

ALMA MATER STUDIORUM – UNIVERSITÀ DI BOLOGNA
SCUOLA DI SCIENZE

Corso di laurea magistrale in analisi e gestione dell'ambiente

**HYDROGEOCHEMICAL CHARACTERIZATION OF SEEHAUSEN
TERRITORY – BREMEN**

Tesi di laurea in caratterizzazione geochimica dei materiali
contaminati

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III Sessione
Accademico 2012/2013

*If you are, you breathe
if you breathe, you talk
if you talk, you ask
if you ask, you think
if you think, you search
if you search, you experience
if you experience, you learn
if you learn, you grow
if you grow, you wish
if you wish, you find
and you find, you doubt
if you doubt, you question
if you question, you understand
and if you understand, you know
if you know, you want to know more,
if you want to know more, you are alive*

Acknowledgments

A lot of people helped me with this thesis, I just had the chance to write it down.

Starting from the beginning, I would like to thank my Italian supervisor Enrico Dinelli: you have always been present and you have always trusted in me.

Ich möchte mich mit folgenden Mitarbeiterinnen der Universität Bremen bedanken: Laura Knigge, Christian Breuer, Kai Gruber, Alexandra Vowinkel and Nick Liedtke. Ohne die Unterstützung von meinem deutschen Betreuer Kay Hamer hätte ich diese Arbeit nicht verfassen können. Danke für alles.

Dann möchte ich mich noch mit den Geologischen Dienst für Bremen für die hohe Bereitschaft bedanken, insbesondere mit Björn Pantaleit, Sven Jensen und Günther Schmidt.

Ein besonderer Dank an die Firma Dr. Novak für die Grundwasserprobenentnahme hilfe und an die Bremer Hafenbehörde.

A special thanks is owed to all the developers of open source software: thank you guys to write tons of code lines and to keep on thinking that world can be a better place.

Un ringraziamento sentito va a tutti i miei compagni di corso che mi hanno supportato, ma soprattutto sopportato in questi anni: Riccardo, Diego, Michela, Emanuela, Chiara e Caterina. Accanto ai compagni di classe, un posto speciale va riservato ai miei conquilini Francesco e Roberto (senza di voi mi sarei divertito sicuramente di meno).

Un ringraziamento speciale va a Elena che sempre mi ha spronato, consolato, aiutato, ma soprattutto è sempre stata presente in questi anni di intenso lavoro.

Infine, senza i miei genitori, niente di tutto quello che ho fatto sarebbe stato possibile. Quindi questo lavoro non è mio, è vostro.

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1 Introduction and aims

The aim of this master thesis is to carry out an hydrogeochemical characterization of the study area and to verify potential emissions of pollutants from a sediments landfill located in Seehausen, Bremen.

The landfill is made up of heterogeneous and salty material dredged from the harbor zone of the bed of the river Weser and from the port of Bremerhaven and might be a source of contaminants to the groundwater.

The first step of the work included the recovery of background information about the geological and the hydrogeological features of the whole region. Indeed, natural condition could also influence the quality of the groundwater due to the aquifer nature and to processes active in the subsurface.

This study will be conducted in following steps:

- identification of the piezometers;
- determination of the hydraulic heads and construction of a contour map;
- measurement of some water parameters directly in the field (temperature, pH, electrical conductivity, dissolved oxygen);
- measurement of conductivity at different depths in several piezometers; this way it could be possible to define a geological pattern;
- water sampling and further measurement in laboratory (cations and anions, isotopes);
- comparison of current geochemical data with historical data.

With this information it will be possible to identify the geochemical peculiarities of the groundwaters, to compare them and describe this way the hydrogeochemical characteristics of the area of study.

Moreover, a better definition of the hydrogeochemical characters and a possible identification of the landfill effect will hopefully be obtained from the analysis of historical data collected from the same piezometers (time series starting from comparison with older 1996 datasets).

1.1 Dredged sediments management

Dredging is the act of removing sediments from a waterway, almost always from an authorized navigation channel, berthing area, or coastline.

All over the world, the continued need to dredge for the maintenance of existing channels and harbor facilities produce millions and millions of cubic meters of dredged material every year. All this material has to be managed in order to protect both the environment and the local social-economical aspects.

National (see Deibel, 2007 for German laws) and European regulations (Water Framework Directive and Soil Communication) provide guidelines on how to manage and treat dredged material. Furthermore, research facilities, non-profit organizations, local authorities and the Sednet association contribute in the dredged material management and treatment thanks to the results and the publication of their researches.

Dredged sediments represent a very complex environmental issue because of their development modalities, their heterogeneous physical-chemical characteristics and their diversified chemical composition.

Very often sediments contain a great variety of both organic and inorganic pollutants and contaminants. The occurrence of pollutants depends above all on the dredging location that reflect environmental peculiarities (for example an area naturally rich in lead) or anthropic impacts (harbor areas).

Organic pollutants are represented mostly by polycyclic aromatic hydrocarbon (PAH), polychlorinated biphenyl (PCBs) and pesticides while heavy metals and phosphates are the most frequent inorganic compounds (De Vivo, Lima, 2009).

Dredged material can be managed in many different ways. Some of them are well known methods that describe how to treat and dispose dredged materials. All these disposal and treatment methods can be divided into two main categories: *in situ* and *ex situ* treatments.

In situ treatments are done directly in place without removing dredged material while *ex situ* techniques mean that sediments are moved in other location from the original settling place.

Each technique involve many different aspects and has different complications, the most important are:

- social – economic aspects;
- environmental impact and benefits;
- technical criteria;
- engineering issues.

The following table (Table 1) summarizes several treatment worldwide used:

Table 1 – Treatment and disposal techniques (adapted by Sustainable Management of Sediment Resources)

Category	Technique	State of the art for treatment of dredged material
in situ treatment	chemical	pilot & full scale
in situ treatment	biological	pilot
in situ treatment	physical/capping	pilot & full scale
physical treatment	separation	full scale
dewatering	natural dewatering	full scale
dewatering	mechanical dewatering	full scale
thermal treatment	desorption	full scale
thermal treatment	bricks	pilot
thermal treatment	light weight aggregates	pilot & full scale
thermal treatment	artificial basalt	pilot
thermal treatment	cement	pilot
washing extraction	biogenesis	pilot
chemical treatment	stabilization/immobilization	full scale
biological treatment	bioreactor	pilot
biological treatment	landfarming	full scale
biological treatment	phytoremediation	pilot
confined disposal	upland	full scale
confined disposal	Sub-aquatic	full scale

Given the large amount of sediments dredged every year, this material is increasingly seen as a resource rather than a waste. Some of the techniques listed above are methodologies that consider the beneficial reuse of sediments and other technologies are being continuously developed (Hakstege, 2007).

Reusing dredged material has many benefits:

- *economical*: saving raw material means cost reduction. Furthermore, disposal (both inland and offshore) are often expensive options (see Elskens, 2007);
- *environmental*: offshore disposal of dredged material has a strong impact on all the environmental branches (organic and inorganic). Reusing this material means sparing negative impacts;
- *social*: dredged sediments has to be put somewhere or treated with some methods. Avoiding the construction of landfill or treatment plant will have a benefit on local population.

Not all the dredged material can replace raw material: several physical, chemical and biological tests have to be made in order to characterize its quality. If the contaminants content is too high, the material cannot be used and has to be disposed in special landfills.

Natural *dewatering* is the technique used in the Seehausen landfill of Bremen. In particular, this method is done by optimizing the natural dewatering by actively handling the sediments mechanically in order to increase evaporation and water drainage.

Briefly: the incoming dredged sediments are put on land in dewatering fields (also called treatment lagoon) where they can dewater and consolidate. During this process, oxygen can penetrate into the sediments and oxidation of organic matter and minerals take place. The energy consumption is very low and limited for cranes and specials windrow turners that handle the sediments. Furthermore, there is no water consumption.

However, natural dewatering requires large space and time: space depends directly on the amount of the dredging sediments while time depends on the weather of the region and on the grain size of the material. This can take from few months up to a year (almost one year in Seehausen).

The costs of this method is quite limited: 10 to 25 €/m³: nevertheless, the cost depends on: the incoming wet material (especially the dredging technique used), the area available for the dewatering fields, the time needed for the total dewatering and the quality of the end product (sale potential). Dewatered sediments can be used in many different ways: construction material, foundation material, sealing material in disposal sites, covering of

disposal sites, construction of dikes and noise barriers and as substitute of bricks.

In particular, the employment of dredged sediments as clay replacement in brick production is a developing process that is worth to be mentioned (Hamer et al, 2007). This methodology consists in the pretreatment and homogenization of dredged material in special furnace. The greatest environmental benefit is the total destruction of organic pollutants and the fixation of most of the inorganic contaminants. Furthermore, a large part of raw material (clay) is replaced with secondary material. This has advantages on all the life cycle: no extraction of new material (energy and material saving), reducing of the disposal sites and economic advantage (calculated in large time interval).

1.2 Why open source software

This small paragraph doesn't want to be a debate between the use of closed and proprietary software and open source software. There are lots of books and article about this topic, first of all the excellent book *The Cathedral and the Bazaar* (Raymond, 2000).

The choice to use entirely open source software on a notebook with GNU-Linux operative system installed (Ubuntu and Debian distributions) for the development of this thesis derives first all all from the “sharing option” that only open source software can offer. Especially in the scientific field it is essential that people can share their work without forcing other people to buy expensive software licenses. Public administrations should use open source software (when possible) and share data in an open format (e.g. for text files .odt files instead of .doc ones). This way every person can **freely** download the dedicated software and read the document or elaborate the data.

A second idea beyond open source is the chance for everyone to customize the software to its own needs: this seems to be a merely secondary option, but it is not. The possibility to look into the source code of a software means having the complete knowledge of the software itself.

A third important option is code quality: this is probably a more technical case, but the fact that lots of people have access to the source code implies that bugs and errors are discovered (and fixed) earlier than proprietary software.

Last but non least, I think that if all past knowledge was to be available only against payment, the whole scientific world would suffer from it.

2 Geology and hydrogeology of the North-West Germany

2.1 Geology

The subsurface geology of the north-western Germany is characterized by different types of materials deposited during the last 250 myr, that form a several thousands of meters thick sequence of sediments and rocks. The recent ice ages have influenced the north of Germany, as the whole Northern Europe, giving to the environment of this region the typical glacial deposition frame.

The superficial salt structures (from the Permian period) along with the channel network system formed by the movement of the glaciers are typical of the Northern Germany.

2.1.1 Devonian and Carboniferous

The Devonian era is mainly characterized by alluvial clastic sediments and terrigenous sediments. The latter originate from the erosion of the inland rocks and are transported by rivers into the sea. The coarse sediments (sand) deposit in coastal areas, while the fine-grained ones (silt and clay) need a calmer marine environment to be settled.

The border of the oldest Devonian layers and of the earliest Carboniferous ones is situated at 7000 meters depth (Fig 1) (Ortlam, 1985).

2.1.2 Permian

The Permian include the lithostratigraphic units of Rotlingend and Zechstein. Rotlingend is the oldest one and is made up of sandstones and porphyry, while the youngest layers of Zechstein include evaporite deposits, created by the precipitation of salts from the inland Zechstein sea (260-250 myr).

The Zechstein sea was located in the north side of Europe and covered partially Germany and the present North Sea. Due to the interruption of the connection with the other seas and the increasing temperatures that led to an arid climate, the Zechstein sea began to evaporate with a consequently increasing of salts concentration in the water. This strong evaporation lead to the accumulation of halite, gypsum and other evaporite minerals. This process of sedimentation caused the "salt sequence" Werra, Straßfurt, Leine and Aller and salt layers have a variable thickness from 100 to 1500 meters (Walther, 2007).

2.1.3 Triassic, Jurassic and Cretaceous

Over the salt layers of the Zechstein unit there are the deposits of the Triassic, Jurassic and Cretaceous. Together they are 3500 meters thick and are very deformed nearby the salt structures. The deformation of the layers that surround the salt deposits is due to the up climbing of these ones to the surface (see Fig 1).

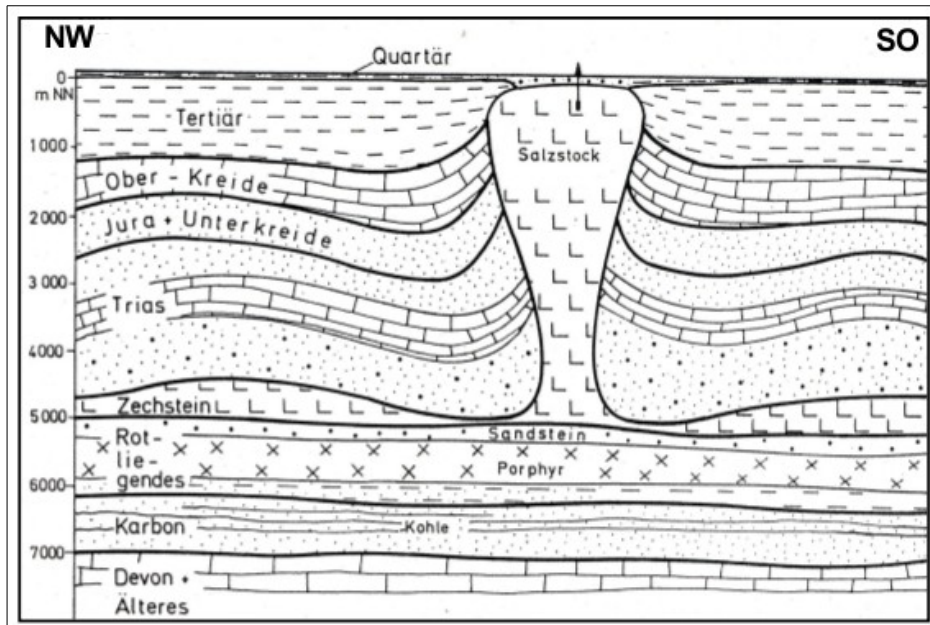


Fig 1 – North-west Germany stratigraphy (Ortlam 1985)

The re-climbing is caused by the phenomena of halokinetik: salt layers are buried under a 5000 meter load that causes an increment of pressure and temperature. Thereby salt assumes a plastic behavior and thanks to its lower density compared to that of the above layers, it can climb up to the surface (Ortlam, Schnier, 1980). The maximum period of the uprising occurred in the Cretaceous and in the Neogene (Walter, 2007). Salt layers form this way two types of structures: salt domes and salt walls. Both of them are mostly covered by a gypsum cap (caprock).

In Bremen it is possible to find two salt domes (Lesum and Lilienthal) and a salt wall (Demelhorst-Osterholz): both climb up from a depth of 4500 meters to 150 meters (Ortlam, Schnier, 1980, Fig 2).

