Handbook for Field Hydrological Measurements

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Part VIII

Hydrochemistry

Chapter 11

Hydrochemical field investigation procedures

11.1 Background

Water is a transport medium for all kind of substances, including nutrients, pollutants, gases and sediment. The chemical composition of rain water infiltrating in soil or rock is changed by many processes, including evaporation, dissolution of minerals, redox reactions, mixing processes (*e.g.* fresh water and sea water) and biological and anthropogenic processes (*e.g.* pollution, agriculture). As dissolution of minerals is a generally a very slow process, the residence time of the water in the medium is a factor of importance. All these processes lead to a certain enrichments or depletions of ions in river and ground water. Studying the hydrochemistry of precipitation, river and ground water in an area may therefore give clues to the importance of the various processes determining the water quality. Studying the chemistry of water is therefore often considered a very useful aid to improve our understanding of the hydrological processes acting in an area.

In this chapter we shall describe the procedures for obtaining reliable analytical results from collected water samples. This includes planning, laboratory sample preparations and descriptions of field measurements of certain parameters that are sensitive to changes between sampling and analysis. Following these procedures increases the quality of the data that you will collect and ensures a successful hydrochemical field work.

11.2 Pre-sampling procedures and planning

It is good practice to reflect on the following questions before you are going out to the field to collect water samples for hydrochemical analysis:

- What is the research question, can it be addressed through sampling of water?

- What are the minimum and optimum sets of parameters that you should include in the sample analyses? Remember that sample analysis is a time consuming and costly activity (at least 50 euro per standard sample analysis).

- What is the optimum number of samples to be collected in time and space to solve your research question?

Part of the planning of your research programme is to make sure that your samples are analysed in a timely fashion. This is also because the chemical composition of your sample is likely to change to a certain extent during storage (*e.g.* pH, HCO_3^-, etc.). When you are collecting samples for fieldwork or laboratory studies that need to be analysed certain procedures need always to be followed.

If samples are to be analysed in a commercial laboratory, you need to contact them about sample procedures and delivery and the timing of the analysis. If the analysis is done at the water chemistry laboratory of the Institute of Earth Sciences at the VU, you should do the following:

a. Make an agreement about your planning with the laboratory analyst (Mr. John Visser) and inform the laboratory manager (Dr. Boris van Breukelen) about the number of samples, the desired analysis and the time frame for your sample analysis.

b. Make the necessary preparations for avoiding sample contamination and for the conservation of your sample between the time of collection and the actual analysis. To avoid changes in your sample chemistry during storage, acidified sample bottles are used for the analysis of cations (ask the lab analyst for full details). The procedure for preparing your sample bottles is in short:

    - Rinse all sample bottles/caps in advance with a concentrated HNO_3solution, then flush them several (5) times with demineralised water and finally rinse with distilled water.
    - Dry the cleaned bottles/caps
    - For sample conservation add 0.7 ml concentrated HNO_3(65% suprapur) per 100 ml sample volume to your cleaned bottles. If you use 50 ml sample bottles, add 0.4 ml of HNO_3.
    - Always mark the acidified bottle and its cap with a large red dot to indicate that it contains acid!
    - In consultation with the lab analyst, stickers can be made that list the laboratory numbers.
    - Download the excel template sheet from the Laboratory for Water Chemistry link at http://ecohydro.falw.vu.nl (get user name and password from Boris van Breukelen or John Visser) and study it so that you know what to measure and note down in the field. You are required to upload this file containing the metadata for your sample before your samples can be analysed.

11.2.1 Required material

Make sure that you have the following packed before you leave for the field.

I. Sufficient clean sample bottles, as well as acidified sample bottles. For the laboratory analysis of a single sample for main cations and anions you will need:

   - 1 clean and acidified 50 ml bottle for cation analysis
   - 1 clean 10 ml bottle for anion analysis
   - 1 clean 50 ml bottle for laboratory alkalinity determination and laboratory pH and EC measurements (optional)
   - 1 clean 30 ml amber-coloured glass bottle for δ^{18}O and δ^2 H analysis (optional).

