwater quality could easily be shown by comparing actual values to baseline values. Nevertheless in practice, problems appear when defining baseline due to the common variability of the significant different chemical parameters. It is necessary to know whether a given concentration is natural, the result of hydrologic changes due to human activities or the result of introducing substances from outside into the groundwater body.

Any adverse change in physicochemical properties is called contamination, and the substances producing this change are called contaminants. If these substances are artificially introduced in some way they can be called pollutants, and the result is pollution (see Chapter 1). These are the definitions that will be used in this chapter, although they are not universally admitted.

Natural variability can be taken into account by describing the statistical distribution of values for any given parameter of interest reflecting the water's natural quality of a groundwater body. This implies that a large enough number of unbiased measurements were made, which is not an easy task in a large, three-dimensional groundwater body. For a given chemical or physical parameter, the range and distribution of values can be described by a set of statistical magnitudes like the mean, median, standard deviation, percentiles, maximum, minimum, *etc.*, or by its full statistical distribution. In practice, this can be done only for a limited number of samples and for a small number of characteristic parameters, which may vary from case to case. Although this is not a new problem, existing experience is currently limited. However, statistical values are badly needed to correctly and effectively apply the recently adopted Groundwater Water Framework Directive (WFD),[1] and especially the recently adopted Groundwater Directive.[2]

The situation explained above was in mind when the European Union BaSeLiNe (Natural Baseline Quality in European Aquifers, EVK1-CT1999-00032 and EVK1-CT-2002-00527) project was elaborated. The project started in 1999 and closed in 2003.[3] In this project the following definition of baseline was adopted: "groundwater quality baseline is the concentration range in water of a given element, species or substance, derived from natural geological, biogenic or atmospheric sources."

Thus, chemical concentrations are considered, taking into account water-rock interaction and the natural behaviour of chemical compounds along groundwater flow lines. Both atmospheric contributions and chemical reactions are time dependent, and not all components have the same residence time in the system. As a consequence, the quality baseline of a given aquifer shows a range—sometimes a wide one—of values that varies in space and evolves slowly with time. For a given groundwater body, lithological heterogeneity and the fact that groundwater moves following more or less well-defined flow lines are the main contributors to baseline spatial variability. The main actions controlling baseline temporal variability are chemical reactions (redox, mineral solubility and surface processes such as adsorption and ionic exchange) and recharge conditions. This one involves evapo-concentration of airborne and soil-released salts, as well as solutes contributed by surface water.

Groundwater pollution may clearly appear when looking at specific substances introduced as pollutants (tracers) and non-existing (to some extent) from baseline, especially those of fully artificial origin. Substances such as NO_3, NH_4, F, As, heavy metals, some radioisotopes (and isotope changes) may not be suitable tracers for pollution, since they may also appear naturally in groundwater under some hydrogeological conditions.

The objective of the BaSeLiNe project was twofold: (i) setting scientific criteria to define groundwater quality baseline, and (ii) developing standard methods to

be applied in the European Union territory in order to guide in the fulfilment of the WFD requirements. The project, coordinated by researchers of the British Geological Survey, initially consisted of a consortium of 11 research groups of 9 European countries: Denmark, Spain, Portugal, Belgium, France, Estonia and Poland, United Kingdom and Switzerland as an associate country; later on, in 2002, they were joined by three other countries: Malta, Bulgaria and Czech Republic, which at the time were in the process of joining the European Union. The main objectives of the project were attained by means of theoretical and practical conceptual approaches, based on experience and real data from 21 aquifers of the consortium countries. It is clear that each aquifer is unique and its baseline quality depends on a particular combination of geological, hydrodynamical, climatic and soil cover characteristics. This means that results from a given aquifer cannot be used to accurately characterise any other aquifer. Nevertheless when climatic conditions, including distance to the coast, are not too different and of secondary importance, it is possible to establish some typologies, based essentially on the dominant lithology, in order to help defining baseline quality and planning analysis sampling, monitoring and study. But lithology is only one of the many factors influencing baseline quality. It becomes dominant in well-recharged aquifers by continental rainfall, but climatic conditions may dominate in semi-arid and arid areas, especially near the seashore, reducing and even overcoming the importance of lithological influence. This is a common situation in many peri-Mediterranean areas. Furthermore the residual influence of the sea on sediments may exert an important influence on groundwater quality, as happens in numerous coastal areas. Figure 5.2.1 shows how the airborne chloride deposition rate varies on continental Spain and how this is translated into groundwater chloride content due to water evapo-concentration in the soil.

In this chapter some of the main methodological and conceptual results of the BaSeLiNe project are mentioned to illustrate how to determine the natural quality baseline of groundwater. This includes both the items to be considered and the preventive measures to be taken into account. The final report of the project was made available via the internet.[3]

5.2.2 Rationale to Establish the Groundwater Quality Baseline

The need to define and establish baseline values of groundwater quality, and the criteria to set them, are a consequence of the enforcement, over the years, of different acts and laws. In the USA, the Environmental Protection Agency (EPA) relies on the Federal Water Pollution Control Act Amendments of 1972, amended in 1977 and revised several time through the years. It is known as the Clean Water Act. Although dealing mostly with surface water, this act considers cleaning polluted groundwater in disposal sites and recognises that planning is needed to address the critical problems posed by non-point-source pollution.

In the European Union, the WFD (2000) has been enacted, the main objective of which is setting the framework to protect continental, surface,
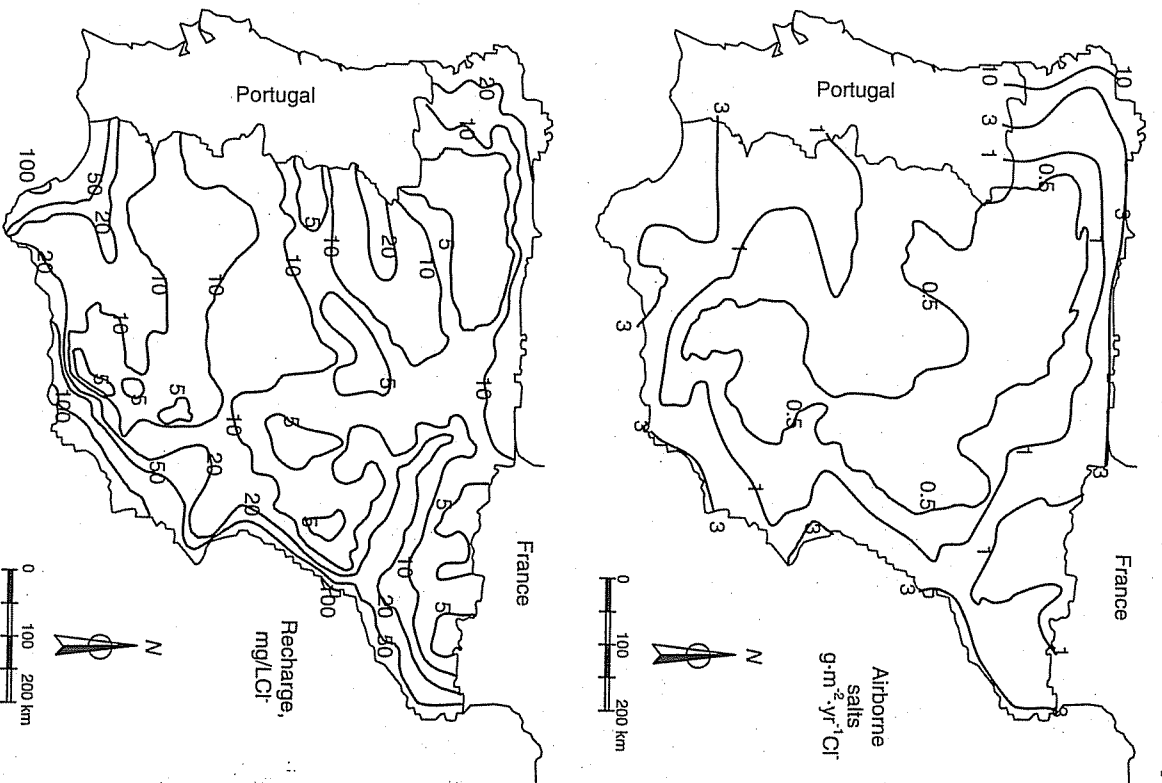
Figure 5.2.1 Change of chloride content in groundwater in continental Spain. The upper panel shows atmospheric airborne chloride contribution in $mg \cdot m^{-2} \cdot yr^{-1}$ and the lower panel shows the result of climatic/pedologic evapo-concentration, once discounted runoff, as reflected in chloride content ($mg\ l^{-1}$) in the upper part of the groundwater table. Chloride baseline changes conspicuously throughout the territory. (Modified from Ref. 4.)