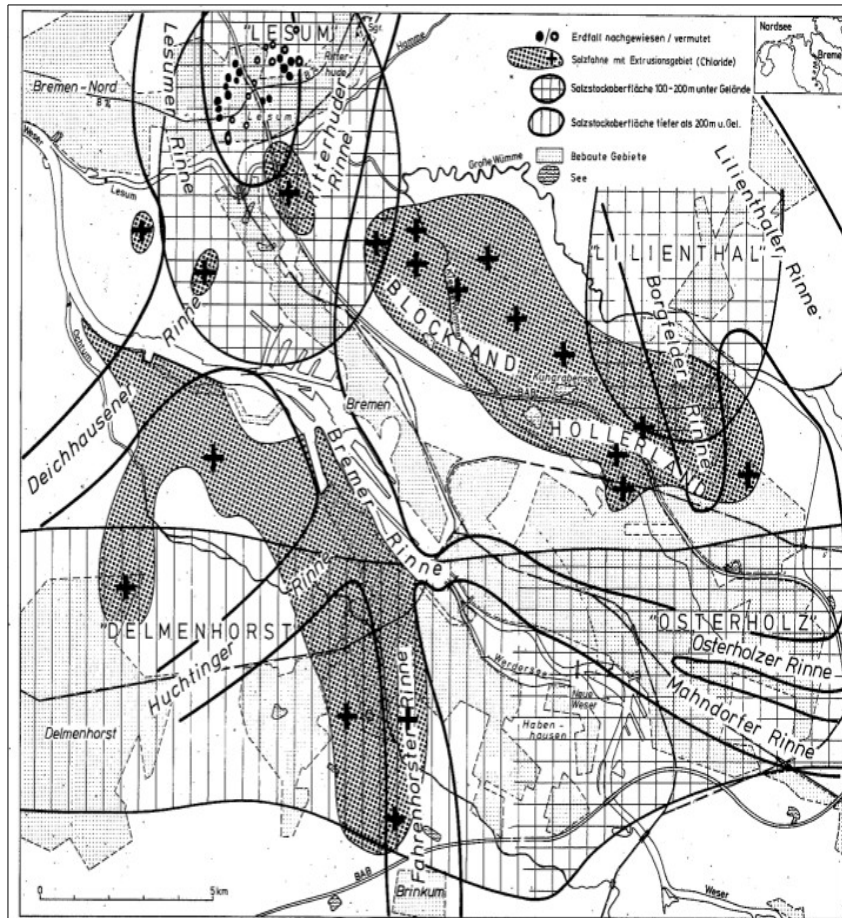


Fig 2 – Salt structures in Bremen (Ortlam and Sauer 1993)

2.1.4 Tertiary

In Lower Saxony the Paleogene and Neogene layers reach a 1000 meter thickness (Lang, 1971) and they are almost all visible on the stratigraphic sequence (see Fig 3). The erosive phenomena destroyed the upper Oligocene, the lower Miocene and the Pliocene layers.

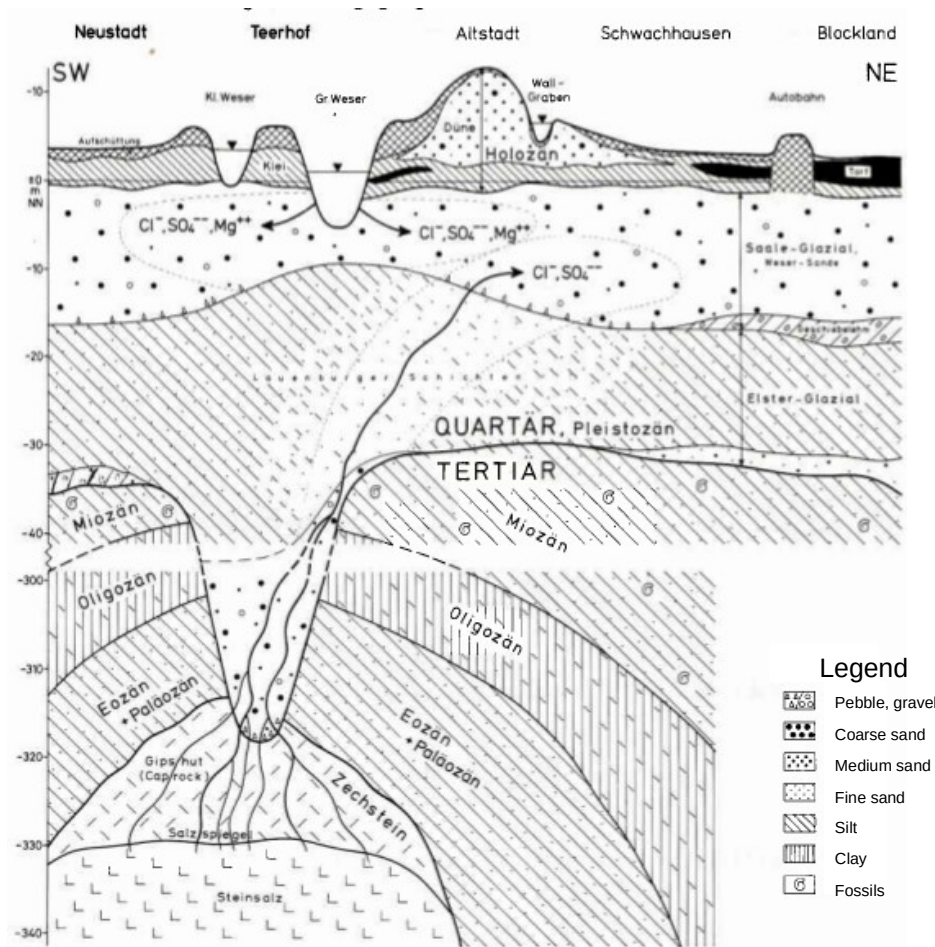


Fig 3 – Subsurface stratigraphy of Bremen (Ortlam 1980)

From the beginning of the Tertiary to the end of the Miocene the majority of the north-western Germany was characterized by a marine environment and the deposits of this period are made up of clay, silt and fine sands with a variable content of carbonate (Ortlam, Schnier, 1980). Paleogene and Eocene deposits are characterized by gray and gray/green sediments color and sometimes one can also find some volcanic ashes (Lang, 1971). Due to the salt tectonic (diapirism) these layers are strongly deformed and in some cases they are positioned just a few meters under the surface (Ortlam, Schnier, 1980).

2.1.5 Quaternary

The youngest Quaternary layers, whose thickness can reach 250 meters (Lang, 1971), cover those of the Paleogene and the Neogene, but the three ice ages (Elster, Saale and Weichsel) had strong effect on the geology and the morphology of the entire region.

The deposits formed during the alternation of ice and warm ages are very heterogeneous both in materials and in grain size. During the ice ages a complex system of sub glacial channels has formed (see Fig 4). The deepest channels reach the Permian salt structures and have enough power to slice their surface.

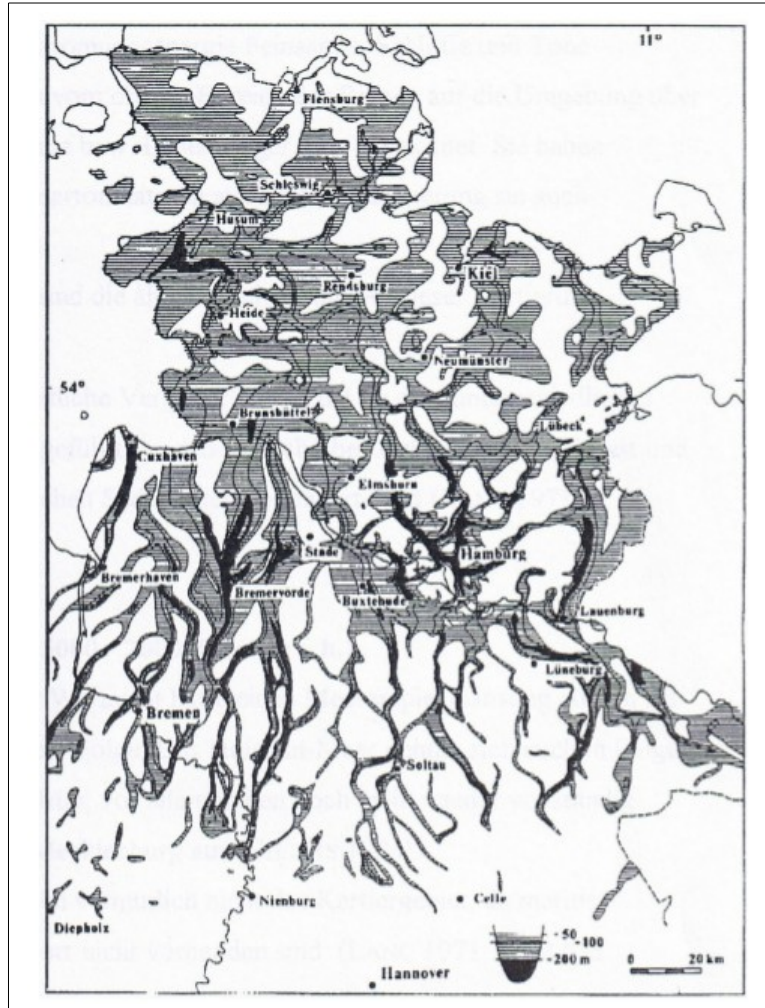


Fig 4 - Sub glacial channel system in north-west Germany (Ehlers 1990; from Kuster and Meyer 1979; Hinsch, 1979; Linke, 1983)

Elster ice age (700,000-370,000 ka) is the first and the most extensive of the three Pleistocene ice ages. It changed the environment so much that it brought to the complete destruction of the pre-existing landscape and landforms (Hammer, 2003).

During the final stage of the glaciation, when ice began to melt, many small lacustrine basins formed. They are filled both with fine-grained (silt and clay) and coarse-grained (Ritterhunde sands) sediments. Fine grained sediments along with coarse ones form the Lauenburg layers characterized by a thickness of 150 meters (Ehlers, 1994).

The heavy and moving ice sheet compressed the sedimentary substratum and was able to dig deep channels (up to 400 meters) in the substratum, forming a complex channel system (Ehlers, 1994 & McCann, 2008). The channels are first filled up with coarse sediments (sand and gravel) and then with fine ones on the top (Lauenburg layers).

Varved clays, glacial till and sediments of melting waters are very common sediments in north western Germany. Till deposits of the Elster ice age are mainly composed by local sediments with a considerable content of sand (Ehlers, 1994).

In the interglacial Holstein age the sea level rose again and the marine transgression covered the most part of the northern plains (McCann, 2008) (see Fig 5). As a consequence of this evolution a deposition of marine and organic sediments took place, including peat, limestone-mud and diatomaceous earth. In the surroundings of Bremen these sediments are almost absent because they have been eroded and transported away by the other ice ages (Ehlers, 1994).

HOLOZÄN	Subatlantikum	Dünensande					Weser- sande und -kiese	
	Subboreal	Auelehm						
	Atlantikum	Klei						
	Boreal	Torf						
	Präboreal							
PLEI- STO- ZÄN	Weichsel-Kaltzeit							
	Eem-Warmzeit							
	Torf Schluff							
	Saale-Kaltzeit	Warthe-Stadium		fehlt				
		Drenthe 2-Stadium						
		Drenthe 1-Stadium		Grundmoräne				
				Rinnensedimente				
	Holstein-Warmzeit							fehlt
	Elster-Kaltzeit							Lauenburger Schichten
								Grundmoräne
						Rinnensedimente		
Ältere Kaltzeiten						fehlen		

Fig 5 - Layers deposition during the Quaternary (Ortlam, 1980)

The following Saale ice age (350,000-135,000 ka) is divided into three main periods: Drenthe I, Drenthe II and Warthe. Moreover, it is quite important to notice that some interstadial periods also occurred during this ice age. In the Drenthe I and Drenthe II periods, the Lauenburg layers have been covered first with 10-20 meters layers of gravel and sand and then with glacial sediments (Ortlam, Schnier, 1980). Till deposits of these first ice age are made up of loam with a variable content of sand (Hammer, 2003).

During the Elster ice age the first part of the channels is covered by the sand, while in the Drenthe II period the melting waters sank the sand forming thus great sandy plains (Ehlers, 1994).

In the final stage of the Drenthe II period and all over the Warthe one, Lower Saxony was completely free of ice and the glacial sediments of Warthe have been transported from the Fennoscandia (Hammer, 2003).

During the interstadial periods in the Saale ice age no deposition of organic sediments occurred. The peat and the silt with organic content developed only during the Eem interglacial age. The following marine transgression settled the marine sediments that covered all the Saale layers. The marine advance is predominant in the east side of Europe and in the north of Germany the Eem deposits are very common (McCann, 2008). The Weichsel is the last and smallest ice age of the Pleistocene (115,000-11,500 ka). Glaciers cover only a small part of northern Europe without affecting the Lower Saxony. The rivers are consequently strong enough to transport coarse sediments such as gravel and Weser sand (Hammer, 2003). The deposition of these sediments continued up to the Holocene.

The gradual increasing of the sea level caused a reduction of the flow strength of the Weser river and therefore the deposition shifted from coarse to fine-grained sediments. Especially in the floodplains, loamy sediments form the so called Auelehm while the raising of the Weser submerges the depressed lands where peat and silt are settled. The west side of the Weser is characterized by the deposition of clay and silt.

Due to the alternation of glacial and interglacial periods, Bremen and its surroundings are represented by some typical landscapes (see Fig 6):

- dune;
- floodplains (Auelehmmarsch);
- bogs (Niedermoormarsch);
- geest (typical northern Germany landscape of sandy and gravelly soils);
- vorgeest of north Bremen:

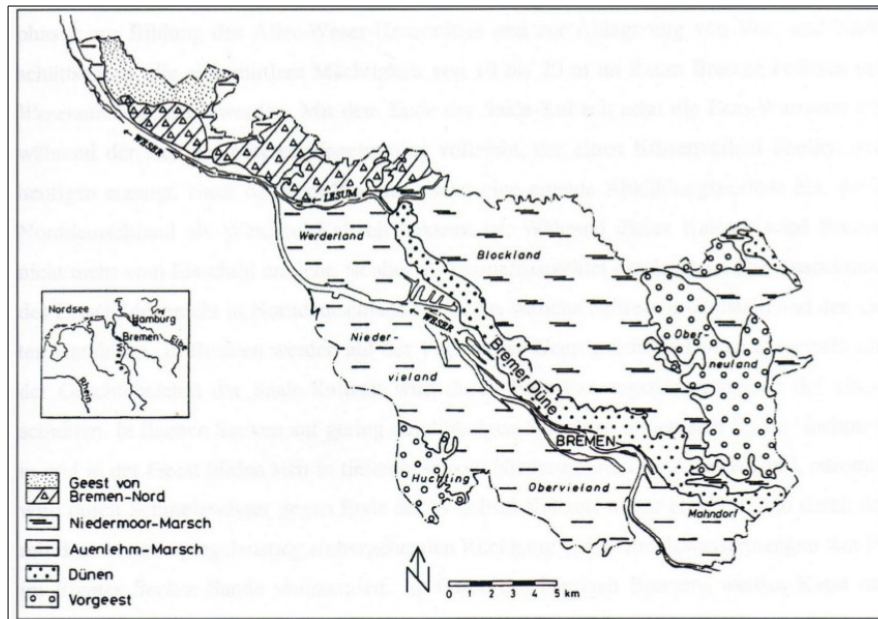


Fig 6 - Landscape forms in Bremen (Sauer, 1995)

The lack of vegetation in the early Holocene promotes the soil degradation and the wind erosion. Indeed, wind of south west forms the so called Bremner Düne (5-15 meters) in north-west, south-east direction (Sauer, 1995).