II. At least one 50 ml syringe for filtering of sample water and sufficient 0.45 µm pore size filters. We use single-use Millipore nitrate-cellulose or nitrate-acetate filters for this purpose. Note: depending on the suspended matter concentration in your sample you may need up to 10 filters to filter 50 ml of sample water. However, usually one or two filters per sample is sufficient.

III. Electrical conductivity and temperature meter

IV. pH meter and calibration buffer fluids. Do not use pH strips as these are not very accurate.

V. Dissolved oxygen (O_2) meter (optional).

VI. Flow through cell or container to place your field electrodes (optional, see Figure 11.1).

VII. A titration kit for field alkalinity (HCO_3^-) determination (and optionally Cl^-, Ca^{2+}, $Ca^{2+}+Mg^{2+}$). You should always determine HCO_3^- while sampling because the concentration will change rapidly in your sample bottle.

VIII. Test strips for nitrate (optional).

IX. A pump and sufficiently long tubing for groundwater sampling in piezometers.

X. A field book, pencil, yellow tape and markers to code sample bottles.

XI. A cool-box to store your water samples cool during their transport to the laboratory refrigerator (optional).

Figure 11.1: PVC–perspex flow through cell with electrodes to measure the pH and EC of water pumped from a well and passing through the cell without being exposed to air.

11.3 Field sample collection procedures

11.3.1 Methods to obtain water samples

In a hydrological study you may want to analyse different types of water, including precipitation, river water and groundwater. The procedures differ slightly and will be discussed below.

Sampling of water from collectors

Rainfall, throughfall, litter percolate or transpired water can be collected in *clean* rain gauges or sample bags made from chemically inert material. The collectors have to be rinsed with a diluted HNO_3 solution to remove ions sorbed to the collector material, followed by thorough rinsing with distilled water (6 times). After a rainfall event the water can simply be sampled according to the normal sample procedures (acidification, filtering) described above. Be sure to sample the water as soon as possible after the rainfall event to avoid changes due to storage and evaporation in the collector.

River and lake water sampling procedure

Sampling of well-mixed turbulent surface water is normally rather straightforward. You must take the surface water sample ideally just below the water surface away

Figure 11.2: Soil moisture suction cup used for the extraction of moisture from the unsaturated zone.

from the river banks, preferably in the river section where flow is most turbulent to ensure proper mixing of the water. Note that the hydrochemistry of water close to the river banks or at the bottom or surface of the river may differ from the overall river water chemistry due to poor mixing.

Sampling in less turbulent water, such as lakes, pools or stagnant rivers, is much more cumbersome as stratification may have developed. This often means that a layer of warm, oxygen-rich water at the surface may be floating on top of cooler bottom water, which may even be anoxic if the lake is deep enough. In such an environment it may not be possible to take a single sample that is representative for the water body and several samples then have to be collected from different depths to get an idea of the hydrochemistry. Such stratification can even be observed in small, shallow lakes with depths of less than 50 cm (*e.g.* Lagoa da Jincosa in Portugal).

Phreatic zone soil moisture sampling procedure

Soil moisture sampling from the unsaturated zone can be done with a *porous cup sampler* (also called *suction lysimeter*). This is a PVC tube with a porous cup glued to one of the ends (see Figure 11.2). A stopper with two smaller diameter tubes is inserted into the other end of the tube. These tubes are used to evacuate the sampler and to collect water from the sampler.

When the sampler is installed into moist soil (pF<2.7), the under-pressure in the sampler will create flow of soil moisture through the porous ceramic cup into the sampler. The water can be sampled by putting air pressure on the short tube, causing water to flow out of the longer tube extending from the sampler.

The porous cup can be made of ceramic, teflon or sintered metal. The first two materials are less suitable because of hydrophobicity (teflon) and high exchange capacities and oxidation (metal) influencing the hydrochemistry. Ceramics (porcelain) is therefore often the best option due to its inertness and toughness.

Alternatively, unsaturated soil may be sampled for pore water extraction. The moisture may be extracted by centrifugal action in the laboratory.