transitional, coastal and ground water, in order to prevent any further environmental deterioration and to improve current status. The Groundwater Directive,[2] which was adopted at the end of 2006, is aimed at establishing strategies to prevent, control and correct groundwater contamination, as stated in Article 17 of the WFD. It neither modifies nor enlarges the WFD objectives, but complements them in a way that presents some difficulties, since it is still insufficiently known by many of the officials that have to apply the provisions. The European directives are obligatory in the European Union territory, and have to be incorporated into national legislations in accordance with the subsidiarity principle. In fact, the WFD is now incorporated into countries' national laws and water acts, and related legislation and rules have been, or will be correspondingly adapted (see Chapter 3.1 for further details).

In North America (USA and Canada), the term baseline applied to natural groundwater quality appears often in documents of the EPA and the United States Geological Survey (USGS), since at least the mid-1990s. But it seems that there is neither an official document giving a definition nor the criteria to establish it. In Europe, the WFD does not use explicitly the term baseline, but the expression "background levels." Moreover, it mentions repeatedly what is called "quality of surface water and groundwater bodies of the different countries." A "groundwater body" is defined as a clearly differentiated volume of groundwater inside a given aquifer or aquifer system.

Furthermore, the new Groundwater Directive[2] incorporates the term "threshold values," meaning "a concentration limit for a pollutant in groundwater, the exceedance of which would cause a body of groundwater to be characterised as having poor chemical status."[2] The baseline or "threshold" should be established in waters participating actively in the hydrological cycle, except if they are already modified by contamination. This participation may be due to natural conditions or created by human intervention, such as pumping or deep drainage.

Taking into account the spatial and temporal variability of natural quality, baseline composition and the current scarcity of monitoring data and knowledge on the functioning of many aquifers, the Groundwater Directive does not provide a list of quality standards to be uniformly applied in the whole European Union, though it prescribes the application of existing nitrate and pesticide norms. In this respect, norms on drinking water, which are useful to protect human health, are not necessarily adequate as environmental guidelines. However, from this derives that groundwater bodies in "poor chemical status" are overcome must be classified as water bodies in "poor chemical status."

Thus, a body or group of bodies of groundwater shall be considered as having good groundwater chemical status when, according to the WFD and new Groundwater Directive,[1,2] the nitrate concentration does not exceed 50 mg l^{-1} NO_3 (or a lower one if established for a nitrate vulnerable zone, following Directive 91/676/EEC), and the total content of active ingredients in pesticides, including their relevant metabolites (degradation and reaction products), does not exceed 0.1 mg l^{-1}. With regard to any other polluting substances, and especially for NH_4, As, Cd, Cl, Pb, Hg, SO_4, trichloroethylene and

tetrachloroethylene, groundwater status has to be below the threshold value set by each country.[2] The member states of the European Union are encouraged to enlarge the list according to identified risks to groundwater.

The rationale for the new Groundwater Directive[2] mentions that the 2003 meeting of the BaSeLiNe project in Funchal, Madeira Island, stressed the difficulty of setting uniform quality standards for groundwater, and emphasised the need to consider aquifer characteristics and actual pressures from human activity. Moreover, the document establishes criteria to identify significant and sustained upward trends in pollution from human activity and to determine if there is a reversal, calling for a common methodology to test the statistical significance of these trends (Article 1 of the directive).

In order to correctly monitor the possible natural baseline deterioration of the different water bodies, following the conclusions of the BaSeLiNe project, some groundwater "types" may be considered, according to the kind of aquifer containing the water and the concentration range of specific baseline indicators. Nevertheless, as already stated, baseline is a complex result and consequently the aquifer type is only one of the factors.

5.2.3 Methods to Establish the Natural Baseline Quality of Groundwater

To establish the baseline quality of an aquifer or groundwater body, the ideal situation is when available chemical data correspond reasonably well to areas unaffected by human activity. Generally this means pre-industrial age water. But this is not always easy or possible to get. Shallow levels of water table aquifers often contain anthropogenic components of diverse origin (acid rain, airborne pollutants, agrochemicals) and must be discarded. Multilayer aquifers present, in theory, some ideal conditions to obtain non-impacted waters from their deepest levels, provided they are not stagnant or contain saline water. However, often wells and boreholes are poorly constructed and grouted, and may produce a by-pass between exploited deep and shallow contaminated levels. This means that, sooner or later, young contaminated water may penetrate pre-industrial age water levels. Nevertheless, in some cases, there are aquifers containing pollution-free, young water, which are fully acceptable to characterise the reference natural baseline quality.

In order to distinguish water of natural origin from anthropogenically impacted water, the BaSeLiNe project[3] recommended the following approaches to be adopted, if applicable: (1) looking for the evidence that water age (or mean residence time) exceeds 50 to 100 years; (2) extrapolating available chemical data time series backwards, until it reaches a (theoretical) initial time in which there was no anthropogenic activity in the area; and (3) looking for substances that are clear indicators of human activity. These substances may be agrochemicals and their degradation compounds (including metabolites of pesticides), industrial products or an increase of dissolved nitrogen species or of total dissolved organic carbon. In order to identify the existence of a fraction

of young water with an anthropogenic influence, fully artificial substances are especially useful, such as many organic solvents, SF_6, CFSs, etc. Even though the presence and the impact intensity of anthropogenic contaminants in water can be currently easily identified through modelling, this approach allows taking reasonable initial decisions on the way, provided that the significant compounds are analysed with the needed analytical sensitivity, at least in the survey stages, independently of being part of the monitoring program.