Niedermoormarsch are situated in the north-east side of Bremen (Blockland): these bogs are made up of stagnant and poorly oxygenated waters where peat is deposited. Niedermoormarsch and Auelehmmarsch have a thickness of 2-4 meters and their less compacted sediments cover the Lauenburg layers (Sauer, 1995).

The geest is a typical hilly landscape of north Germany and it is composed mainly by till deposits resistant to erosion. It is less fertile compared to the bogs but it is more protected by floods because more elevated on the territory.

2.2 *Hydrogeology*

In the Lower Saxony the aquifer is made up of the Weser sands, deposited during Saale, Weichsel ice ages and mixed with other holocenic sands. The silt and clay layers of the Lauenburg (Elster ice age) are characterized by a low permeability and form the base of the aquifer. However, the Lauenburg layers include also sandy parts (Ritterhude sands) that form the deepest aquifer: there are not others aquifers in the deeper Tertiary layers (Ortlam, Sauer, 1993).

The subsurface of the whole region is characterized by channels that were dug during the Elster ice age. In some rare cases groundwater storage can be found in the coarse sediments of these channels.

The aquifer is covered by the Quaternary sediments, made up mostly by both loamy material (Auelehm) and silt deposits.

Further information about the hydrogeology of the area of study are available in the next section.

3 Area of study

3.1 Location of the study area

The Seehausen area is situated in the western part of the city of Bremen, in the Niedervieland territory. The area is included between river Weser (east and north side) and the smaller river Ochtum (west side). Seehausen is a flat territory with an extension of approximately 10 km², many of which are farmlands.

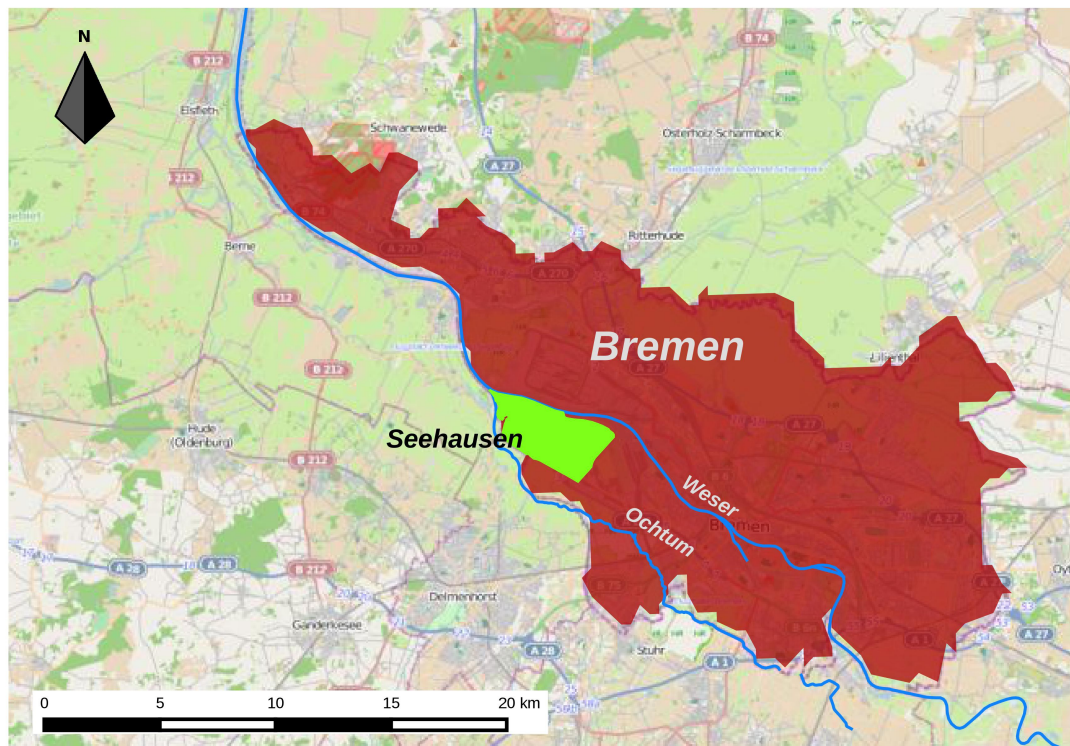


Fig 7 - Seehausen location

3.2 Trade and harbor in Bremen

Harbor activity is one of the most important economic activities for the city of Bremen. Every year million of tons of goods transit through the Bremen and especially through the Bremerhaven ports: in 2011 a total amount of 80,000,000 tons of wares were moved (www.bremenports.de [1]). The transport of these goods is provided by a total amount of 7194 cargo ships; 1048 of them hosted in the port of Bremen and 6146 in the port of Bremerhaven.

In order to navigate, ships require a free environment, this means that a huge amount of

sediments have to be dredged from the river Weser and from the harbor basin of Bremerhaven every year. Indeed, due to natural processes, sediments tend to accumulate to the bottom of the rivers and to the coast lines. To keep these two dynamic environments in a stationary status, it is necessary to dredge the channel and harbor areas.

However, considering the traffic of the ships, these sediments could be heavily polluted, especially by heavy metals and organic contaminants. Also significant concentration of dissolved salts can be found and this is because the sediments are essentially marine sediments. However another source of pollution, especially heavy metals, comes from the Harz mountains (Monna et al., 2000). To avoid the contamination of the environment, particularly of soil and groundwater, the dredged sediments have to be disposed and treated in special landfills.

3.3 *The Seehausen sediments landfill*

The landfill of Seehausen was built in 1996. Till 2001 there were accumulated only sediments dredged from the river Weser, but since 2001 also the sediments coming from the Bremerhaven port are treated and this meant a significant increase of incoming material. Around 340,000 m³ of sediments are treated every year (2003).



Fig 8 - Seehausen landfill overview

The dredging procedure is quite a simple process (Fig 10). It begins with bucket chain excavators that extract sediments from the interested region and put them on big barges. The barges navigate in river Weser till they arrive to Seehausen where a net of pipeline pumps the sediments in one of the 16 the drying fields. Every field has a surface of around 20,000 m² in which 21,000 m³ of dredged sediments can be deposited. Sediments require almost one year to reach the optimal dryness. During the year sediments are turned and crumbled by special machines in order to accelerate the drying time. Once dry the volume of sediments is reduced by about a third.



Fig 9 - Bulldozer and sediments drying procedure

During the drying time, the water coming out from the sediments is drained in a complex network of channels: water is pumped in a large basin before being purified in a phytodepuration facility and pumped back into the river. Nevertheless a part of this waste water is used to pump the sediments in the drying fields in a “closed cycle”.

Periodically, sediments are sampled and different analysis are made to evaluate the content of pollutants and other dangerous substances. A large fraction of the dry and clean sediments is accumulated in hills and later use directly for construction purposes (e.g. for the constructions of dikes) while another part is treated in a special *conditioning structure*.

In this structure sediments are treated in different ways: the procedure simply consist in the adding of material in order to create a final product that can be used for building purposes. Depending on the final aim, creation of bricks or material for the bottom of streets, different raw materials are added (e.g. loam or cement). The conditioning structure is able to treat 200 m³ of sediments every hour.

On the other hand, all the sediments that have a significant content of contaminants are disposed inside the landfill.

All the base of the landfill is composed by clay that should protect the groundwater from an eventual transport of contaminants leached from the sediments and from the drying fields. However it is possible that in some places the protection is depleted and chemical species have the possibility to flow in the aquifer and contaminate it.

The closure of the landfill, due its to the capability, was planned in 2018, but the continuous removal of clean sediments extended its life (today the landfill has a capacity till 2025).

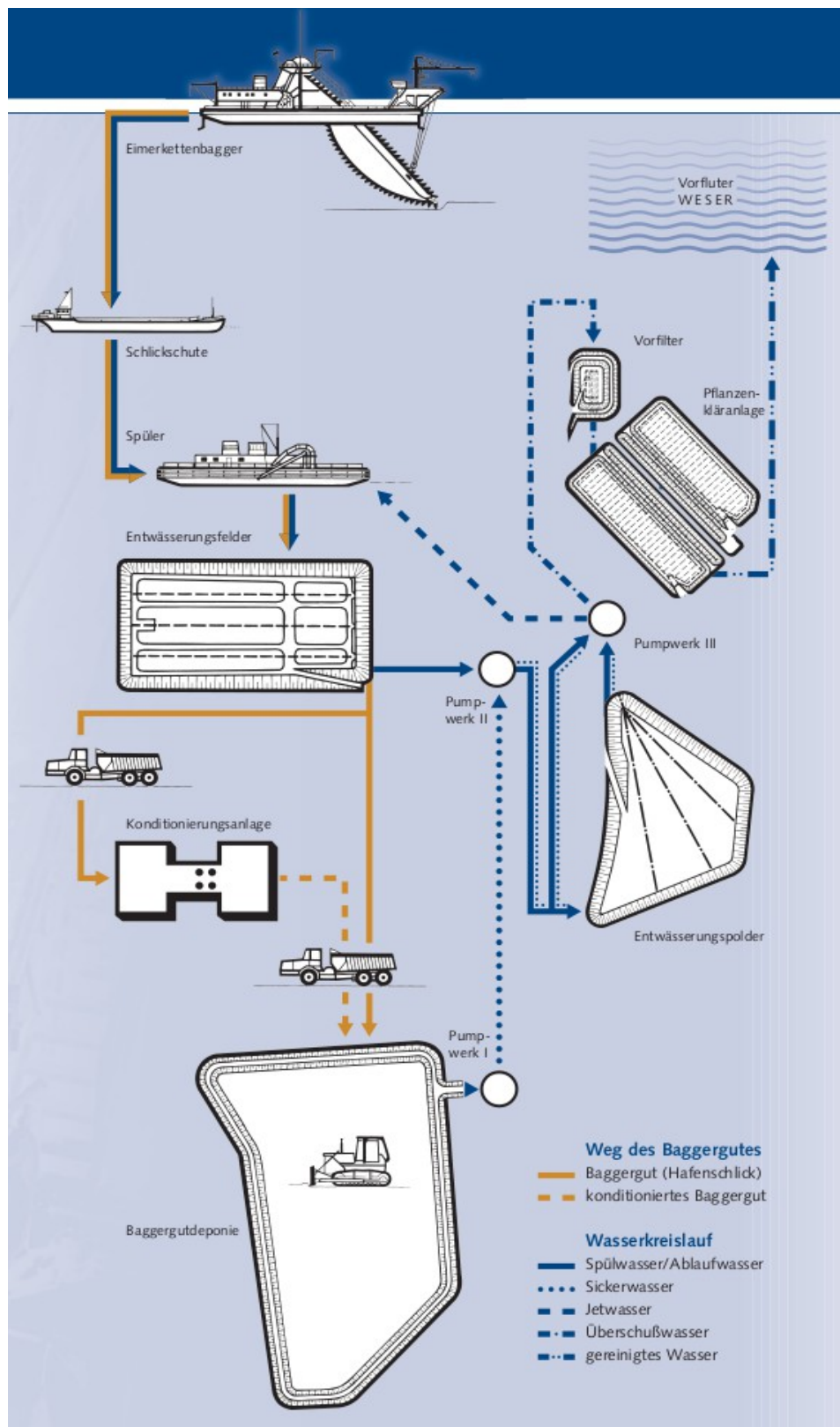


Fig 10 - Dredging and treatment procedures summary (www.bremenports.de [2])

3.3.1 Landfill location in the Seehausen territory

The landfill (included the drying fields, the constructed wetland, roads, etc...) has a total surface of 127 hectares and is surrounded mostly by farmlands. However, in the southern side one can find one of the many logistic areas of the harbor, while in the northern side is located the small neighborhood of Seehausen (see Fig 11).