The use of porous cups allows for the development of hydrochemical time series for soil water, whereas this is not possible using the destructive soil sampling method.

Ground water sampling

Various methods exist for groundwater sampling. Groundwater bailers (Dutch: *water happer*) are very useful to take samples from large-diameter open wells, which are abundantly present in the Portugal field work areas (Portuguese name: *nora* or *poço*). The closed bailer is slowly lowered below the water level to the desired sampling depth and opens when rapidly pulled upwards. Note that the water composition in open wells may not truly reflect the aquifer hydrochemistry as the well also collects rain water (dilution) and is affected by evaporation and oxidation.

Before sampling groundwater from a piezometer, always remove at least three times the volume V (in l) of standing water ($V = 3\pi r^2 l$), where r is the diameter of the piezometer and l the length of the piezometer filled with water. This ensures that you obtain a water sample representative of the aquifer. The standing water in the piezometer may have a different chemical composition than the aquifer because evaporation and oxidation may have occurred and stratification may have developed.

In Portugal, some deep wells (called *furos*) may have taps installed. Springs (called *fonte*, Figure 11.3) may have been captured and and have taps installed that drain water from a storage reservoir. In this case, let the water run for a while before you start sampling.

Several types of pumps are available to extract water from wells for groundwater sampling. The most frequently used pumps are *peristaltic pumps* (small volumes, for instance for sampling through minifilters), *submerged pumps* (large volumes) and *inertial pumps*. Examples of such pumps are shown in Figure 11.4. Avoid the use of a vacuum pump to extract water from a piezometer, as its use results in strong degassing, associated pH increases and mineral precipitation during sampling. A peristaltic pump creates much smaller suction forces and can safely be used if the water table is less than a few meters below surface. It is better to use a submersible Grundfos pump or a mechanical inertial pump when the water table is at a depth of more than 5 m. These pumps push the water up and cause no degassing at all. Small-diameter (2.5–10 cm) groundwater piezometers can easily be sampled manually with a simple *inertial pump* consisting of a couple of meters tubing with a ball-valve attached at the end. By moving the tubing rapidly up and down, it fills with water each time you move it downwards and the ball-valve ensures that water cannot flow out of the tube once it has entered during the downward movement (a mechanical version of the system is shown in Figure 11.4).

If there are no other means of sampling your aquifer water, you can install your own observation piezometer (see Chapter 8 on how to drill holes and install wells). Please take a moment to reflect on the diameter of the piezometer. Larger diameter (5 cm) piezometers provide access to submersible pumps (see later) or the EM-39 borehole sounding device (Chapter 9). At least two small diameter (2.5

Figure 11.3: Fonte 006 in the Vagos research are near Aveiro.

Figure 11.4: Overview of pumps available to collect groundwater: Barnant Company E/S portable water sampler with a peristaltic pump (left), Grundfos submersible pump (center) and Waterra inertial pumps with ball valves (right).

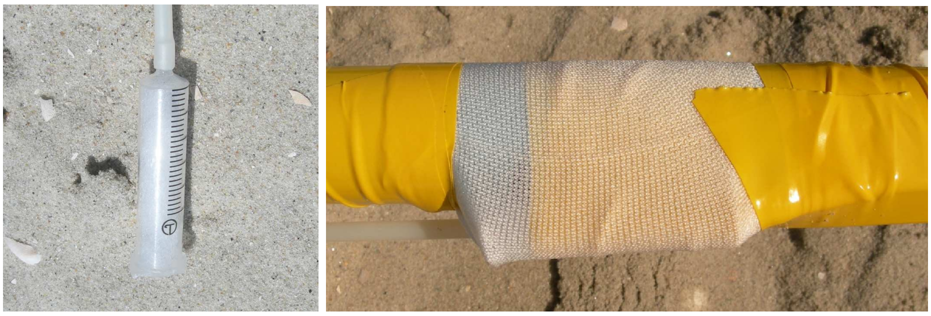

Figure 11.5: A minifilter (right) consists of plastic cylinder (part of syringe) filled with filter wool. One end is attached to the sampling tube and the broad end is open. This filter is attached to the exterior of a piezometer, covered with filter cloth and taped in place on both sides at the desired depth (right).

cm) piezometers fit in one manually drilled borehole (diameter 10 cm). Usually, you will have to delay sampling for at least a week after installation, but preferably for several months, before reliable groundwater samples can be obtained. This stabilisation period is required because the local aquifer hydrochemistry has been disturbed by the drilling. If you can not wait that long, be sure to pump as much as water until the groundwater becomes clear.