One of the more frequent contamination forms is the arrival to the recharge area of a given aquifer or water body of airborne contaminants external to the zone. This complicates the determination of natural quality baseline in small, intensively exploited aquifers, which are often an essential local water resource characterised by the short turnover time. The BaSeLiNe project suggests using, as a reference for these aquifers, the natural baseline established for other aquifers under similar geological, hydrogeological, climatic, etc., characteristics, reinforced when needed with the help of hydrogeochemical modelling, and the drilling of new monitoring boreholes for sampling, when some parts under natural conditions can be expected to be found.

Since the same non-impacted aquifer may contain groundwater bodies of different chemical composition (e.g. due to the presence of redox fronts, ion exchange gradients, waters of diverse marine continental origin), in practice the natural baseline quality of specific water bodies and their characteristic values should be explained by means of some main geochemical processes and the heterogeneities existing in the aquifer. In order to explain correctly a given baseline quality composition of a water body inside an aquifer, it is convenient to use ambient descriptor properties (and terms) such as "confined," "water table," "oxidant," "reducing."

The different integrated tools applied in the BaSeLiNe project are commented on below. They constitute a proposal of methodology to establish the natural groundwater baseline quality, and contain the main conceptual and applied results of the project.

These tools are:

- to study the major and trace inorganic components chemical data, in order to establish the variation range of natural baseline quality;
- to study the organic carbon data in order to establish the variability range of baseline quality and its usefulness as a contamination indicator;
- to carry out hydrogeochemical modelling, in order to identify and establish the types and characteristic times of the basic reactions controlling the baseline quality of the different aquifer types;
- to use tracers and dating techniques to know the time scales that control the variation ranges of the different components under consideration;
- to study baseline trends to know their causes and how to discriminate between those due to natural processes and those due to contamination.

Adequate sampling, which is a key issue to know aquifer water quality, has to address the three-dimensional character of groundwater flow and the importance of surface processes.[5,6]

5.2.1 Study of Major and Trace Inorganic Component Chemistry

Natural water quality depends on characteristic concentrations of different components, represented by the statistical mean or median of a set of values and their distribution (dispersion) around these central values. If the distribution is normal or log-normal, it is possible to define their dispersion by means of the standard deviation. However, often this is not the case due to the simultaneous or correlative presence of more than one physicochemical process. In the BaSeLiNe project, in order to define the baseline quality, and after a first evaluation of available data, it was decided to adopt the median as the most characteristic value for a parameter or component, and the 2.3% and 97.7% percentiles to show the variation range. Thus, most of the studied population (95.4% for a normal distribution) is inside the range.

In order to reasonably describe the possible spatial variation of baseline quality, the chemical study of an aquifer or groundwater body should be carried out by using a large enough number of groundwater samples. This implies that new samplings may be needed. Moreover, this means that historical data prior to 1985 should be evaluated before being integrated to the younger ones, since many analytical techniques were less accurate than the current ones, and detection limits were too high for some components.

An approach based on simple statistical, univariant techniques is proposed to establish characteristic values and variation ranges. In the BaSeLiNe project the cumulative frequency representation of data was selected in order to identify the main processes controlling the observed distributions (Figure 5.2.2). This type of representation was already used by Davis and de Wiest[7] to show the distribution of elements in fresh groundwater. Figure 5.2.3 is a simple case. Other graphical representation types, which were considered adequate to show the natural baseline, are the box or whiskey plots (Figures 5.2.4 and 5.2.5) and that of time/space evolution of concentrations.

Some of the main methodological remarks are the following.

- For populations not following the normal or log–normal distribution, outliers may be part of groundwater composition natural baseline quality and not necessarily the result of contamination. Such are the appearance of dissolved Fe^{2+} and Mn^{2+} in reducing groundwater ambients, the disappearance of NO_3^- and SO_4^{2-} in similar environments or the high concentrations of sulfate when sulfide-rich sediments are supplied with dissolved oxygen or become desaturated. Thus, a careful study of these data is needed.

- The baseline quality variability may be of the same order of magnitude or even larger than that produced by contamination.

- The natural baseline quality being established depends on available data, and it is often biased due to diverse circumstances, such as taking samples by pumping (selection of the most permeable layers) or carrying out samplings with preference for some depths, or by mixing different flow lines (Figure 5.2.6).
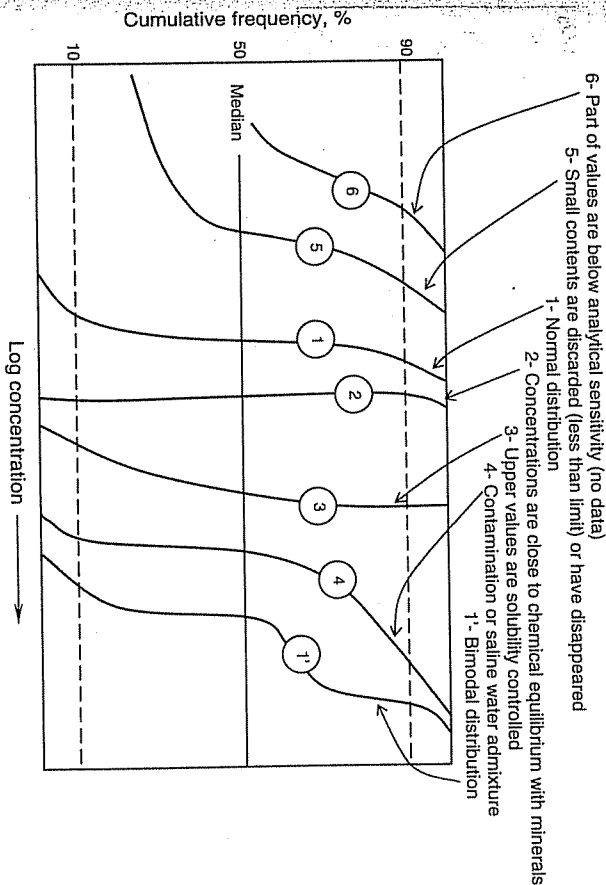
Figure 5.2.2 Plot of cumulative frequencies of chemical parameters, showing some typical circumstances. The median is used as the regional reference level, or the value to compare different parameters. Type 1, normal distribution; type 1', multimodal (bimodal as shown) distribution, both reflecting variability of recharge, water–rock interaction and turnover (residence) time in natural flow systems. Type 2, small variability due to closeness to chemical equilibria with relevant minerals (for Si, Ca, Mg, etc.). Type 3, small variability at high concentrations reflecting that mineral solubility exerts control (e.g., fluorine content due to fluorite dissolution). Type 4, large variability of high concentrations resulting from addition of contaminated or saline water to a small fraction of samples. Type 5, fast decrease of low values pointing to the preferential reduction or elimination of a component by a geochemical reaction (e.g. nitrate reduction or sulfate reduction). Type 6, low values are below a threshold due to analytical conditions. (After Ref. 3.)

As a consequence, the following guidelines are proposed to determine the baseline quality of an aquifer or water body.