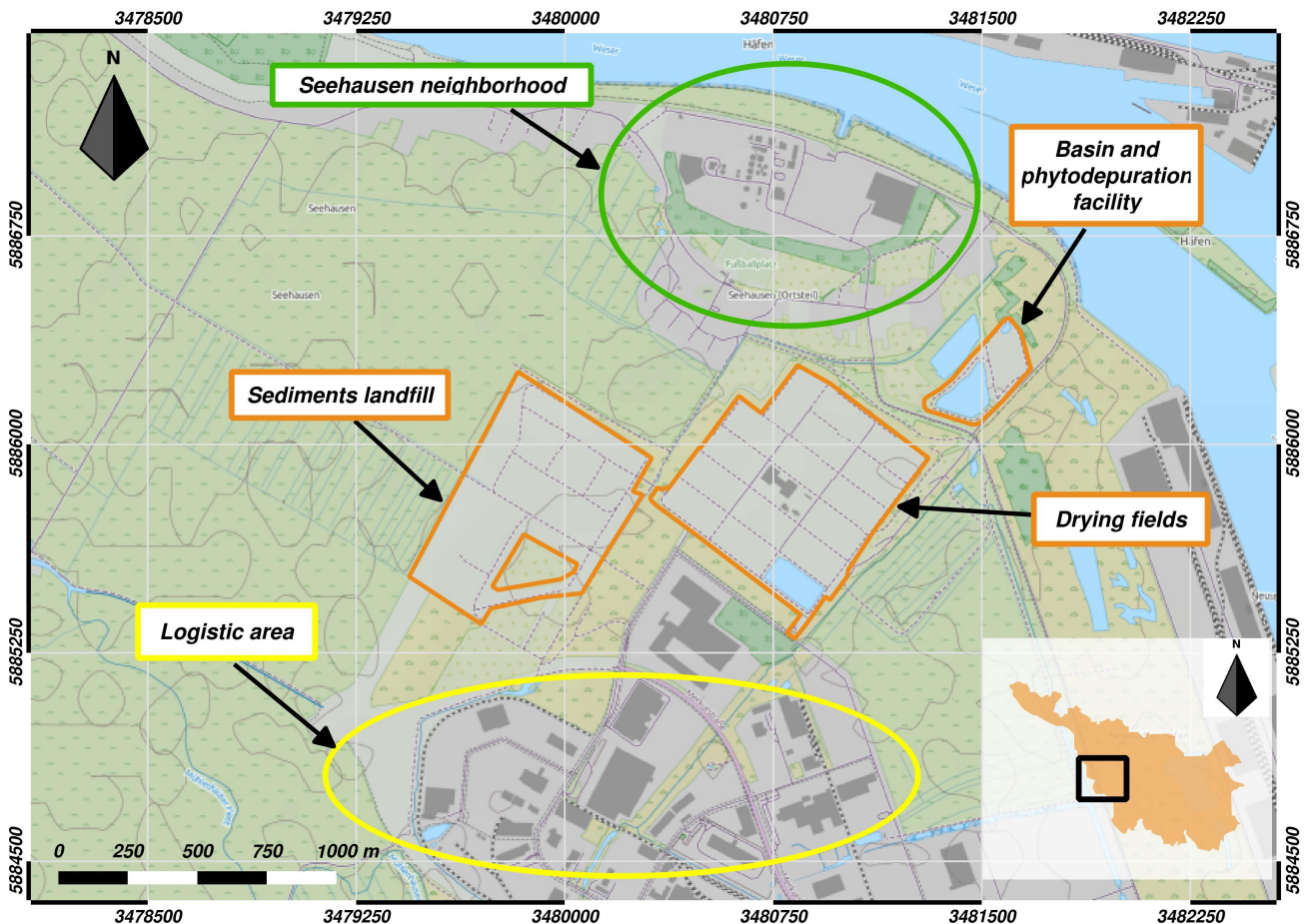


Fig 11 - Overview of the landfill in the Seehausen area

The ground level of the area of study varies from 1.30 m above middle sea level (MSL) in the central part of the area of study to 10.00 m above MSL in the south-east side of the territory.

3.4 Geology of the area of study

The old Lauenburg layers, settled in the Elster ice age and made up of clay, silt and sand, are situated under the Weser sands and can be found at depth from 9 to 25 below the

surface (Sauer, 1995). Weser sands deposited in the Saale and Weichsel ice ages can have a total thickness that varies from 5 to 15 meters (Sauer, 1995). Between the Weser sandy layers and the Lauenburg ones, sometimes the residual of glacial sediments of till deposits (Saale ice age) (Sauer, 1995) can be present. The Quaternary deposits are the most important sediments of the whole area. They cover the Weser sands and are mostly made up of loamy material (Auelehm) deposited in the recent Holocene period. These loamy sediments can have a thickness that varies from 1 to 10 meters

Seehausen is located in the left part of the figure Fig 12 corresponding to the Neustadt territory.

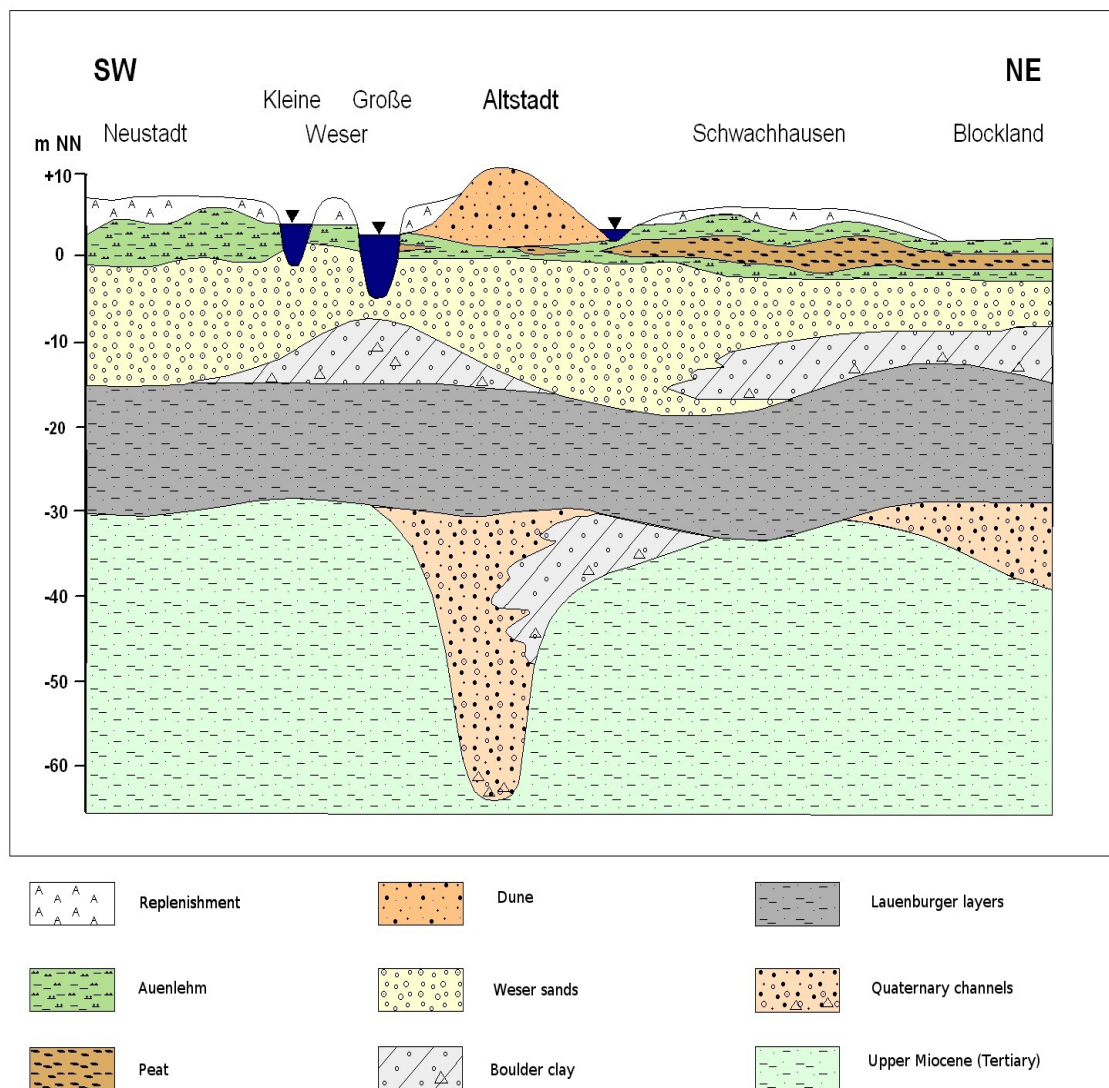


Fig 12 - Bremen geological overview (Adapted from Senator für Bau, Umwelt und Verkehr , 2006)

3.5 *Hydrogeology of the study area*

The Seehausen area is included between the Weser River and its tributary Ochtum. The aquifer is in very close contact with the Weser and meet the Ochtum only in the northern side. Anyway, the Ochtum does not influence the aquifer status (Sauer, 1995).

The Weser sands that form the upper aquifer are from 2 to 21 meters thick and the aquifer has a flow velocity that vary from 20 m/y to 30 m/y (Roth et al., 2007). The permeability of these sands has wide ranges (from 10^{-3} m/s to $5 \cdot 10^{-5}$ m/s) because of the large grain size spectrum of the grains.

The bottom part of the aquifer borders with the Lauenburger layers. These layers are made up essentially of low permeable clay sediments (permeability $< 10^{-7}$ m/s) and by sandy layers (see section 2.1.5) with a permeability of about 10^{-5} m/s (Klinge et al., 2002) that form the lower aquifer. The flow velocity is pretty low and varies from 5 m/y to 10 m/y (Roth et al., 2007).

The southern part of the territory is affected by the saline structure of Delmenhorst-Osterholz that can be found at a depth of 300 meters. Given that, groundwater flowing through it are enriched of salts and can consequently influence the global salt concentration of the lower aquifer (Sauer, 1995).

The whole territory is drained due to industrial and domestic uses. This water management can have a strong influence on the depth of the fresh and salty water interface.

The sandy lenses of the Lauenburger layers allow the communication between the upper and the lower aquifer that in fact form a unique water body. In these contact areas the more salty waters of the lowest aquifer can mix with those of the upper one and increase the salts concentration of the aquifer. The up climbing is caused by the difference of density between salty and fresh water (Gyben-Herzberg effect).

Another natural source of salt in the aquifer could be related to a tidal effect. In low tidal condition the water level of the Weser is lower than that of the aquifer, therefore water flows from the aquifer to the river. But in high tidal condition, the water level of the Weser is higher than that of the aquifer and Weser water flows into it (Sauer, 1995).

Due to these two last features, the communication between the aquifers and the tidal effect, the hydrogeological setting of the area of study is very heterogeneous and complicated to analyze.

4 Materials and Methods

A detailed survey of the whole territory has been made in order to find the best sampling points. The Harbor Authority offered to share all the piezometers used for the landfill monitoring. Furthermore, chemical data from 1996 to 2012 are available for these piezometers and will be used in the discussion.

Additionally it has been made a research in the database of the Geological Survey of Bremen in order to find other useful piezometers outside the landfill area.

The information collected for all the piezometers consist basically in: a unique ID, X and Y coordinates in the Gauss-Krueger Zone 3 coordinate system and finally the height of the pipe reported in meter over the middle sea level. The data collected has been elaborated in order to transform them in a readable table format for QGIS software, that allows the creation of a map of all the sampling points scattered in the territory.

4.1 *Monitoring net*

Initially, 38 piezometers seemed to be available for the sampling, but after field surveys the real number of available piezometers lowered to 22 (18 of the Harbor Authority and 4 of the Geological Survey), see Fig 13. The main reason is that Seehausen is a territory in big expansion and due the continuous constructions of buildings, roads and industrial facilities many piezometers have been destroyed. Nevertheless the 22 piezometers offer a good coverage of the territory: some of them are placed directly in the landfill, while some others are placed outside the landfill boundaries. The latter ones could reflect the natural environmental condition. A complete table resuming the characteristics of all the piezometers is available in Attach 1.

All the piezometers used for this work have different characteristics, the most important are the filter installation depth and the position (relative to the landfill). This two main criteria have been used in order to categorized piezometers into four different classes:

1. shallow – upstream
2. shallow – downstream
3. deep – upstream
4. deep – downstream

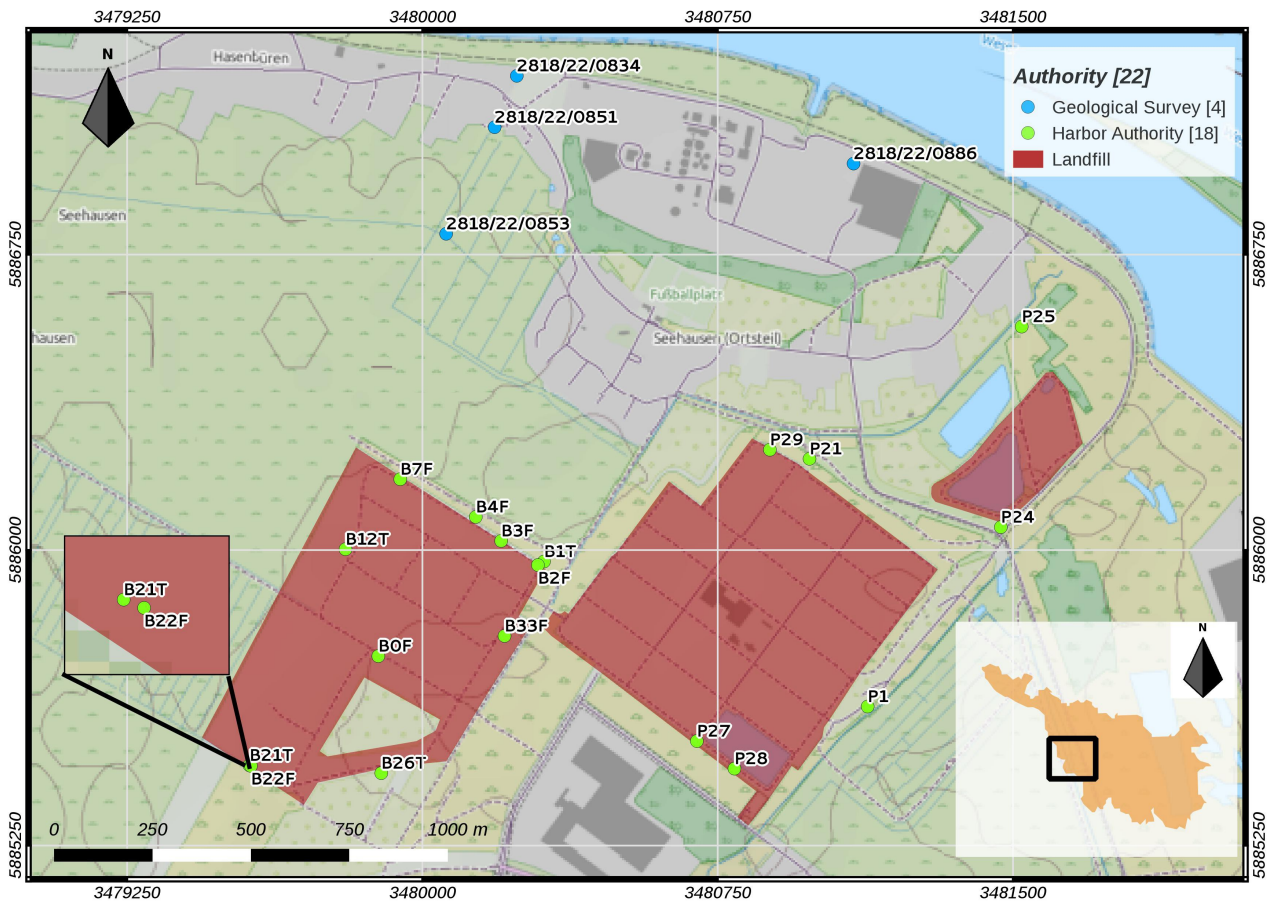


Fig 13 - Piezometers in the area of study

See map in Attach 2 for a complete view of all the piezometers.