If you want to obtain information on the variation in hydrochemistry with depth, we advise you to attach minifilters at the outside of a piezometer. These can be made easily by taping a few cm length of filter cloth to a 2–3 mm diameter tubing (or syringe casing) that is taped to the outside of the piezometer at the desired depth (Figure 11.5). Do not forget to clearly label the tubing at the surface: indicate the number of the miniscreen and its depth. Make the tube of each shallower minifilter around 5 cm longer than the one on a deeper level, so that you always know the depth order of the miniscreens in case the labels have become unreadable after time.

On-site hydrochemical analysis

Because several key parameters may change rapidly during storage of a water sample, acidity (pH), temperature, electrical conductivity (EC), alkalinity (and optionally oxygen concentration) have to be determined during sampling. Fortunately, these parameters are easily determined with electrodes (except for alkalinity). Monitoring these parameters during sampling (via flow through cells) also enables deciding when the ground water well has been sufficiently flushed to begin sampling. Always calibrate the electrodes before use (check the manuals for calibration procedures). pH meters show considerable drift and must be calibrated at least once a day, but preferably before each samples is taken. EC and temperature meters are very stable and only need to be calibrated before you leave for field work. Only alkalinity must be determined, preferably in duplicate, via titration by means of a field *digital titrator* (Hach, Germany). You can check nitrate/nitrite concentrations using nitrate test strips (Merck, USA), especially if nitrate analysis is not possible the next day.

If a project does not allow time for laboratory analysis, or if samples cannot be shipped to a laboratory, some parameters may be determined via titrations as soon as possible after sampling and preferably on the same day(!) by means of a field digital titrator set (Hach, Germany). These include Ca^{2+}, hardness (Ca^{2+}+ Mg^{2+}) and Cl^-.

Conservation of water samples

Water samples must always be conserved in some way, because otherwise the concentrations of the hydrochemical parameters may change during storage until analysis. If a (potentially anaerobic) groundwater sample is brought to the surface the following physical-chemical conditions will be altered with the following effects:

1. A decrease in pressure causing degassing (of CO_2) and thereby inducing a pH increase and potential precipitation of minerals like calcite.
2. Oxidation of ammonium (to nitrate by microbial oxidation) and reduced metals (lowering their concentration by precipitation to mineral phases), while alkalinity becomes lowered if reduced ferrous iron (Fe^{2+}) oxidises.
3. A higher temperature enhances microbial activity, induces precipitation of carbonate minerals, and may lead to evaporation and thereby higher concentrations of all solutes.
4. Light may result in growth of algae and corresponding hydrochemical changes.

Water samples must therefore always be stored under preferably cool conditions, out of direct sunlight, with the bottle filled completely and capped tightly to avoid leakage.

In general two sample bottles are used, one for anion and one for cation analysis. The first 50 ml(or 10 ml) sample tube, for anion analysis, must be filtered to make the sample optically clear. This allows good colorimetric analysis in the laboratory. You need at least 50 ml, if this water is also used for laboratory EC and pH measurements and, optionally, for laboratory alkalinity titration. The sample bottle should first be flushed three times with sample water before the sample is taken, filling up the bottle completely whenever possible.

The second 50 ml sample bottle, for analysis of cations, must also always be filtered and acidified down to a $pH < 2$ (by adding concentrated HNO_3 in a 1:100 dilution). Filtering and acidification prevents mineral precipitation and impedes oxidation processes and bacterial activity, thereby conserving the sample. Filtering is required before acidification because the strong acid will dissolve suspended matter, resulting in increased concentrations.