- To exclude samples known to be contaminated (information provided by some components).

- To carry out samplings along a flow line and normal to it. The data used must take into account the three-dimensional distribution of water characteristics in the aquifers. This means considering the sample position with respect to the groundwater flow network. In many cases what matters is the flow configuration existing under prevalent aquifer conditions, due to the slow movement and replacement of groundwater, and not the current flow regime under disturbed conditions. This may be a major handicap for studies lacking scientific support.
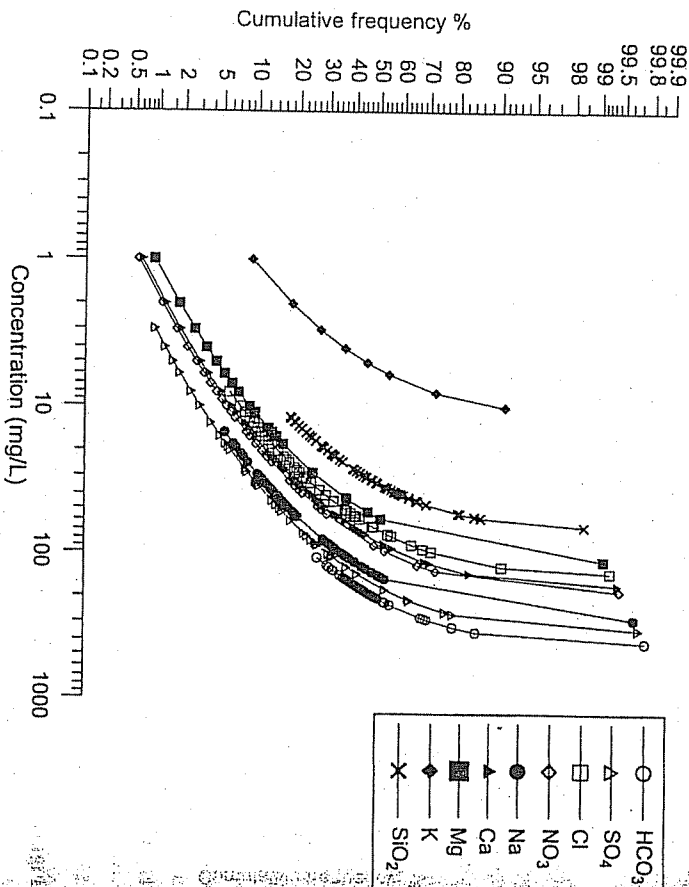
Figure 5.2.3 Plot of cumulative frequencies for major ions in Madrid's basin aquifer. Fresh recharge water from the basin sides mixes with saline remnants in the central basin sediments, derived from old playa lake situations. The higher values are controlled by reactions with sedimentary silicates. (After Ref. 8.)

• To compare local data to information from other areas that are surely not affected by human activity.
• To use times series, when existing, to detect early time conditions.
• To use hydrogeochemical modelling as a tool to know if the assumed and deduced processes are natural or need artificial conditions to be active.
• To make a limited use of statistical techniques, since hydrologic and hydrogeochemical considerations are generally not taken into account and thus not enabling key processes to be clearly identified.

5.3.2 Organic Component Chemistry

Organic carbon dissolved in groundwater is an important reactant in natural geochemical processes. Furthermore, it may be useful to determine the natural or uncontaminated status of a given water as a contamination indicator, e.g. of disposal sites and used waters, and may be a potential contaminant as well. It is a source of energy and food to bacterial populations, both in aquifers and in distribution networks, and also plays an important role in the mobilisation of trace metals, radionuclides and biogenic components coming from outside.
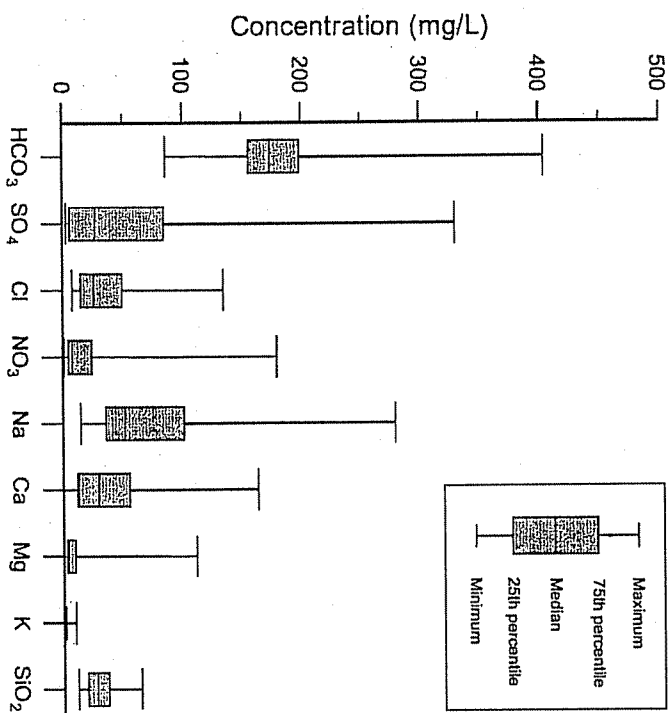
Figure 5.2.4 Box plot (whiskey plot) of major ion concentrations in groundwater samples from Madrid Tertiary Detrital aquifer. Groundwater is predominantly of the sodium bicarbonate type, in agreement with the arcosic nature of sediments, but there is also some saline groundwater formed in old evaporating playa lakes, of mostly the sodium-calcium sulfate type. Excess sodium is part of baseline. (After Ref. 8.)

Additionally, its presence and concentration is important for the evolution of underground redox fronts.