4.2 Sampling and field parameters

19 groundwater samples of 22 piezometers available were collected during two different field trips: the first one in the dates 11-12 of June 2013 in collaboration with Institut Dr. Nowak company and the second one on the 13th of August with the university equipment. A Grundfos® pump model “MP1” pump has been used in both field trips for the water sample collection. The sampling procedure begins with the measurement of the water table height, then the pump is inserted at about 2 meters below the water surface and the extraction begins. The power of the extraction was controlled checking regularly the measure of the water table height.

Physical parameters such as pH, dissolved O₂, temperature, electrical conductivity and water table height have been measured directly on field during the sampling, but also

subjective measures like smell, color and turbidity were taken for all the 22 piezometers.

WTW® Multi 3430 Multiline instrument combined with 3 electrodes has been used for the measurement of the field parameters, in detail:

- pH, electrode SenTix 940
- dissolved O₂, electrode FDO 925
- electrical conductivity, electrode Tetracon 925

For each piezometer, 2 samples were collected and filtered at 0.45 µm, each of 100 ml: one for the anions and isotopes analysis while in the other sample it has been added HNO₃ (65% concentrated) for the cations analysis.

4.2.1 Alkalinity

Alkalinity is the capacity of the water to neutralize an acid. In a normal water sample the major anion capable of neutralizing acid is the bicarbonate (HCO₃⁻) and for this reason, alkalinity is expressed as equivalent concentration of HCO₃⁻ (in mg/L or meq/L).

Alkalinity values has been taken directly on field for only 8 piezometers; for all the other piezometers, it has been calculated through a regression line model based on the concentration of chlorine, sodium, calcium and potassium. For the 8 in field samples, alkalinity has been calculated through the Gran Titration technique. It consists in lowering the pH of the solution adding HCl (0.1 M) in at least 5 steps: pH must reach 4.3 because hereafter all HCO₃⁻ is transformed in CO_{2(aq)}. The HCO₃⁻ concentration is deduced through the calculation of the point of equivalence: this point is reached when the solution cannot neutralize the acid added and so the concentration of protons rise linearly. It is possible to calculate the concentration of protons from pH and from the total volume of the solution:

$$[H^+] = 10^{-pH} \cdot (V_0 + V_{HCl})$$

where V₀ is the initial volume (100 mL) and V_{HCl} is the total volume of acid added.

Plotting the values of H⁺ versus the volume of HCl one can calculate the regression line and the point at which this line cross the x axes, that is, the value at y=0. Knowing all these values it is finally possible to deduce the alkalinity value through:

$$\text{Alkalinity} = X \cdot (C_{HCl} / V_0)$$

where:

Alkalinity is expressed in [mol/L]

X is the point at $y=0$ expressed in [L]

C_{HCl} is the concentration of the strong acid in [mol/L]

V_0 is the initial volume of the solution in [L]

Alkalinity can be easily transformed in HCO_3^- multiplying its value by the molecular weight of HCO_3^- (61 g/mol):

$$[\text{g/L}] \text{HCO}_3^- = [\text{mol/L}] \text{Alkalinity} \cdot [\text{g/mol}] \text{Molar weight}$$

An example of the spreadsheet used for the Gran Titration is available in Attach 3.

4.3 Continuous monitoring of groundwater parameters

In order to have a better and more completed knowledge of the whole territory, additional dataloggers (CTD Diver and Mini-Diver of Schlumberger Water Services® company) have been installed into 13 piezometers for about one month (3rd July – 5th August). 7 of them were set to take a measure of pressure (expressed as mm of water column plus air pressure), temperature (°C) and electrical conductivity (mS/cm) every 5 minutes, while the other ones 5 were set to take a measure of only pressure and temperature every 10 minutes. The depth at which the data loggers have been installed depends on the fresh – salt water interface (measured with a long probe instrument): where possible, they have been placed exactly on this interface. Thanks to the data loggers placed in the north side of the area one can see the influence of the river in the aquifer. Furthermore, with the huge amount of data collected it should be possible to notice the general trend of those parameters and highlight unusual behaviors. A summary of the data loggers data and a map of the area are available in Attaches 4 and 5.

4.4 Laboratory analysis

Analysis of cations, anions and isotopes (stable hydrogen and oxygen) have been made in the Geochemical Laboratories of the University of Bremen. Complete tables of the values for all the piezometers are available in Attaches 6, 7 and 8.

4.4.1 Anions

Following anions have been measured: chloride, sulfate, fluoride, bromide, nitrates, phosphates and nitrites. It has been made an additional filtration through a 0.2 μm filter paper for all the samples because of the presence of suspended material that could disturb the analysis.

It has been used an ionic chromatograph Metrohm®, model “883 Basic IC plus” equipped with column “Metrosep A Supp 5 – 150/4.0”.

For the analysis, the instrument takes a small portion of the sample that is transported by an eluent till the separation column: depending on the mass and the size of the anions, they require more time to pass through it. Every anion requires a precise interval of time to go through the column and knowing this time it can be easily detected by special detector placed at the end of the column.

A multi element standard (MES) has been used for the calibration. It have been prepared 7 samples containing the standard solution of the element to be measured in different grades of dilution: concentrated, 1:2, 1:4, 1:8, 1:16, 1:32, 1:64 (MES to MilliQ water respectively). Two certified reference materials (K15 sea water and CRM sea water high purity standard) with know concentration, have been included in the analysis to verify the calibration. Complete data of the calibration and the standards used are available in Attach 9.

4.4.2 Cations

ICP-OES (inductively coupled plasma optical emission spectrometry) technique has been used to measure following cations: K, Mn, Ca, Fe, Mg, Na, Li, Al, Be and Ni. The instrument used is a Perkin-Elmer® c “Optima 7300 DV”.

The procedure of analysis consists in the vaporization of the sample that is transported by an inert gas to a plasma flame fueled by argon. The flame can reach temperature up to 8000°C that supply enough energy to ionize the elements: this way, outer electrons are completely dissociated from the atom that is left with a positive charge. When the energy is

removed, electrons return to the original position releasing energy in form of electromagnetic radiations. These radiations are unique for each element and can be detected by the detector of the instrument and their intensity quantified.

For the calibration, it has been used a MES made up by the 10 elements to be measured and a 1% solution of HNO₃. 3 standard samples have been prepared in different dilutions: concentrated, 1:2 and 1:5 (MES to 1% HNO₃ solution). The certified reference material (CRM SRM 1643 E) has been used to validate the calibration curve. All the values are available in Attach 10.

4.4.3 Isotopes

Water stable isotopes have been analyzed with the “tunable diode laser absorption spectroscopy” (TDLAS) technique with the instrument “LGR DT-100 liquid water stable isotope analyzer” of Los Gatos Research Inc®. Basically the analysis consist in the emission of a precise wavelength radiation that passes through the water sample: a portion of the emitted radiations are adsorbed by the isotopes and a detector identifies the lack of radiations transforming them in concentration according to the Lambert-Beer law.

As for the anions analysis, the samples have been filtered through a 0.2 µm paper due to the presence of suspended material.

3 samples of the standard “Vienna Standard Mean Ocean Water” (VSMOW) have been used for the calibration of the instrument. The instrument gives the results directly in δ-values of the samples: δ-values consist in the ratio between the heavier and the lighter isotopes of the sample and of SMOW expressed in ‰.

$$\delta = \frac{R_{sample} \cdot R_{VSMOW}}{R_{VSMOW}} \cdot 1000$$

where R is the ratio in which the heavier isotope is at the numerator and the lighter one is at the denominator (e.g. ²H_{sample}/¹H_{sample}) and δ is the value expressed in ‰.

Isotopes analysis are very useful to understand the source of the water in the samples: Craig (Craig, 1961) discovered a linear relationship between δ values of ¹⁸O and ²H in the rainfall water:

$$\delta^2H = 8 \delta^{18}O + 10$$

global meteoric water line

so, one can draw a $\delta^{18}O - \delta^2H$ graph and, if the points plotted are in the proximity of the line, then the source of the water is rainfall. Indeed, sea water or river water intrusion would reflect a change of the isotopic ratio due to dilution and other fractionation processes.

4.5 Data analysis

4.5.1 Statistical analysis

Statistics is essential to understand and comment the data. Basically, two software has been used: Libreoffice Calc for the preparation of the dataset and RStudio for the data elaboration.

Libreoffice Calc (basically the open source equivalent of Office Excel) offers a quick and easy way to prepare data that will be imported in RStudio. The hard part of the work was to make all the data consistent and coherent: historical dataset sheets didn't have the same layout and data missing or data mistaken were difficult to elaborate.

Once that all the data have been cleaned, they have been uploaded in RStudio (Van der Loo, De Jonge, 2012). RStudio is an open source IDE (integrated development environment) for the world known R programming free statistical software. This means that all the R functions and packages are available also for RStudio but with a very simplified graphical interface.

Univariate statistical analysis has been used essentially for the plotting of boxplots and scatterplots. Boxplots help to see the spreading of the plotted variable, e.g. the variation of chlorine in the same piezometer depending on time or the variation of electrical conductivity depending on the piezometer depth.

Almost all the plots have been created with the *ggplot2* package (Hadley, 2009, <http://docs.ggplot2.org>). *ggplot2* is a data visualization package which breaks up graphs into semantic component (scales and layers): the extremely basic language and the powerful versatility have been very useful for data plotting.

Several multivariate statistical analysis have been performed in order to understand geochemical behaviors. Correlation matrix is a quick and powerful statistical method to see the relationship between all the variables. Through the correlation matrix one can see which variables are related and so try to understand some strange behaviors. Multi-dimensional-scaling (MDS) is the statistical method that allows to plot in 2 or 3 dimension data with more than 3 variables. Thanks to this method one has the chance to see if single observations belong to specific groups. Clustering is another graphical way that allows to gather together single observation into groups depending on the input variables: e.g. it is possible to see how many piezometers groups can be distinguished and see if there is a depth correlation rather than a spatial one. Clustering method is based on a distance matrix, so it is necessary to specify which distance is used for the calculation: distance type depends on the purpose of the analysis. The clustering plot, also known as *dendrogram*, links with lines the single observations and offers a graphical distinction of the different groups. Multivariate linear regression has been made just to infer the HCO_3 concentration of those piezometers where it has not been measured directly in field. The theory beyond this multivariate method does not differ from a *normal* linear regression: the model consists in finding the relationship between a *dependent variable* and more *explanatory variables*.

All these methods have been applied in chapter 6.

4.5.2 Spatial analysis and GIS

Spatial analysis has been performed with QGIS software: working with the development version of this software has allowed to take all the advantages of the new implemented features.

QGIS is a powerful cross platform open source software (the source code is available online, see github.com/qgis/QGIS) entirely developed by volunteers (I'm one of them): in the last years it has been adopted by a growing number of public administrations, universities and governments. QGIS offers a complete suite of geospatial algorithms which allow to implement essentially all kind of spatial operation. If there is the need to use more functions, with QGIS it is possible to use other software such as R, SAGA-GIS, GRASS,

OTB and the complete Python programming language with all its features. Furthermore, additional plugins offer other specific functions. So basically, there is no spatial operation that cannot be performed with QGIS.

The background map of all the map compositions comes from OpenStreetMap which is a complete and growing spatial free database made up by single users (like Wikipedia). OpenStreetMap data and all the other data used in this work are under the Creative Commons license (CC-BY-SA).

Spatial interpolation has been used extensively: it consists basically in the process of using points with known values to estimate values at other unknown points. There are many interpolation algorithms available and their use depends on the data type. Among other, two methods are widely used: Inverse Distance Weighted (IDW) and Triangulated Irregular Network (TIN).

In IDW the sample points are weighted during interpolation such that the influence of one point relative to another declines with distance from the unknown point you want to create (see Fig 14).

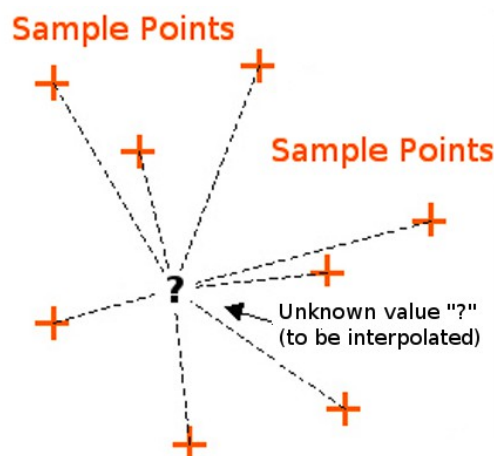


Fig 14 - IDW interpolation method

The major disadvantage of IDW is that the quality of the interpolation result can decrease if the sample points distribution is uneven: in other words the more the dataset is big and well spatial distributed the better will result the interpolation.

TIN interpolation tries to create a surface formed by triangles of nearest neighbor points. To do this, circles around selected sample points are created and their intersections are connected to a network of non overlapping and as compact as possible triangles (see Fig 15).

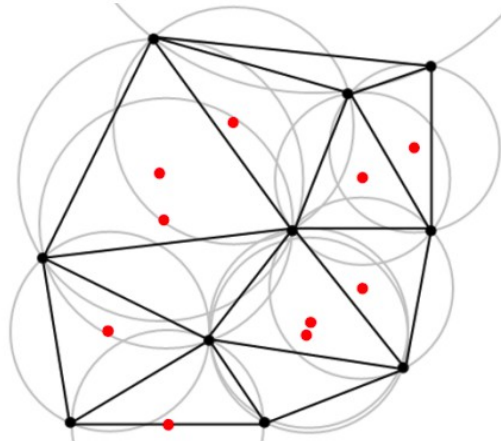


Fig 15 - TIN interpolation method

The big disadvantage of TIN is that the surface is not smooth and give a jagged appearance. This is caused by the discontinuous slopes at each triangle edges and sample data points.

For this reason IDW interpolation has been the method used for the creation of all the maps (if another algorithm has been used, it is specified).

The excellent book of Neteler and Mitasova (Neteler, Mitasova, 2004) explore deeply interpolation techniques explaining in detail when to use them in order to get the best result.

Interpolation has been used in order to create a groundwater flow map of the whole Seehausen territory. After the measuring of the piezometer water table height it has been possible to create the interpolated map. Contour lines have been easily extracted from this map: each line corresponds to a certain table height value and so it is possible to see in which direction the water is flowing. Contour lines have been compared with those of the WMS Service of the Geological Survey of Bremen (see Section 5.2.4 for further details and for the map comparison).