Table 11.1: Water type codes for sample descriptions.

Water type	Code
Soil core water	CW
Groundwater observation well	GWO
Groundwater abstraction well	GWP
Groundwater infiltration well	GWI
Laboratory experiment	LAB
Litter leachate	LL
Lake water	LK
Precipitation (bulk)	PB
Precipitation (wet only)	PW
Sea water	SEA
Soil moisture	SM
Stem flow	SF
Solid phase	SP
Surface water (river, spring, etc.)	SW
Throughfall	TF

Always start with the anion analysis sample bottle and fill the acidified sample bottle afterwards, because you may accidentally transfer some HNO_3 to the non-acidified bottles (contamination), increasing nitrate and lowering the pH. Use a syringe and 0.45 μm filter for filtering. Use a fresh filter for each new sample. When you need to refill the syringe with sample water, first detach the filter and then pull out the plunger. If you pull out the plunger with the filter attached, the vacuum created will tear the filter.

11.3.2 Water sample coding

Code water sample bottles with a waterproof marker on both bottle and cap. Give each sample a short clear code that also identifies your initials/name, student group, or study area and the water type. Note down all measured information at the sampling location in a notebook and determine the coordinates with a GPS. For instance, if your first sample is of river water, and your name is Jack Jones, then you may want to call the sample JJ-SW1 (SW for surface water), whereas your second sample would be JJ-SW2. A list of water types used by the Laboratory for Water Analyses is given in Table 11.1.

11.4 Laboratory analysis

11.4.1 Sample metadata requirements

Before the samples can be analysed, the laboratory staff needs some details about the samples for determining if dilution is needed, or if there are any other specifics about the sample that require special treatment. It is to upload the sample data before analysis can start. Details about the procedure can be found on the Water Laboratory web page at http://ecohydro.falw.vu.nl.

Single samples can be entered in the laboratory database using a form, whereas a template spreadsheet file is available for multiple samples. Be as complete in your sample description as possible and do add remarks on sample colour, filtered/non-filtered, acidified, specifics of sample site, discharge or volumes (mm) in case of river water, rainfall, throughfall, litter percolate, etc. The required fields are: Sample code, Site or well ID, Filter no., Date, Time, Country code, UTM Zone, Latitude, Longitude, Sample type, Discharge (or flux in case of rainfall, throughfall, etc.), Upper filter level, Lower filter level, Topographic height, Remarks, Field pH, Field EC, Field Temperature, Project name, Sub-project name/SAP number, Investigator name, Observer, Alkalinity, Field Cl, Field Ca, Field Mg, Field NO3 and Dissolved O_2.

In the laboratory you will receive stickers to place on your sample bottles and you will have to assist the laboratory analyst with filling analysis vials, making sample dilutions, and measuring the laboratory pH, EC and alkalinity.

All metadata and analytical results are stored in a database and can be retrieved through the water laboratory web site at http://ecohydro.falw.vu.nl.

11.4.2 Analytical procedures

Anions (Cl^-, NO_3^-, NO_2^-, SO_4^{2-}) and nutrients (NH_4^+, PO_4^{3-}) are analysed on a Labmedics Aquakem 200 discrete analyser (DA; Figure 11.6). This instrument can also be used to measure alkalinity via colorimetry. However, alkalinity is usually measured via inflection point titration on a Radiometer Titralab TIM840 titration workstation (automatic titrator; Figure 11.6). All DA methods are based on colorimetry, i.e., the adsorbance of a sample at a certain wave length (colour) after addition of certain reagents is taken as measure of the concentration of a certain chemical. Anions (+ Br) can also be determined via ion chromatography (IC; Figure 11.6) on a Dionex DX-120 IC equipped with IonPac AS14 column. Cations (Ca, Mg, Na, K, Fe, Mn, Al and Si) are determined using the acidified samples by means of a Varian 730-ES inductively coupled plasma-optical emission spectroscopy (ICP-OES, Figure 11.6). If you wish, ICP-OES can also simultaneously measure a whole suite of spore elements and heavy metals (B, Ba, Be, Sr, Li, Mo, As, Cd, Co, Cr, Cu, Ni, Pb, Se, Sb, V, Zn) together with total P and S. For some projects you may be interested in measuring other parameters such as methane, dissolved organic carbon (DOC), or H_2S. Contact Boris van Breukelen for details on sampling conservation and analysis.