Organic carbon is part of the organic matter present in groundwater, which is of two types: humic and non-humic substances. The latter group includes decomposable plant material, living biomass and woody plant material. Both types can be present as solved species or as particles. All natural waters contain some dissolved organic carbon (DOC), here considered—from a practical approach—as that remaining in water filtered through a 0.45 μm sieve. The total organic carbon (TOC) is that measured in unfiltered waters and includes both the dissolved and the particulate fraction (larger that 0.45 μm), such as bacteria and phytoplankton. For correctly sampled groundwater, in most cases DOC is about the same as TOC since the sieving effect takes place in the aquifer, except for coarse formations, in which even some micro-organisms could be transported. Work carried out mostly in the last decade recognises the significant role of TOC in some important hydrogeochemical processes, such as natural weathering or redox reactions, which control the evolution of some hydrogeochemical environments in aquifers. Furthermore, the particulate matter, especially that of colloidal size (most of it smaller than 0.45 μm),
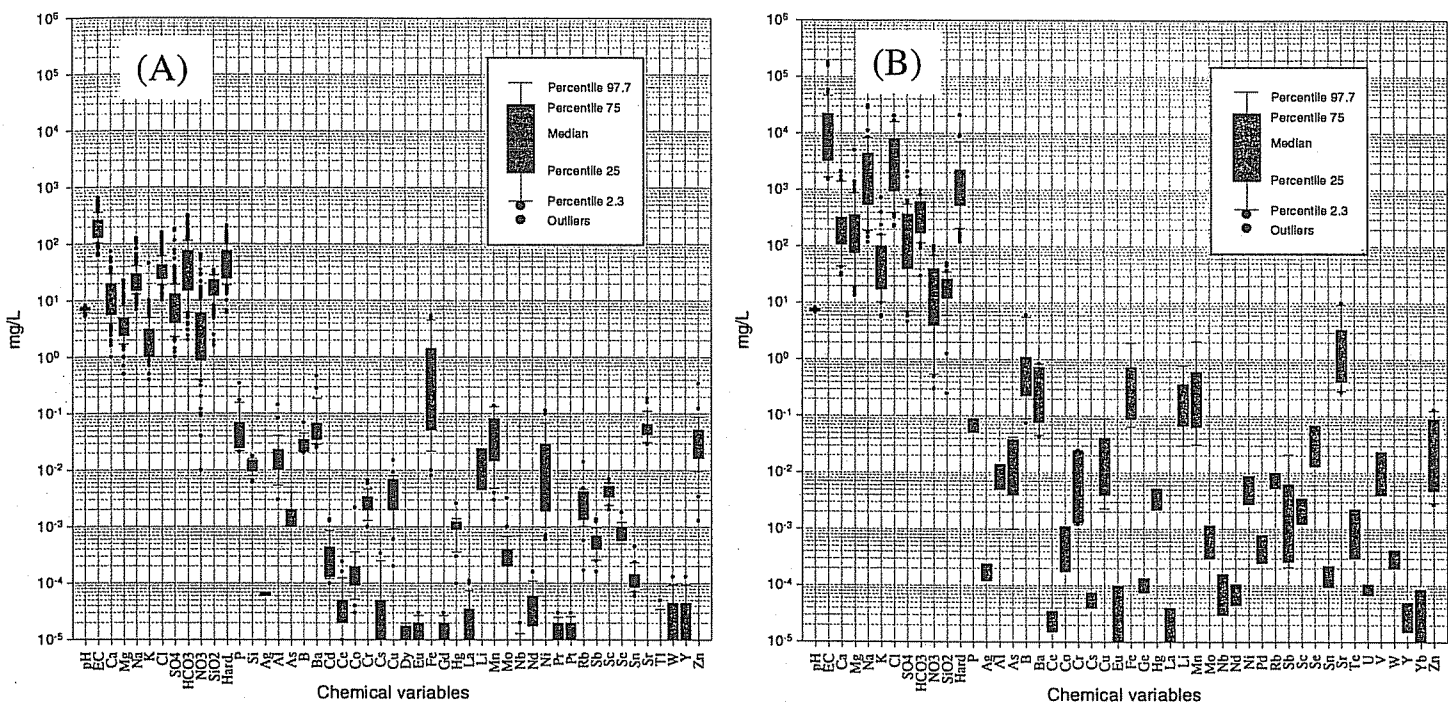
Figure 5.2.5 Whiskey plots (box plots) to show median and range variation of different major and trace components and physicochemical parameters of interest for baseline quality in fresh water (A) and saline water (B) of the same aquifer (Doñana, southwestern Spain). The aquifer system has at least two hydrogeologically different water bodies. (After Ref. 9.)
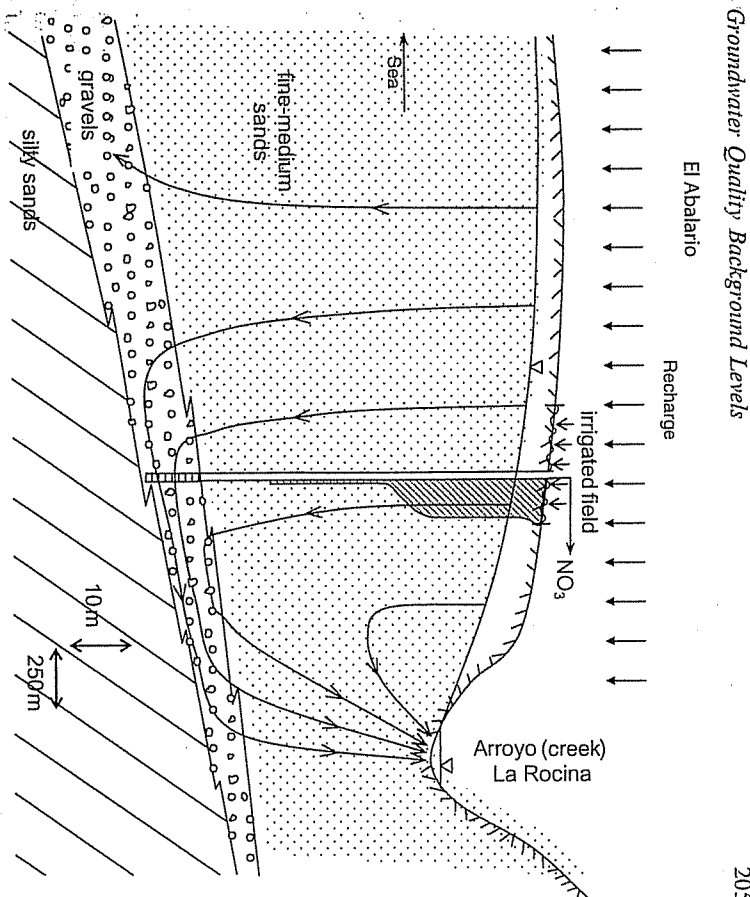
Figure 5.2.6 Schematic representation of aquifer behaviour in El Abalario, Doñana Natural Park (Huelva, Spain), showing a cross-section between El Abalario dome and La Rocina creek. The water table aquifer consists of fine–medium sands with a thin coarse layer of a much more permeable gravely formation, where wells have their screens. The flow lines (lines with arrows) have an important vertical component, which is downwards in most of the area. Nitrate contamination in irrigated fields (mostly fruit trees and strawberries under plastic cover) moves downwards in the sands, at about 0.5 m per year. Currently a large part of the sands is contaminated by high concentration of nitrate, but this still does not appear in many wells that are deep screened nor in deep discharges into the main water course, though it does in the shallow local creeks. Well water still shows baseline values but the water body is seriously damaged, and it will progressively worsen. The medium is oxidant, so nitrate is not reduced. In other areas, in which the aquifer is thinner, nitrate pollution attains the full thickness.

plays an important role in the transport, mobilisation and degradation of contaminants.

Natural groundwater often has TOC concentrations less than a few milligrams per litre, although values higher than 50 mg l⁻¹ can be occasionally found. Data studies carried out within the BaSeLiNe project show that TOC concentrations decrease with increasing depth, and that differences between median values of natural water from siliceous and carbonate aquifers containing young and old water are small. The measured values vary between 0.7 and 1.8 mg l⁻¹, which are significantly smaller than those measured in clearly

contaminated aquifers, in which the values may be of the order of several tens to some hundred milligrams per litre.