Ortlam and Sauer (Ortlam, Sauer, 1993) have created some concentration maps (interpolation maps of ion concentrations) of several elements of all Bremen territory in 1991 (so, 5 years before the landfill construction). To compare those maps with current data maps, I had to computerize the old maps and to re-create the interpolation. All the interpolation maps are raster layers: they are composed by pixels and each pixel represents a numerical value of the original layer. In other words a layer is handled just like a numerical matrix and one can perform mathematical operations between them. Mapalgebra is the QGIS tool that allows to do these operations: it creates a new raster layer that is the result of the mathematical operation between the other layers. The following figure (Fig 16) explains how Mapalgebra works:

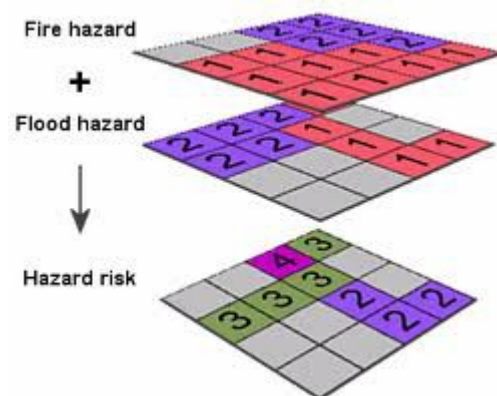


Fig 16 - Mapalgebra

5 Results

This chapter shows the complete dataset of the physical-chemical parameters collected by both the Harbor Authority and myself during the sampling trips. The harbor authority has collected the data in the last few years while I took the data in this current year (June and August 2013).

The data collected by the dataloggers (see 4.3) will be also shown in a section of this chapter.

Furthermore, Piper and Schoeller diagrams will be used in order to classify the different water types.

5.1 *Field campaign 2013*

In this section a brief summary of all the physical-chemical data will be reported. These data have been collected in the June and August 2013 field trips (see Attach 6, 7 and 8 for a complete view of the data).

5.1.1 *Temperature*

The temperature ranges varies from 10.5°C (in B21T and B26T) to 14.4°C in 2818/22/0886. However, this parameter is very homogeneous in all the piezometers and there are no outliers to report.

5.1.2 *pH*

The water in all piezometers shows neutral pH values: 2818/22/0853 has the lowest value (pH=6.49) while B1T has the highest one (pH=7.69).

5.1.3 *Electrical conductivity*

Electrical conductivity is a fundamental parameter for the study of the groundwater behavior. The values are very heterogeneous: higher values occur in deep piezometers while shallows piezometers show lower values:

Table 2 - EC depending on depth

	Min	Mean	Max
Deep	2410	5707	9700
Shallow	867	1937	3190

P1 has the lowest value while B12T has the highest one. With the following boxplot it is possible to better notice the difference:

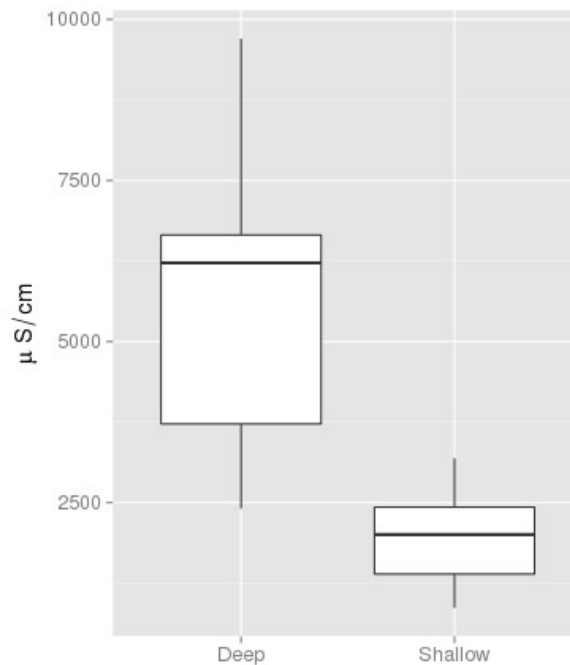


Fig 17 - Electrical conductivity boxplot

5.1.4 Dissolved oxygen

Dissolved oxygen range varies from 0.03 mg/L (B3F and B4F) to 0.93 mg/L (B12T). While it seems there are differences among shallow and deep piezometers, the values are rather homogeneous.

5.1.5 Subjective measures

Beside the physical-chemical parameters, information about color, odor and turbidity have also been collected. The majority of the samples don't have any odor, the color is transparent and there is no turbidity.

Refer to Attaches 6, 7, and 8 for more detailed information.

5.2 Field campaign 2013 – chemical analysis

This section summarizes all the chemical data collected during the laboratory analysis.

5.2.1 Anions

As described in section 4.4.1 the major anions have been detected with IC technique. Just like historical data, a big difference in the anions concentration can be noticed between the deep and the shallow piezometers, especially for the chlorine, sodium and sulfate concentration (higher in the deep ones). The following plots show the anion related data:

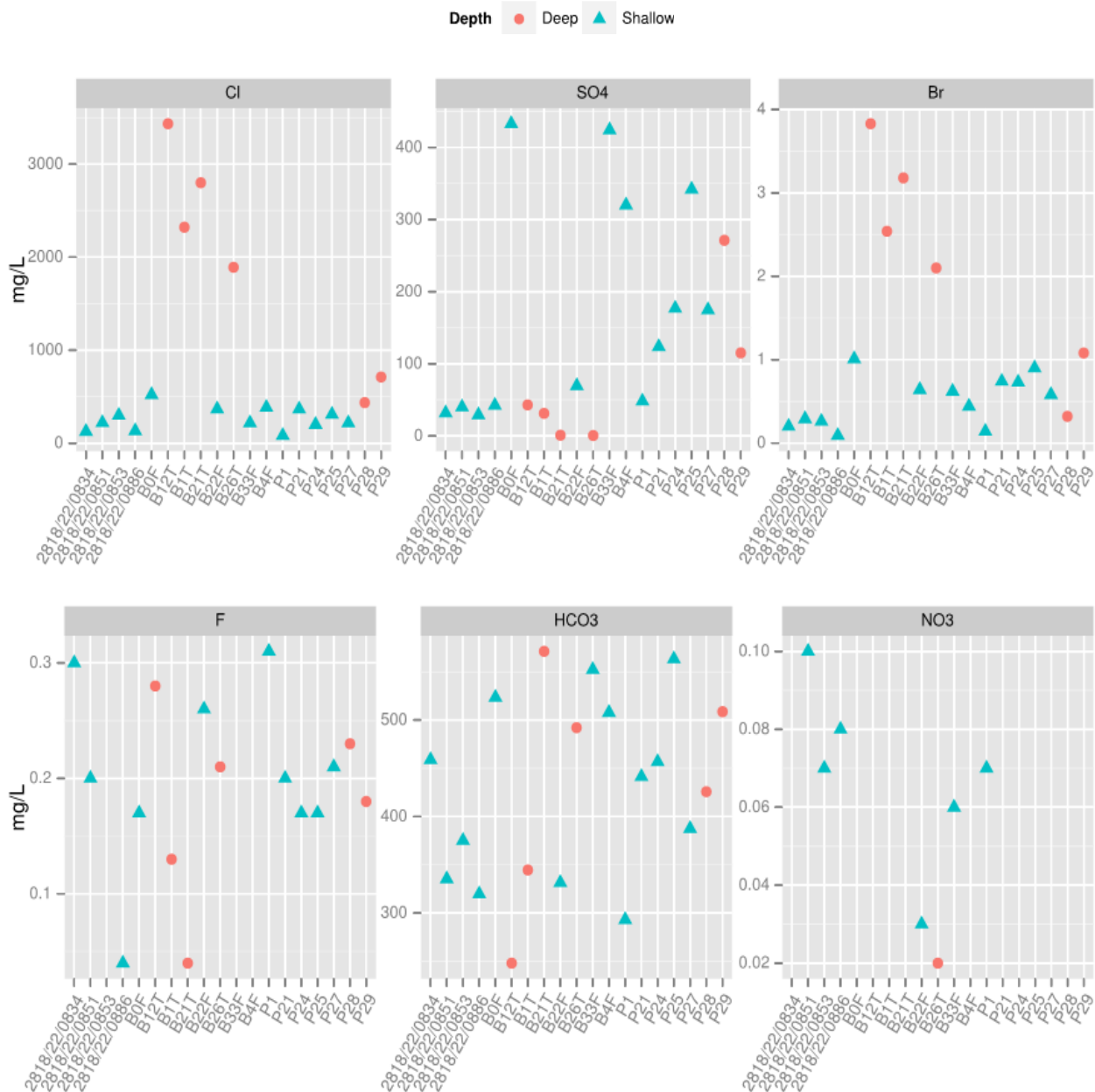


Fig 18 - Anions concentration in all the piezometers

As one can see, B12T has the highest chlorine concentration (3435.49 mg/L) while P1 has

the lowest one (82.01 mg/L). Values are related to the electrical conductivity. Another interesting trend is the sulfate one whose highest concentrations can be found in shallow piezometers.

5.2.2 Cations

Cation concentrations are not as spread as those of anions. The most visible difference is the sodium content, which is much higher in the deep piezometers. The following plots show, in a logarithmic scale, cations concentrations according to the piezometers depth:

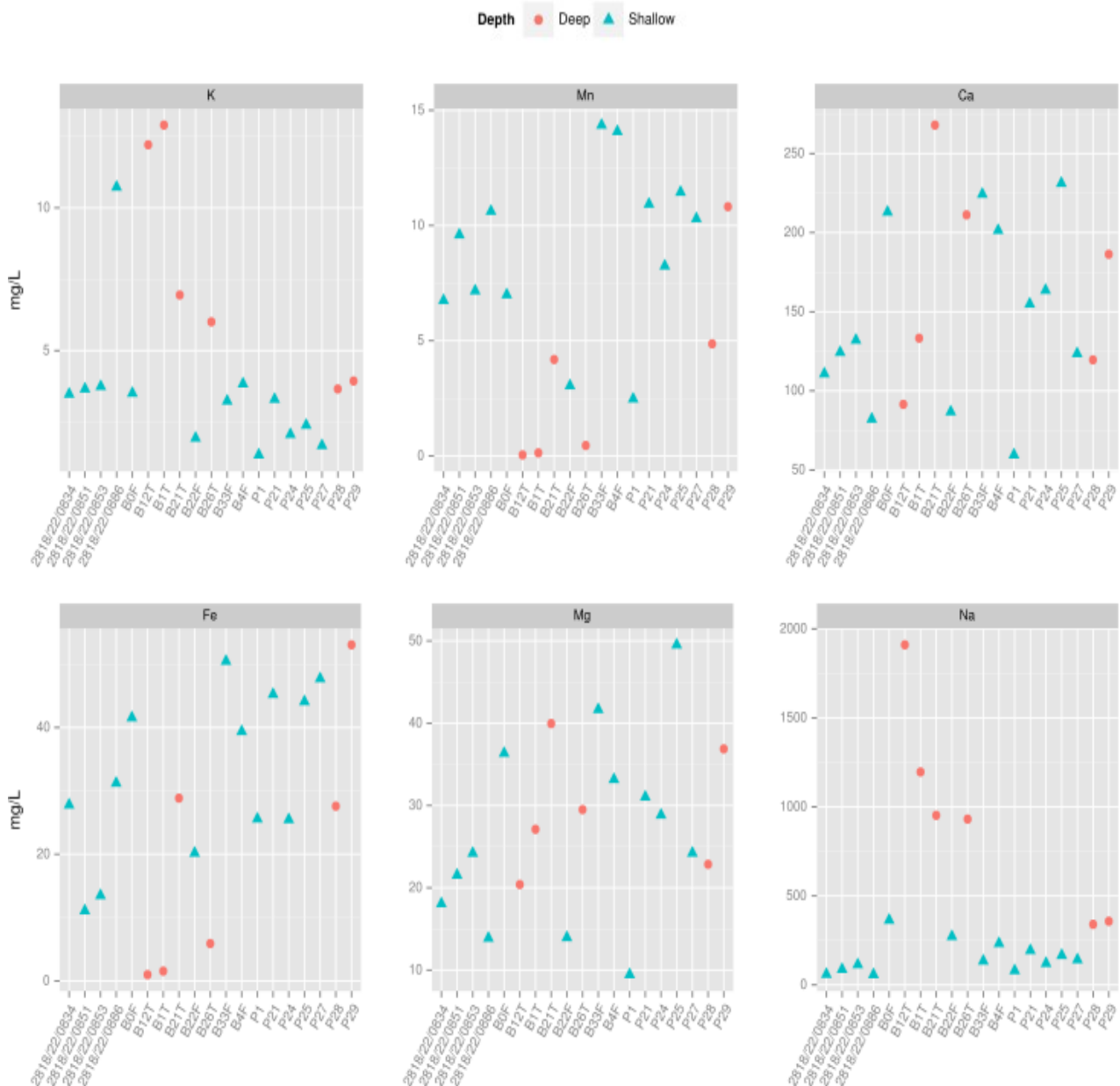


Fig 19 - Cations concentration in all the piezometers

Moreover, it is possible to notice the different spreading of iron and manganese while lithium has been found in very low concentration only in the deep piezometers (lithium plot is not displayed, see Attaches 6, 7 and 8 for detailed information about the values).

5.2.3 Isotopes

Water stable isotopes have been analyzed as well. According to section 4.4.3, the study of these isotopes is useful to understand where the water comes from.

The global meteoric water line has been plotted on the same graph of the isotopic concentration (Fig 20):

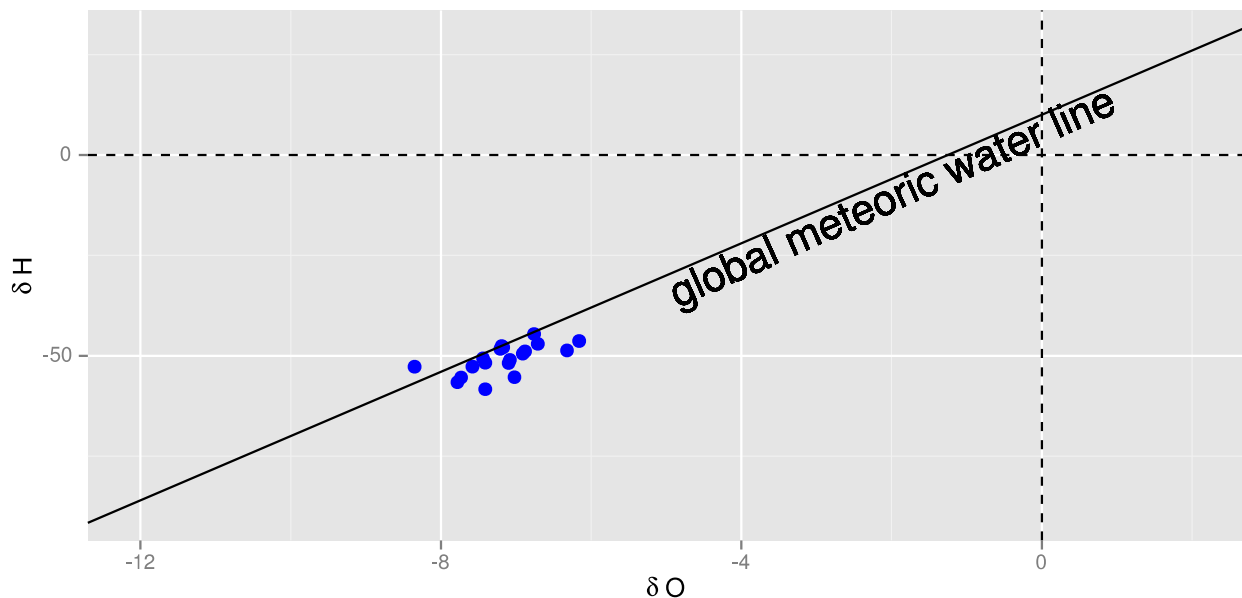


Fig 20 - Isotopic content

As one can see, all the samples are close to the global meteoric water line. It means that rainwater infiltration is mostly responsible for the aquifer recharge.