11.5 Checking the accuracy of analytical results

Usually you analyse or obtain your analysis results in weight units like mg l^{-1} or ppm. Note that mg l^{-1} equals ppm (part per million by weight of sample) for dilute fresh waters (density = 1.0 g cm^{-3}), while mg l^{-1} is slightly higher than ppm for waters having a salinity of seawater (density = 1.023 g cm^{-3}; 1 ppm = 1.023 mg l^{-1}). To assure that errors were not made during lab analysis you can:

1. Calculate the electrical balance (EB, in %, see Equation 11.1 with concentration units in meq l^{-1}) of the water samples after having recalculated the concentration units to meq l^{-1}, together with

$$EB = \frac{\sum \text{cations} + \sum \text{anions}}{\sum \text{cations} - \sum \text{anions}} * 100 \qquad (11.1)$$

2. the EC rule-of-thumb (Equation 11.2). Try to determine what went wrong if errors are too large (> 5%). Probably some parameters must be re-analysed once it is ascertained that no errors were made during sampling and/or conservation.

$$\sum \text{anions} = \sum \text{cations} \approx EC/100 \ (\mu S\ cm^{-1};\ \text{for } EC < 1500\ \mu S\ cm^{-1}) \qquad (11.2)$$

The unit mmol l^{-1} is useful to detect the stoichiometry of reactions; meq l^{-1} enables checking the accuracy of analysis; water quality norms are usually given in weight units like mg l^{-1} or ppm.

Recalculation of analytical units:

- mmol l^{-1} = mg l^{-1} divided by gram formula weight
- gram formula weight = weight in grams of 1 mol of atoms or molecules
- 1 mole = Avogadro's number = $6*10^{23}$ atoms or molecules
- meq l^{-1} = mmol l^{-1} * charge of ion

For example, 1 mmol l^{-1} Ca^{2+} = 2 meq l^{-1} Ca^{2+} = 40.08 mg l^{-1} Ca^{2+}

Alternatively, the EB & EC rule-of-thumbs can also be used to estimate the concentrations of some major ions that are not easily measured with the available field methods: $Na^{+}+K^{+}$ and sulphate (SO_4^{2-}). Hereto, it is assumed that your analyses were done perfectly and the EB equals zero. You will estimate $Na^{+}+K^{+}$ and SO_4^{2-} in this way during the Dinkeldal fieldwork, as only EC, Cl^{-}, NO_3^{-}, HCO_3^{-}, Ca^{2+} and Mg^{2+} can be analysed with the field kit.

Figure 11.6: Equipment of the VU water laboratory to perform hydrochemical analysis. Aquakem 200 discrete analyser (upper left), Radiometer Titralab TIM840 titration workstation (upper right), Dionex DX-120 IC equipped with IonPac AS14 column (lower left) and Varian 730-ES inductively coupled plasma-optical emission spectroscope (lower right).

Table 11.2: Concentrations (90^{th} percentiles) of key water quality elements that are typical for groundwater found in non-calcareaous aquifers under different land use and land cover types in The Netherlands (Pers. comm. Igor Mendizabal). TH is the total hardness, *i.e.* the sum of all calcium and magnesium compounds expressed as calcium carbonate and usually given in mg l^{-1}.

Land use category	90^{th} percentile of water quality					
	NO_3^- mg l^{-1}	SO_4^{2-} mg l^{-1}	Al^{3+} μg l^{-1}	Ni μg l^{-1}	TH mmol l^{-1}	As μg l^{-1}
Intensive agriculture	218	139	2065	51	4.5	7.5
Extensive agriculture	81	172	625	29	4.7	6.9
Intensive urbanization	89	161	124	20	5.1	11.9
Extensive urbanization	79	119	55	4	5.2	17.8
Nature	0	60	46	1	3.4	6.3
Forest	36	102	4008	72	2.5	4.5

11.6 Interpretation of hydrochemical regional data-sets

Now that you have your hydrochemical regional data-set, you want to extract the information that it contains out of it. Some common research questions are:

- What different types of water are present?
- Which processes have caused the water compositions?
- What are the relations between the water types/chemistry and spatial information such as land use/geology/soil type/geomorphology/hydrology?