A clear relationship between TOC and other similar parameters such as assimilable organic carbon, halogenated organic compounds or the bacterial counting has not yet been found, and the scientific knowledge about the different organic molecules and their reactivity, toxicity and ability to mobilise various contaminants is still being developed. Though early work was done more than 40 years ago,[10] research intensification has occurred during the last ten years, producing excellent manuals[11] and a good number of scientific papers. Published work is mostly related to biodegradation in natural remediation, paying attention to some compounds (plaguicides, halogenated organic carbons, hydrocarbons) and their metabolites, as well as selective behaviour through ^{13}C isotope evolution.[12,13] The knowledge gained in upcoming years could be relevant.

5.2.3.3 Hydrogeochemical Modelling

As already stated, groundwater natural quality is the result of complex interactions between the solid, gaseous and liquid phases. The resulting composition may be in some places of the same or of a higher order of magnitude than that due to contamination in other places. Hydrogeochemical modelling coupled to water flow is a necessary tool to get a qualitative and quantitative knowledge of the main and more frequent processes controlling groundwater quality (dissolution/precipitation, ion exchange, redox reactions, adsorption; Figures 5.2.7 and 5.2.8). Once the significant processes are known and quantified, modelling can be used to predict future water quality changes, both due to ambient
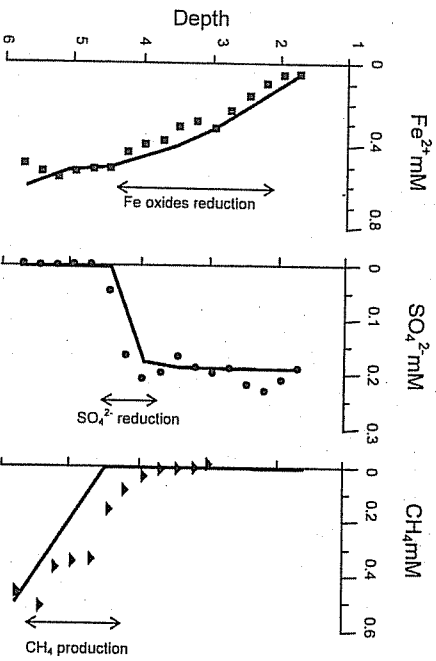
Figure 5.2.7 Interpretation of chemical logs along boreholes to show hydrogeochemical changes when going through a redox front. Data points are experimental values and the continuous curves are the result of flow and transport modelling. Values are in mmole l⁻¹ (mM). (After Ref. 3.)
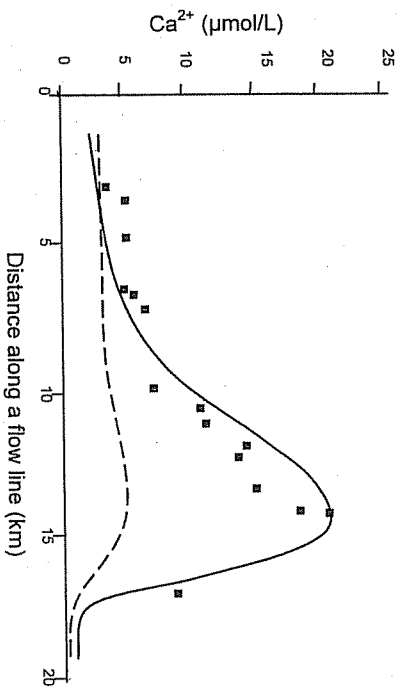
Figure 5.2.8 Interpretation of measures along a flow line to show hydrogeochemical changes when there is water-rock interaction. Only Ca^{2+} evolution is shown. Data points are experimental values and the curves are the result of flow and transport modelling, with only one process (insufficient to explain results) and with two processes. (After Ref. 3.)
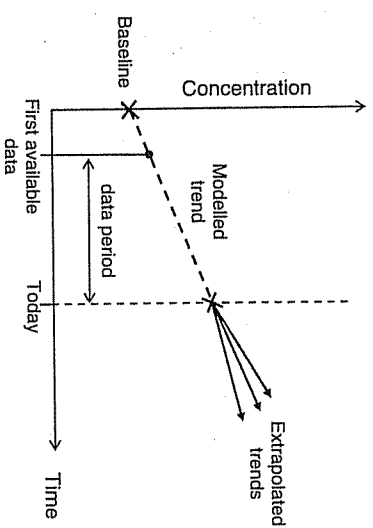
Figure 5.2.9 Schematic representation of trend modelling using the data period. Extrapolation backwards until anthropogenic processes are not present or a steady state is observed allows the approximate knowledge of baseline quality for the chemical parameter being considered. Extrapolation forwards allows visualisation of trends under given scenarios or hypothesis. (After Ref. 3.)

natural variations (e.g. natural climatic changes, tectonically induced flow modification, subsidence, sedimentation, erosion) and to the impact of different human activities, including the future removal of some of the current ones (Figure 5.2.9). Modelling facilitates the study of spatial and temporal trends, and helps in the correct design of expensive monitoring programmes.

In the BaSeLiNe project, programme PHREEQC was used to study the processes responsible for the natural composition observed and its evolution, especially the changes occurring along a flow line in three aquifer types that illustrate frequent situations in Europe: silica-dominated sedimentary aquifers with rare carbonates; carbonate aquifers or aquifers containing abundant carbonate; and aquifers with old saline water being displaced by younger fresh-water. More sophisticated approaches, although not necessarily more effective, are those simulating flow and reactive mass transport. Nevertheless a detailed insight to processes allows one to define more accurately what is happening[14] or to identify controlling facts, e.g. in seawater intrusion into aquifers.[15] The most significant conclusions related to modelling are the following.

• Many patterns and trends appearing often in natural waters, such as ion exchange gradients, are the result of processes occurring at geological time scale and are generally due to flow conditions that preceded those existing today, even if equilibrium is quickly attained. Under such conditions the supply of reactants may be the limiting factor. This means that the "time" parameter must be carefully used in simulation works. Independent dating measures using different tracers are desirable to limit uncertainty. When this information is not available and time is derived from a modelling exercise, the uncertainty associated must be clearly shown.

• Groundwater development distorts natural chemical gradients, and this is very difficult to correct and simulate. Mixing processes between old and young waters also change the original composition. Therefore, some discontinuities in the natural composition of some aquifers may be due to "age gradients," while smooth changes following the groundwater head gradient show the existence of continuous processes.

• When an aquifer does not contain water of natural origin, modelling may yield a realistic estimation of the original concentration of some elements.

5.2.3.4 Tracers and Temporal Scales

In order to interpret water quality changes referring to variation of the natural baseline quality, the knowledge of the age – the turnover time – of groundwater in the flow system is needed, as well as the temporal scale at which the different hydrogeochemical processes explaining natural baseline chemistry occur. Under favourable conditions water age may be reasonably estimated with sufficient accuracy, but this may be often impossible, due to the unavailability of suitable ideal tracers. In order to solve these difficulties, the use of several tracers and the numerical simulation of water flow and solute transport are necessary. The dating principles are the following.

• It is interesting to measure the components whose concentration in water varies along time, due to known causes distinct from water-rock inter-action.