5.2.4 Groundwater contour map

The comparison between the two following different contour maps shows only small local changes probably due to the different number of piezometers measured and to the different scales used for the interpolation.

Both maps show that the groundwater flows directly into the river (so, SW – NE direction):

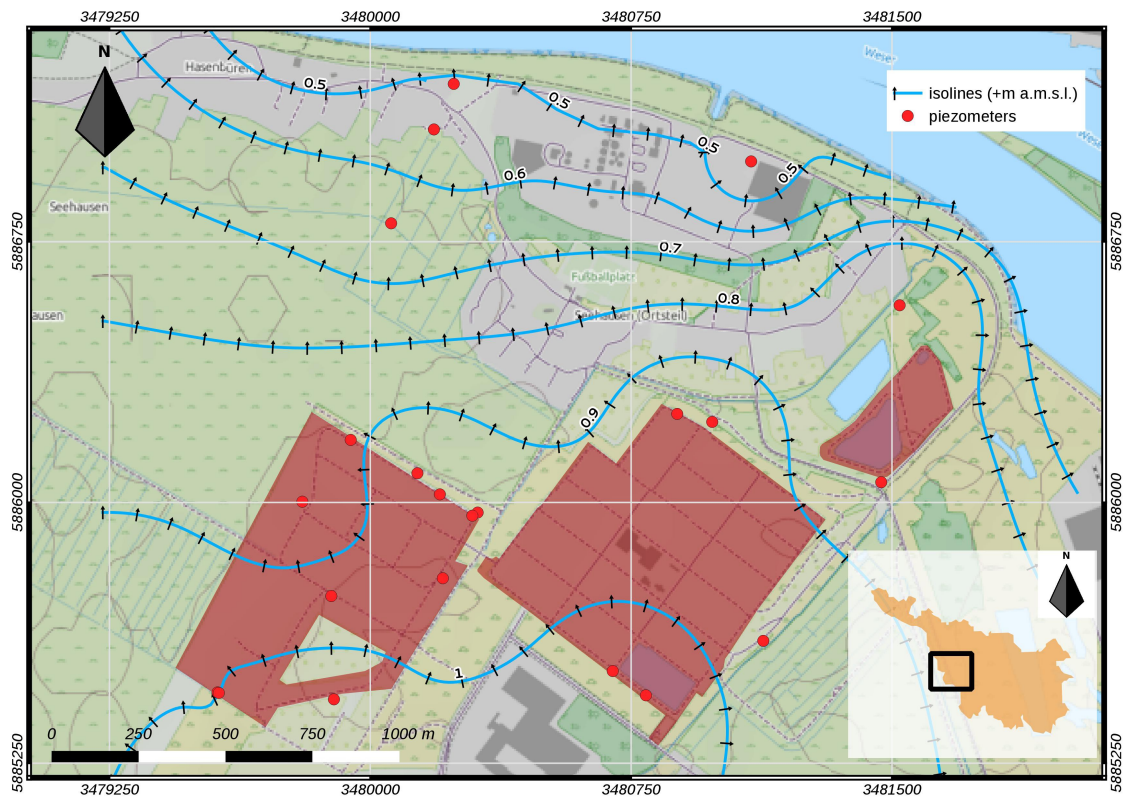


Fig 21 - Contour map, my data



Fig 22 - Contour map, WMS data (Geological survey, 2011)

However, it is also possible that the landfill modifies the behavior of the groundwater flow due to infiltration of leaching water, especially in the dewatering fields area.

5.3 Field campaign 2013 – dataloggers

Thanks to dataloggers installation it is possible to see monthly trends as well as discover unusual behaviors and external influence sources (e.g. the river and consequently the tide influence). All the plots legends refer to dataloggers ID: for complete information on piezometer, installation depth and measurement see Attach 4.

5.3.1 Temperature

Temperature measurements are available for all the piezometers. One can see a soft temperature increase in all the piezometers. In some piezometers one can see daily fluctuation: these are likely due to the tide influence. Figure 23 summarizes the temperature for all the piezometers:

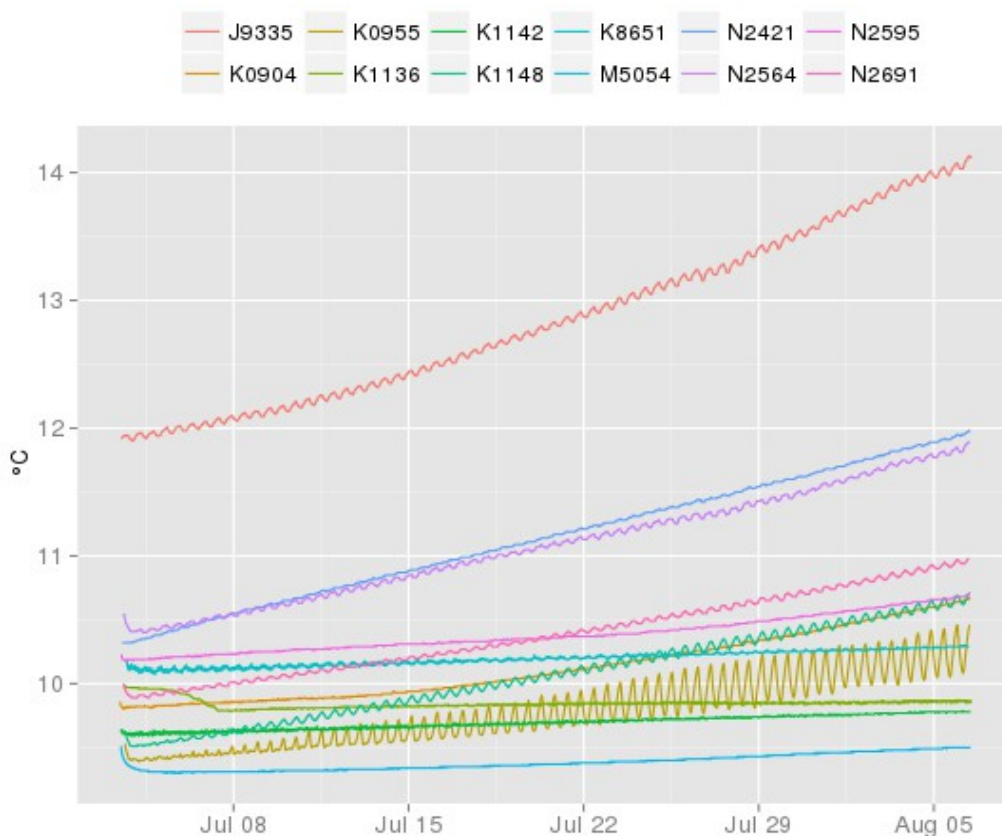


Fig 23 - Temperature in piezometers

5.3.2 Pressure

All the piezometers show an overall pressure loss with a resulting water table height decrease in the time. The apparent non-linear trend of the line can be explained by the groundwater recharge delay, due to the infiltration rate.

In 8 piezometers the loosing pressure trend is almost the same, while in the 4 piezometers located next to the river, one can see the tidal effect caused by the river infiltration. However, even in these latter piezometers, the general trend is pressure loss in the time.

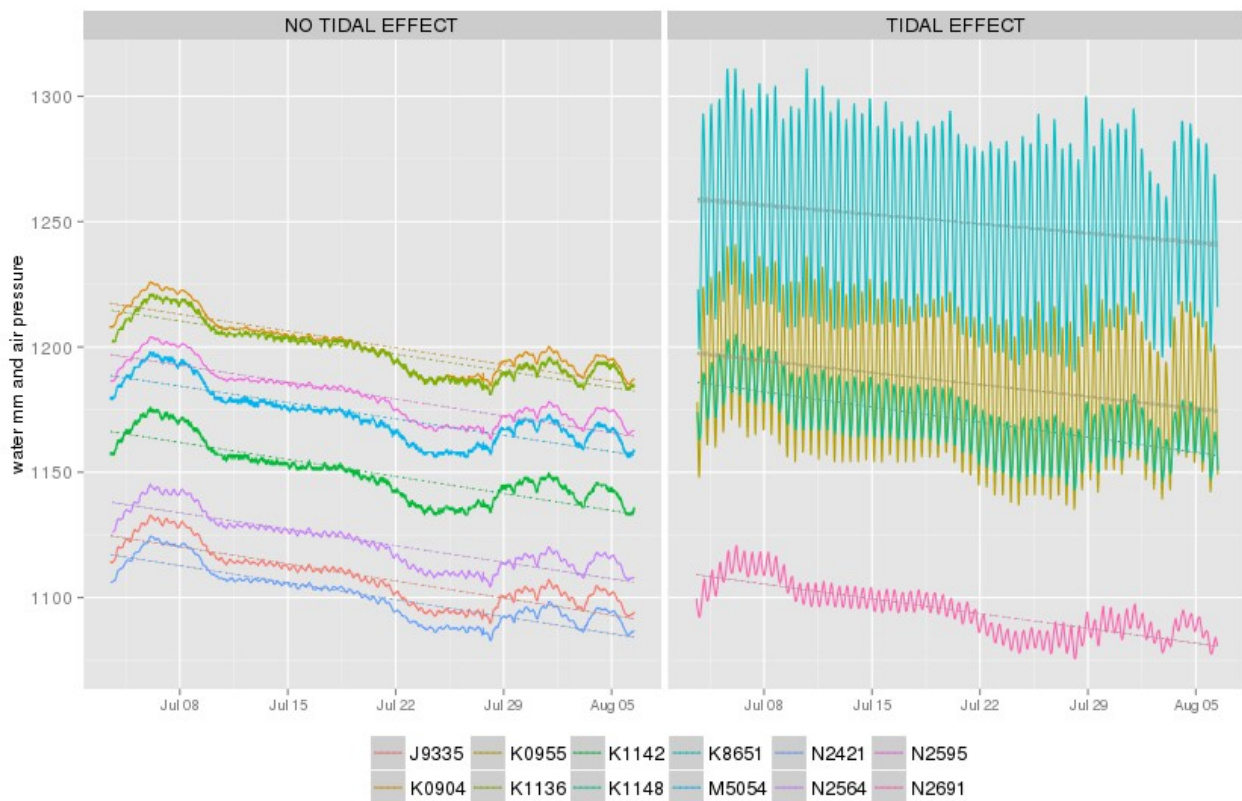


Fig 24 - Pressure and tidal effect

5.3.3 Electrical conductivity

Electrical conductivity trends could help to understand unusual behavior in the piezometers, like an input from an external source. This parameter has been measured in 7 piezometers (see section 4.3 for further information). Each piezometer has its own electrical conductivity value (depending on the place and depth of installation) and for 6 piezometers it cannot be noticed any trend during the month of measure (Fig 25).

However, one piezometer shows a fluctuating trend (Fig 25).

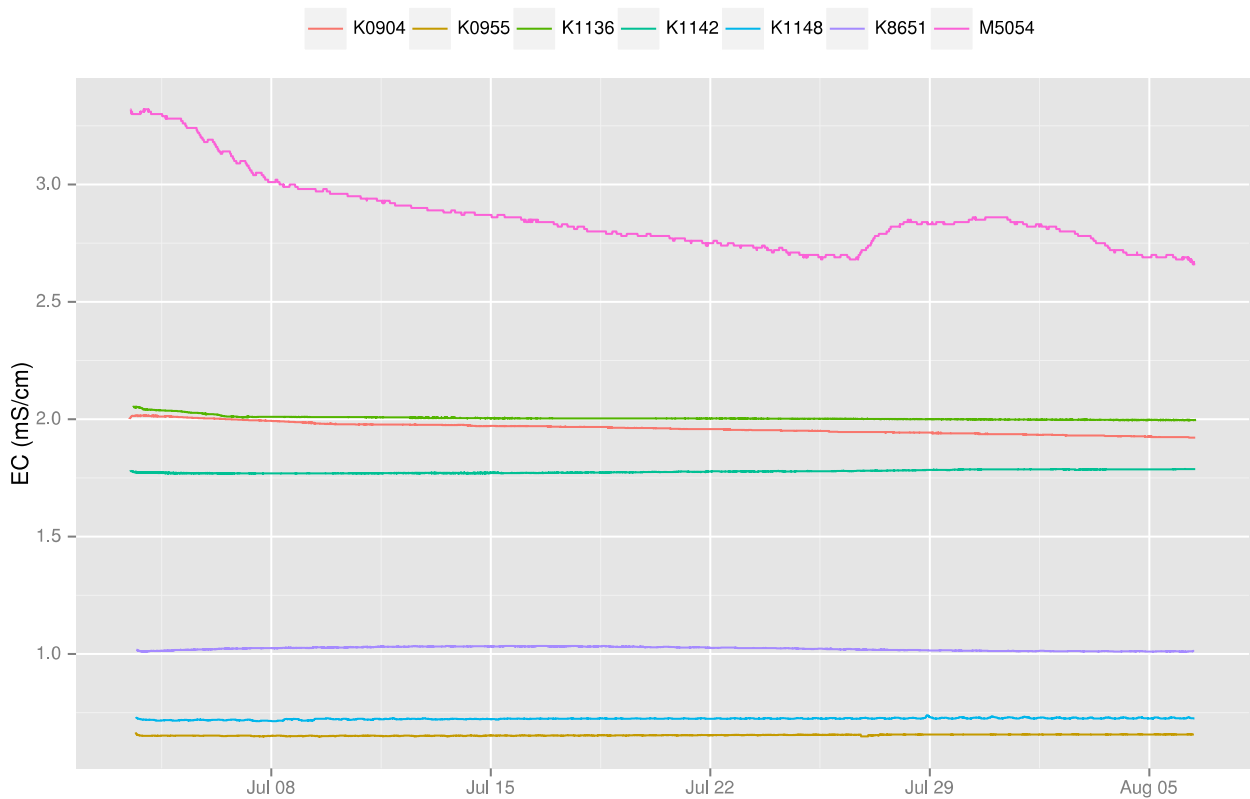


Fig 25 - Electrical conductivity trends

5.4 Historical data

Harbor Authority made available the physical-chemical data gathered from 1996 (year of the landfill construction) to 2011. Some piezometers have been sampled each year since 1996 while others have been installed only in the last few years.