Igor Mendizabal has created a classification system based on hydrochemical data of groundwater from hundreds of water supply pumping stations in The Netherlands. An overview of his findings related to groundwater quality and land use are presented in Table 11.2.

The following list presents some ideas for calculations and graphs you can make to aid your interpretation:

a. Give a general description of the hydrochemical data-set:
   a. Average, median, (5% and 95%) percentiles, and range of concentrations of the various parameters (summarized in a Table via a spreadsheet). Do this separately for each type of water (e.g. rainwater, seawater, and various types of groundwater as determined via, for example, cluster analysis (see later)).
   b. Compare concentrations to water quality norms (cf. Table 1.1 in Appelo and Postma [2005]).
   c. Dominant cat- and anions (HYFA analysis); or make Collins bar or pie diagrams like Figures 1.3 or 8.3 in Appelo and Postma [2005] for the group means.

  d. What are the redox conditions, type of water (fresh, brackish, saline), pH?
  e. Include a hydrogeological and geochemical (type of material: limestone, clay, organic matter, gypsum, etc) description.

b. Calculate saturation indices (SIs; plus total inorganic carbon (TIC)) for selected minerals using PHREEQC (via HYCA optionally) to find out which minerals may have dissolved in the water. Use *SOLUTION SPREAD* and *SELECTED_OUTPUT* keywords (-saturation_indices calcite, dolomite, gypsum, etc (see database for more relevant minerals); check phreeqc practicals and/or manual). Which mineral is the main buffer against soil acidification: calcite or Al-hydroxides? Make cross-plot of their SIs.

c. Compare rainwater and groundwater samples to determine the extent of evapotranspiration that has occurred in the soil zone.

d. Compare samples to seawater ratios to find clues for processes like cation-exchange, dissolution of minerals, sulphate-reduction, and pollution (acid rain, fertilizer). See Appelo and Postma [2005] pages 29–30, 245–246.
  a. GW_chart (USGS) can be used to make a piper plot but you need to type all data in the program (you cannot import a table).
  b. GeoStiff (USGS) can be used to make Stiff diagrams that can subsequently be imported in ArcView software. HYCA can also be used to make these kinds of graphs.

e. Calculate correlation matrix to find out which parameters are correlated and which are not. For example, components used in fertilizer (K^+, NH_4^+, NO_3^-, PO_4^{3-}) may be correlated or Ca^{2+} and HCO_3^- as a result of calcite dissolution.

f. Make cross-plots (xy plots in excel) to find and show relations between parameters (also calculate the coefficient of determination, r^2). Showing seawater mixing lines in these plots is often useful. For example, cations and sulphate versus Cl^- in coastal areas.

g. Compare time-series: to what extent are samples comparable over various years. A student t-test (TTEST function in excel) can be done to determine whether groups of samples are significantly different (in time or space).

h. Multivariate statistics analysis: principal component analysis (PCA), cluster analysis, factor analysis (FA) to find out which samples are related and which ones are different as well as the parameters that correlate. You can use the free 30 days trial version of statistiXL (http://www.statistixl.com) to perform all these multivariate statistics tests in excel.

i. Visualization of results in GIS: how do parameter values correlate with spatial information such as geology, topography, and land-use?

11.7 Hydrochemistry during MSc Hydrology fieldworks

11.7.1 Dinkeldal fieldwork, Twente, Netherlands

The learning goals are that you:

- Know how to take groundwater and surface water samples and to conserve them.
- How (and why) to determine some parameters directly in the field and at the field lab.
- How to check the accuracy of your analyses.
- How to make a chemical mass balance of a watershed via discharge and chemical measurements. For example, a salt balance will be constructed based on EC measurements of the streams.
- Know how to make a simple interpretation of a regional hydrochemical data-set: relations to land use and major hydrochemical processes (like occurrence of calcite dissolution?).