• These components are like "clocks." The different known types are:
– cumulative processes (^{3}He, ^{4}He, some chemical components, etc.)
– radioactive decay processes (^{39}Ar, ^{14}C, ^{32}Si, ^{3}H, ^{85}Kr, etc.)
– variable but known incorporation to groundwater (^{3}He, CFCs, SF$_6$, etc.).

Within the BaSeLiNe project different tracers (^{13}C, ^{14}C, ^{3}He/^{3}H, ^{85}Kr, ^{39}Kr, CFSs, etc.) and water molecule isotopes (^{18}O, ^{2}H, ^{3}H) are used, mostly to know the groundwater age structure in the studied aquifers (Table 5.2.1). Figure 5.2.10 is an example. Age structure is the result of integrating values derived from different techniques into the hydrogeochemical and hydrodynamical processes responsible for water characteristics, age being one of them. Water age determination implies that processes occurring other than time-dependent ones (e.g. radioactivity) have been adequately corrected to remove other effects such as dilution by dead (non-radioactive) matter or exchange with solid. This is not an easy task. Ages obtained without corrections (or with only partial corrections), namely apparent ages, are only an approximation, and sometimes a crude one. One of the main contributions of time tracers to natural baseline quality determination is the estimation of the residence (turnover) time scale of groundwater in the aquifers being studied. Before carrying out long, extensive and expensive hydrogeochemical studies, this information will help to predict if water will keep in the future its natural composition. This aspect may be shown by determining whether a young water component (^{3}H, ^{85}Kr, ^{39}Ar, CFSs, SF$_6$, etc.) is present or not, taking into account the following.

• If the presence of some (generally various) of these components shows that water is younger than 50 years, this means that it is potentially impacted by human activity. Therefore, it is probable that the natural background has been changed, and consequently the baseline quality. The lack of any young component guarantees that original natural conditions prevail.

Table 5.2.1 Substances (asterisk indicates radioactive) potentially useful for groundwater to date under favourable circumstances and range of years that can be dated.

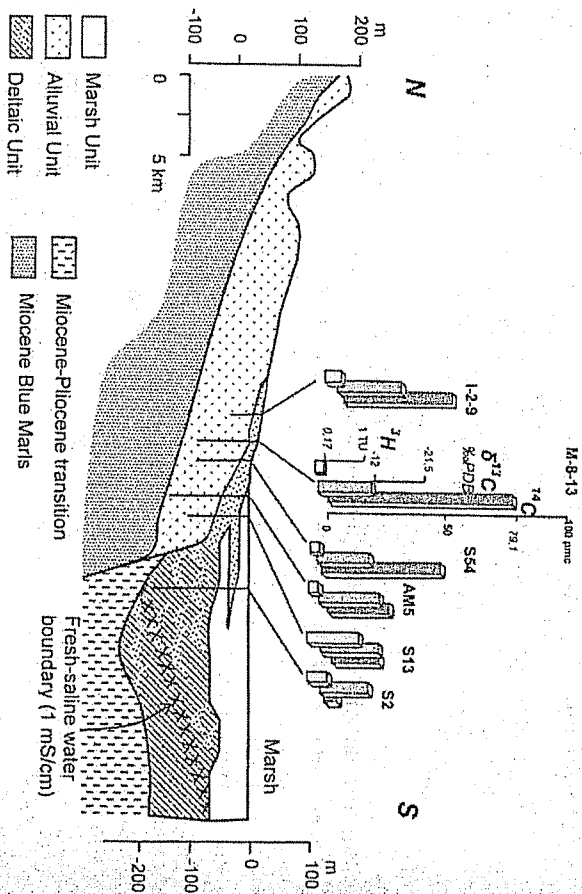| Substance	Origin	Range (years)	Application
^{3}H* (tritium); ^{3}H*/^{3}He	Natural, nuclear bombs, nuclear reactors	5–50 (200)	Easy
^{85}Kr*	Nuclear reactors	10–50	Difficult
CFCs, SF$_6$	Industrial, domestic	10–50	Medium
^{39}Ar*	Natural	50–2000	Difficult
^{14}C* (radiocarbon)	Natural, (nuclear bombs)	1000–20 000	Easy
^{4}He	Natural	200–10 000 000	Medium

Figure 5.2.10 Simultaneous measurement of three isotopes to date in a north-south cross-section in Doñana National and Natural Parks, southwestern Spain. The figure shows tritium (half-life of 12.43 years) in tritium units (TU), radiocarbon (^{14}C, half-life of 5730 years) in percent modern organic carbon (pmc), and ^{13}C content (stable, indicating origin and behaviour of dissolved carbon in the aquifer) in deviation per mile from the PDB standard. Most samples are mixtures of waters from different depths, where relatively high tritium (young water) may coexist with relatively low radiocarbon (old water). This helps in interpreting chemical data. The measurement of ^{85}Kr and ^{39}Ar at some points allow improved understanding. (After Ref. 16)

- If the lack of young components indicates that water age is greater than 50 years, groundwater quality corresponds to water-rock interactions evolving through time. The knowledge of these reactions needs both hydrogeochemical modelling and dating with adequate tracers.

What has been stated allows for the preliminary classification of any chemical parameter, independently of its variation range, into two groups with different residence times: (1) parameters that are measured in water with young components, and (2) parameters that are measured in water free of young components. This simplifies sampling and data treatment, in order to establish the natural baseline quality.

The main result of the study of water residence time in the different aquifers considered in the BaSeLiNe project is that a unique universal technique or set of techniques does not exist, but each aquifer needs the application of a series of specific techniques, which mainly depend on the time scale of water residence time, the geochemical ambient (e.g. in redox media many of the available

tracers may be not useful), the economic resources and the analytical tools that can be used.

5.2.3.5 Study of Natural Baseline Trends

This activity is a result of what is required in the Groundwater Directive:[2] the use of time series in order to

- observe the possible presence of increasing, sustained and statistically significant trends in the concentration of some chemical components, due to contamination; and
- monitor and detect the reversal in these trends after implementing the corresponding remediation actions.

The use of statistical techniques as a principal indicator is still much discussed in hydrogeological forums. If hydrogeochemical and hydraulic techniques are not considered, there is the risk of mistaking natural increasing trends for contamination. In the framework of the BaSeLiNe project the study of historical data sets has been addressed.

- to know which type of time series can be expected to be found in different European Union countries;
- to observe and define natural baseline trends in order to obtain chemical support to understand the natural functioning of aquifers; and
- based on what has been said above, to discriminate natural changes from those due to anthropogenic activity.

Only a few countries have good time quality series on groundwater quality, except for some special aquifers. Length is often less than 15 years, but some Eastern Europe countries have the longest series, up to 70 years. The study of these series has allowed one to distinguish two types of spatial and time trends.

1. Trends of natural origin:

   - Due to processes that cause changes at the aquifer scale. They depend on solute transport velocities through the medium, and therefore are very slow, such as the replacement of saline water by recently recharged freshwater.
   - Due to small-scale space variability caused by aquifer heterogeneity, also of small scale. This causes fluctuations around some level that may be erroneously interpreted, if only a statistical approach is used, as the result of contamination processes (increasing trends) or as reversals of them (decreasing trends following other increasing tendencies).