11.7.2 Algarve fieldwork, Portugal

The learning goal is that you that you increase your skills in relating hydrochemical information to hydrogeological processes in a regional perspective.

11.7.3 Aveiro fieldwork, Portugal

The learning goal is that you know how to make a strategy for a hydrological/hydrochemical study and obtain water samples for hydrochemistry at optimal locations. In addition, you should know how to perform a (close to) complete interpretation of your hydrochemical data-set (see Section 11.6).

The VU water level logger would produce the following line, where the first values are date/time indicators and the last value is the water level deviation from a certain level:

```
126 05 05 08 11 40 30 -00518
```

The data files can be imported into MS Excel or OpenOffice Calc, but can also be processed and visualised by a Python script (see Chapter 13).

An exception is the *Schlumberger – van Essen* Diver water level logger, which comes with its own software (Logger Data Manager) for setting-up, reading and processing Diver data. The Logger Data Manager software facilitates correction of the measured water level for atmospheric pressure changes and export of logger data to ASCII text file or MS Excel file formats for further processing.

12.1 Using Python to process, analyse and visualise your data

The basics of Python are taught in the Ecohydrology and Groundwater Flow Modelling courses. Several Python scripts have been developed for the processing of data (see also Chapter 13). These include the fitting of layers and resistances based on EM-34 geophysical measurements (vertical electrical soundings) and the calculation of evaporation from meteorological data from the automatic weather station.

To use these scripts, please start *Spyder*, which is part of the Python(x,y) suite of programs, or the more simple *Idle* Python interface. Then open the script and take a look at the comments and instructions in the script that tell you how to use it. In most cases you need to prepare an input data file and assign working and data directories to tell Spyder/Python where your files are. The scripts are:

- *stiff.py* has been developped by Boris van Breukelen to allow you to make stiff plots from hydrochemical data collected in Twente and Portugal field courses.
- *piper.py* has also been developped by Boris van Breukelen to allow you to make Piper plots from hydrochemical data collected in Twente and Portugal field courses.

- *em34.py* was developped by Vincent Post and allows you to fit a model of layers to EM-34 Vertical electrical soundings. An example script file (em34_example.py) is also included

- *meteoscript.py* was developped by Maarten Waterloo and is used to process data from the meteorological tower to obtain estimates of potential and actual evaporation. It uses two function libraries (evaplib.py and meteolib.py) and needs a meteorological data input file. The *meteolib.py* library contains meteorological functions to calculate actual and saturated vapour pressures, constants such as λ, γ, c_p, ρ, and the wind vector. The *evaplib.py* library contains functions for determining daily potential evaporation rates with Penman [Penman, 1956], Priestley–Taylor [Priestley and Taylor, 1972], Makkink [Makkink, 1961] and FAO's Penman Monteith ET_0 reference evaporation for short, well-watered grass [Allen et al., 1998].

A Python manual for beginners, Python scripts and function libraries can be downloaded from our web site at http://ecohydro.falw.vu.nl/python. Installation of Python and other software is discussed in Chapter 13.

12.2 Spatial data processing and analysis

Spatial data is best processed with a Geographic Information System. Examples of such systems are ARC/GIS from ESRI (http://www.esri.com) and the open source, freely available GRASS software (http://grass.itc.it). Quantum GIS (QGIS) is an alternative user-friendly open source GIS package licensed under the GNU General Public License. QGIS is an official project of the Open Source Geospatial Foundation (OSGeo). It runs on Linux, Mac OSX, and Windows and supports numerous vector, raster, and database formats and functionalities.

Spatial data analysis has been the subject of the Basics in GIS (450226, 3 ECTS) and Applied GIS (450227, 3 ECTS) courses within the hydrology MSc programme and will not discussed further. A field application of GIS is discussed in Chapter ??. Note that working with time series is often difficult in GIS systems.