2. Trends due to aquifer development, which have their only cause in natural processes and not in human contamination. The cause is the flow

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velocity increase due to groundwater development, thus accelerating the appearance of natural trends that otherwise would require much longer times to be observed. Groundwater development may also induce natural chemical reactions that otherwise would not be produced if abstraction did not exist. This is the case of water mixing by upconing or by changes in the redox state, pH, *etc.*, related to water table oscillation or the displacement of water bodies of different characteristics.

The former trends are related to hydrodynamic and hydrogeochemical conditions, and have to be interpreted and studied before trying to interpret the latter ones.

Figure 5.2.11 shows a simple example and Figure 5.2.12 shows how different chemical parameters correlate with chloride, indicating processes that may be present in trends.

The main methodological and conceptual conclusions of the study of chemical trends are the following.

- In order to differentiate a natural trend from an evolution due to contamination, the origin of the observed trends has to be understood.
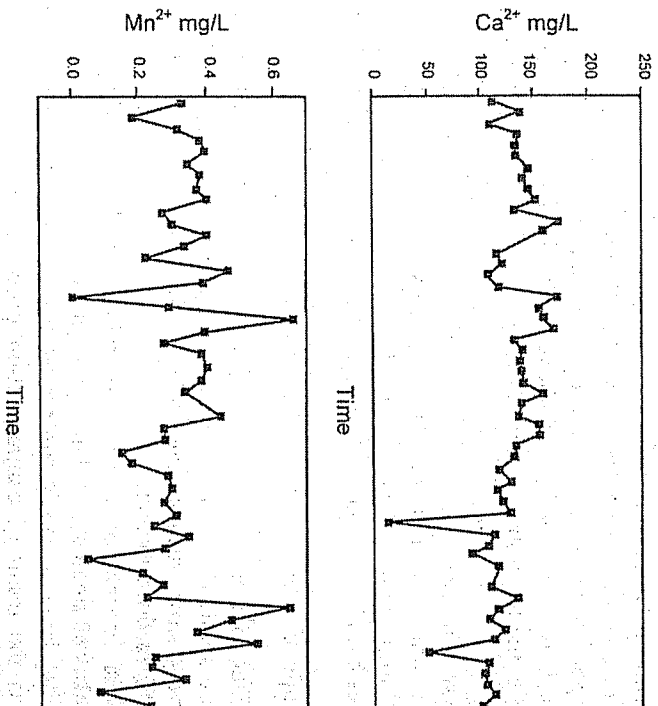

Figure 5.2.11 Chemical trends. The hydrodynamic and hydrogeochemical study is the key to know if there is a trend and if its causes are natural or due to contamination. Time evolution of Ca^{2+} in a pumping well with trend and time series of Mn^{2+} in a pumping well without trend. Central trends are also shown. (After Ref. 3)
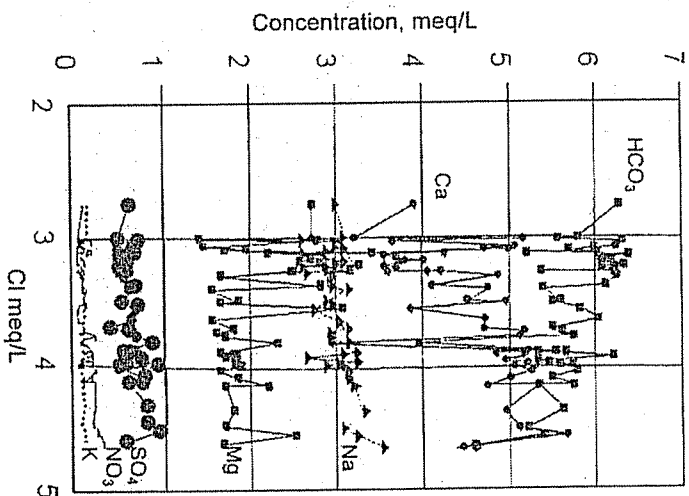
Figure 5.2.12 Plot showing correlations of some ions versus chloride content. It shows the existence of geochemical processes that may not be obvious from the time series plot.

- The main processes producing changes in groundwater quality trends are
  - changes in the mixing proportions between different waters; this happens in the salinisation by lateral flow or saline upconing or when substituting connate saline water with freshwater;
  - changes of redox conditions and fronts, such as the occurrence of pyrite oxidation and the displacement of nitrate, sulfate or iron reduction fronts; and
  - changes in recharge water composition, such as those due to variations of recharge rate or rainfall composition.

- In order to confirm the presence of water quality trends, be they natural or of anthropogenic origin, historical series are needed. When they exist, trends have to be interpreted. Going backwards, the original composition of groundwater can sometimes be determined, which is very important for chemical data interpretation.

- It is recommended that all new drilled wells or boreholes in a given aquifer be adequately sampled, in order to keep this information as an initial reference in databases.

- In the same way, the measurement of initial chemical characteristics will allow future studies to benefit from a highly valued initial reference

information to study the natural trend, and also for numerical modelling and for aquifer management.

• In order to monitor groundwater quality trends in a given aquifer or groundwater body, firstly the different natural trends have to be identified.

5.2.4 Conclusions

The relatively recent enforcement of the European Union Water Framework Directive,[1] and the enforcement of the newly adopted Groundwater Directive,[2] with their strict requirements of member states with respect to the quality status characterisation of different groundwater bodies and the implementation of remediation programmes, need a definition of baseline quality with two clear objectives:

• to distinguish between natural quality and quality modified by the presence of anthropogenic components; and

• to establish the characteristic natural composition of the different aquifers or groundwater bodies to serve as a reference, in case of implementing remediation activities.

In the European Union project BaSeLiNe,[3] carried out between 1999 and 2003, a definition of natural baseline was established, with scientific support, being at the same time usable by managers and policy-makers. Furthermore, a methodology to establish the natural baseline quality and its origin was proposed and tested, appearing to be adequate for application to all Europe. This methodology has been summarily presented above, as well as the main applied and conceptual conclusions derived from the application to 21 European aquifers. As a summary, the main conclusions are the following:

• The interpretation of observed groundwater chemical composition should always be made taking into account the aquifer hydrodynamical functioning. This is the basis to establish natural baseline quality or to deduce which natural or contamination-induced geochemical processes are acting, as well as to detect trends and their possible initial and final time.

• Since the functioning of most aquifers is poorly known, this introduces the need, supported by water law requirements, of carrying out the studies and undertakings adequate to get a basic knowledge in the upcoming 10–15 years. Among these works are (a) the drilling of some new boreholes and their adequate and complete study by means of geological, geophysical, geochemical and hydrodynamical logs, (b) the start of time quality series to monitor baseline quality and to detect any change since the beginning and (c) the use of numerical models, not necessarily sophisticated ones, in order to (i) complete and reinforce

aquifer functioning conceptual models, including water quality origin, (ii) know what is naturally or artificially producing the modifications, (iii) forecast the foreseeable future evolution and (iv) establish the main characteristics of natural baseline quality when it is not reflected in the water currently in the aquifer.

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