Temperature, pH, electrical conductivity, dissolved oxygen, chlorine and sulfate have been regularly measured every year and are available for all the piezometers. Nevertheless other parameters have not been regularly taken every year for each piezometer.

The frequency of the sampling changed irregularly over the years: from twice to four times a year. However, thanks to this dataset it is possible to study the behavior of the groundwater and one should be able to see unusual trends and patterns.

For a better interpretation of the data, piezometers have been grouped together depending on their position (respect to the landfill) and on their filter depth (shallow piezometers have filter < 20 meters under the ground level). This way, 4 groups have been created:

Table 3 - Piezometers position

		POSITION	
		Upstream	Downstream
DEPTH	Shallow	B0F, B22F, P1, P27	B2F, B3F, B4F, B7F, B33F, P21, P24, P25
	Deep	B21T, B26T, P28	B12T, B1T, P29

Refer to section 4.1 and to Fig 13 for a detailed view of all the piezometers in the area of study.

5.4.1 Shallow – Upstream

All the piezometers classified in this category can be considered as non influenced directly by the landfill. They are installed before that the groundwater flows in the landfill area, so they should reflect the natural condition of the shallow aquifer.

B0F is the piezometer that shows the highest values of electrical conductivity and the highest concentration of chlorine and sulfate (actually P27 has the highest value of SO_4 but it is probably due to a measurement error).

Here a brief summary of the data:

Table 4 - Piezometer values summary (shallow – upstream)

ELECTRICAL CONDUCTIVITY ($\mu\text{S}/\text{cm}$)

ID	min	median	mean	90 percentile	max
B0F	885	3040	2888	3368	5370
B22F	740	1984	1906	2117	3090
P1	433	936	987	1051	2170
P27	722	1665	1770	2046	4840

CHLORINE (mg/L)

ID	min	median	mean	90 percentile	max
B0F	400	688	674	800	856
B22F	36	360	377	465	640
P1	47	102	118	134	460
P27	61	290	259	348	630

SULFATE (mg/L)

ID	min	median	mean	90 percentile	max
B0F	104	230	229	310	420
B22F	15.5	150	161	228	340
P1	55	120	132	191	380
P27	38	170	235	470	842

5.4.2 Deep – Upstream

This category is made up of 3 piezometers: B21T, B26T and P28. Considering both the position and especially the high depth of the piezometers, it is very unlikely that this groundwater suffers, in some way, from the anthropic influence.

The highest values of EC and chlorine are probably related to the leaching of the deep salt structures that rise the total salt concentration in the water.

The following table provides a summary of the values:

Table 5 - Summary of the values (deep – upstream)

ELECTRICAL CONDUCTIVITY ($\mu\text{S/cm}$)

ID	min	median	mean	90 percentile	max
B21T	1089	6670	5963	6810	6920
B26T	1225	6230	5540	6330	6430
P28	1131	2810	2786	2930	4670

CHLORINE (mg/L)

ID	min	median	mean	90 percentile	max
B21T	1500	2000	2120	2400	3817
B26T	1307	1900	1897	2300	2600
P28	220	530	536	640	650

SULFATE (mg/L)

ID	min	median	mean	90 percentile	max
B21T	1.2	3	4.24	5.4	41
B26T	1.2	5.1	16.23	37	146
P28	150	260	264.8	350	410

B12T and B26T have higher EC and Cl values than P28. Otherwise P28 shows higher concentration of sulfate.

5.4.3 Shallow – Downstream

This category is represented by 8 piezometers and is the most populated of all. Contrary to the upstream categories, these piezometers could show the eventual contamination of the landfill.

EC, Cl and SO_4 values are rather homogeneous except from B7F that has very low sulfate values (maybe related to analytical errors or laboratory problems). The following table provides a summary of all the values:

Table 6 - Values summary (shallow – downstream)

ELECTRICAL CONDUCTIVITY ($\mu\text{S/cm}$)

ID	min	median	mean	90 percentile	max
B2F	450	2275	2103	2532	2630
B33F	660	2090	1969	2196	2270
B3F	723	2215	2117	2350	2460
B4F	800	2365	2226	2691	2820
B7F	256	3080	2914	3213	3310
P21	838	2220	2192	2473	3630
P24	349	1764	1613	1980	2170
P25	879	2670	2602	3054	3650

CHLORINE (mg/L)

ID	min	median	mean	90 percentile	max
B2F	147	395	377	466	600
B33F	210	305	310	360	580
B3F	280	430	426	480	620
B4F	240	518	518	612	948
B7F	640	800	804	890	1000
P21	310	388	416	517	734
P24	115	310	299	358	600
P25	48	470	483	714	816

SULFATE (mg/L)

ID	min	median	mean	90 percentile	max
B2F	1.9	195	194	280	300
B33F	98	255	271	386	420
B3F	67	110	140.4	254	280
B4F	32	72.25	110.5	244	350
B7F	0.2	0.7	1.12	2.38	5.6
P21	0.8	180	192	270	380
P24	86	190	196	250	380
P25	260	330	340	411	473

5.4.4 Deep – Downstream

Thanks to the great depth of installation, these 3 piezometers should not be directly influenced by the landfill.

Nevertheless B12T and B1T show very high EC and Cl values while they have very low sulfate concentration values. On the other hand P29 has lower EC and Cl values but higher SO_4 values as shown in the table:

*Table 7 - deep - downstream values summary (deep – downstream)***ELECTRICAL CONDUCTIVITY ($\mu\text{S}/\text{cm}$)**

ID	min	median	mean	90 percentile	max
B12T	2560	10180	9573	10349	10470
B1T	1334	6670	6050	6869	7140
P29	1132	3150	3041	3250	3290

CHLORINE (mg/L)

ID	min	median	mean	90 percentile	max
B12T	2400	3100	3277	3694	6152
B1T	1600	2000	2175	2500	4600
P29	250	690	655	740	810

SULFATE (mg/L)

ID	min	median	mean	90 percentile	max
B12T	5.6	54	55	60.0	71
B1T	28	40	41	45	81
P29	150	180	186	210	230

5.5 Water types classification

5.5.1 Piper diagrams

Piper diagram (Piper, 1944) is a common method for representing the chemistry of water samples. It plots the concentration as % meq/L of the major anions (chlorine, bicarbonate, sulfate) and the one of the major cations (sodium, magnesium, potassium, calcium), first in two separate triangular plots, and then in one re-projected diamond central graph.

Thanks to a graphical visualization of all the major ions one can easily find out abnormal samples and, depending on the position of the point in the diamond plot, it is possible to classify the different types of water. There are many characterization methods, for example:

1. Furtak and Langguth (Furtak, Langguth 1967) suggest a classification in 3 mainly group subdivided in 7 categories

This way, the 19 samples can be grouped into 3 categories (see Fig 26):

- **group 4** – waters with increased alkaline – hydrogen carbonatic dominated
- **group 5** – waters with increased alkaline – sulfatic dominated
- **group 7** – alkaline waters – sulfatic dominated

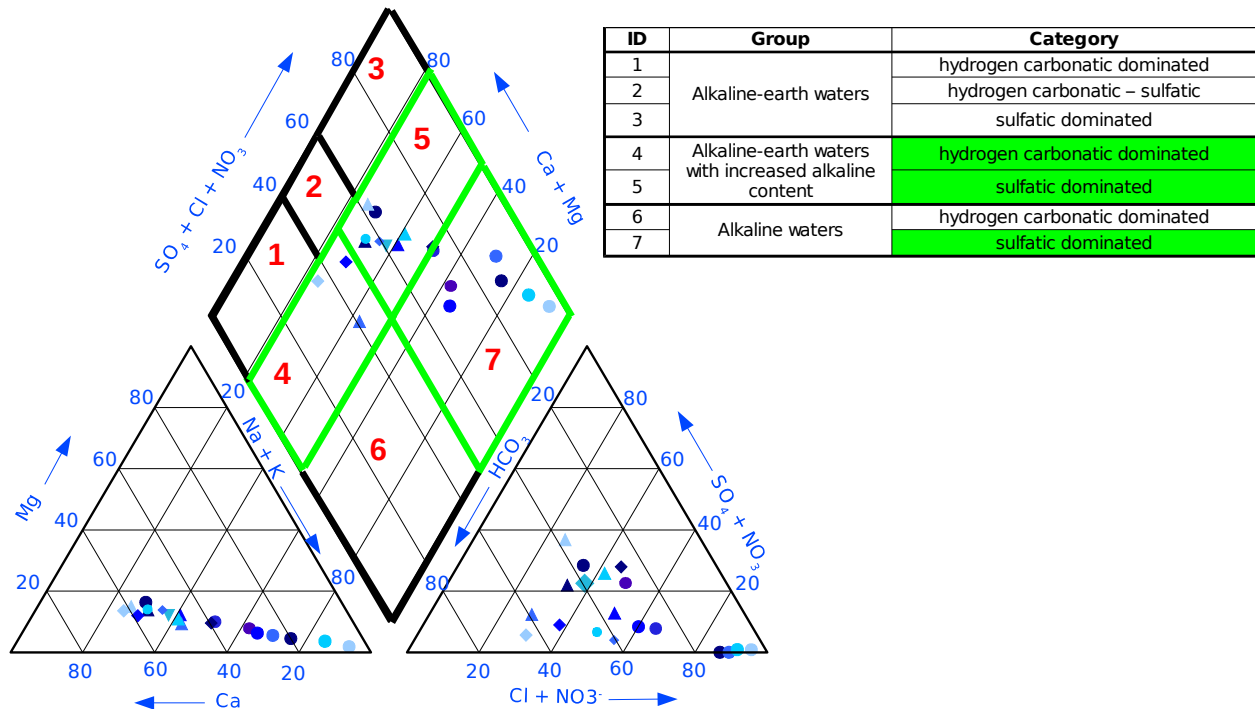


Fig 26 - Water classification (Furtak and Langguth, 1967)

2. Kumar (Kumar, 2013) uses other water characterization criteria: in particular, suggest to divide the central diamond plot in 6 categories

According to this new classification method, the 19 groundwater samples belong to 3 groups:

- **group 1** – Ca-HCO₃ type
- **group 2** – Na-Cl type
- **group 3** – Ca-Mg-Cl type

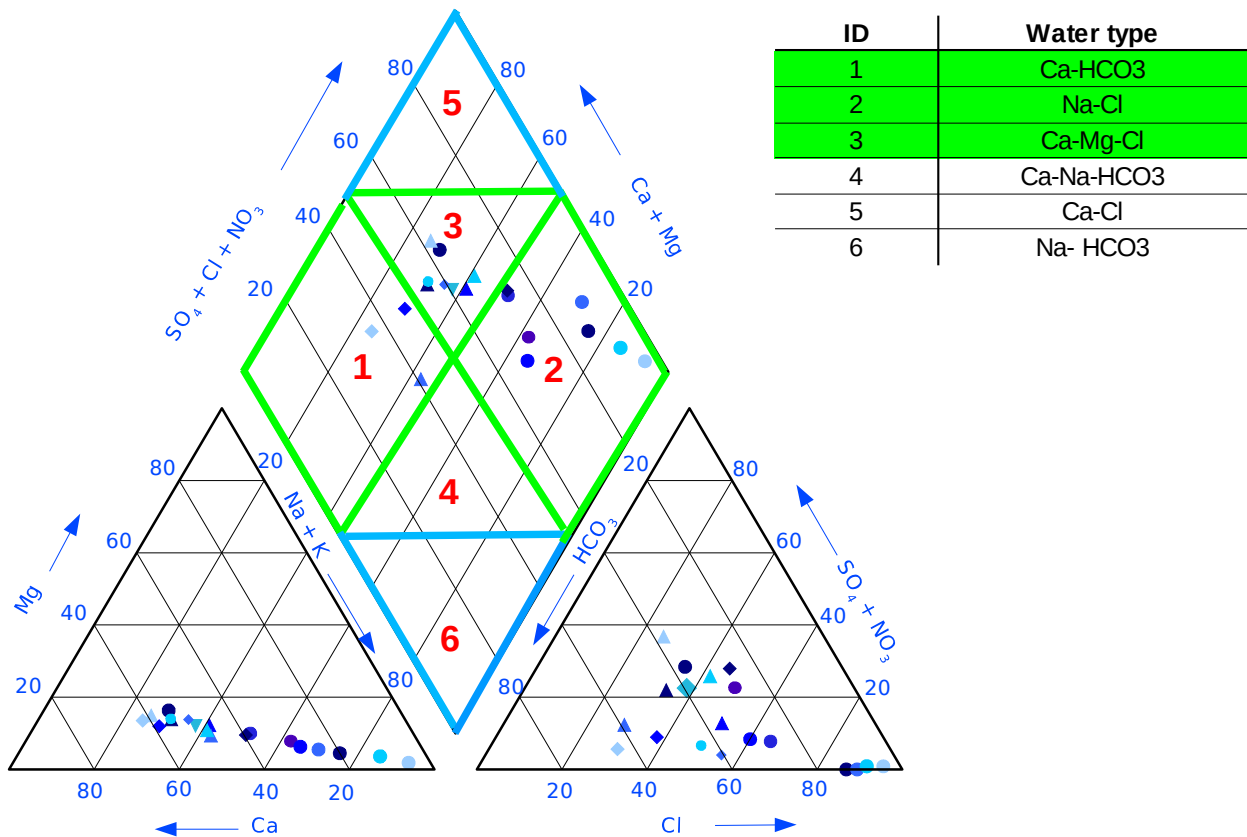


Fig 27 - Water classification (Kumar, 2013)

5.5.2 Schoeller diagram

Schoeller diagram (Schoeller, 1977) is another useful graphical tool for the visualization of the geochemical content of the samples. It compares the logarithmic concentration of the major cations and anions (in meq/L) from the samples with all the different constituents connected with a line. The diagram gives absolute concentrations while the line between two elements gives the ratio between themselves: this means that if a line joining two points from one sample is parallel to another line of another sample, the ratio of those ions in those samples is equal. Moreover, the logarithmic scale allows to plot a wide range of concentrations and this way the samples can be easily compared (Burgos, 1999).

Following plot (Fig 28) is the result of all the groundwater samples taken in field:

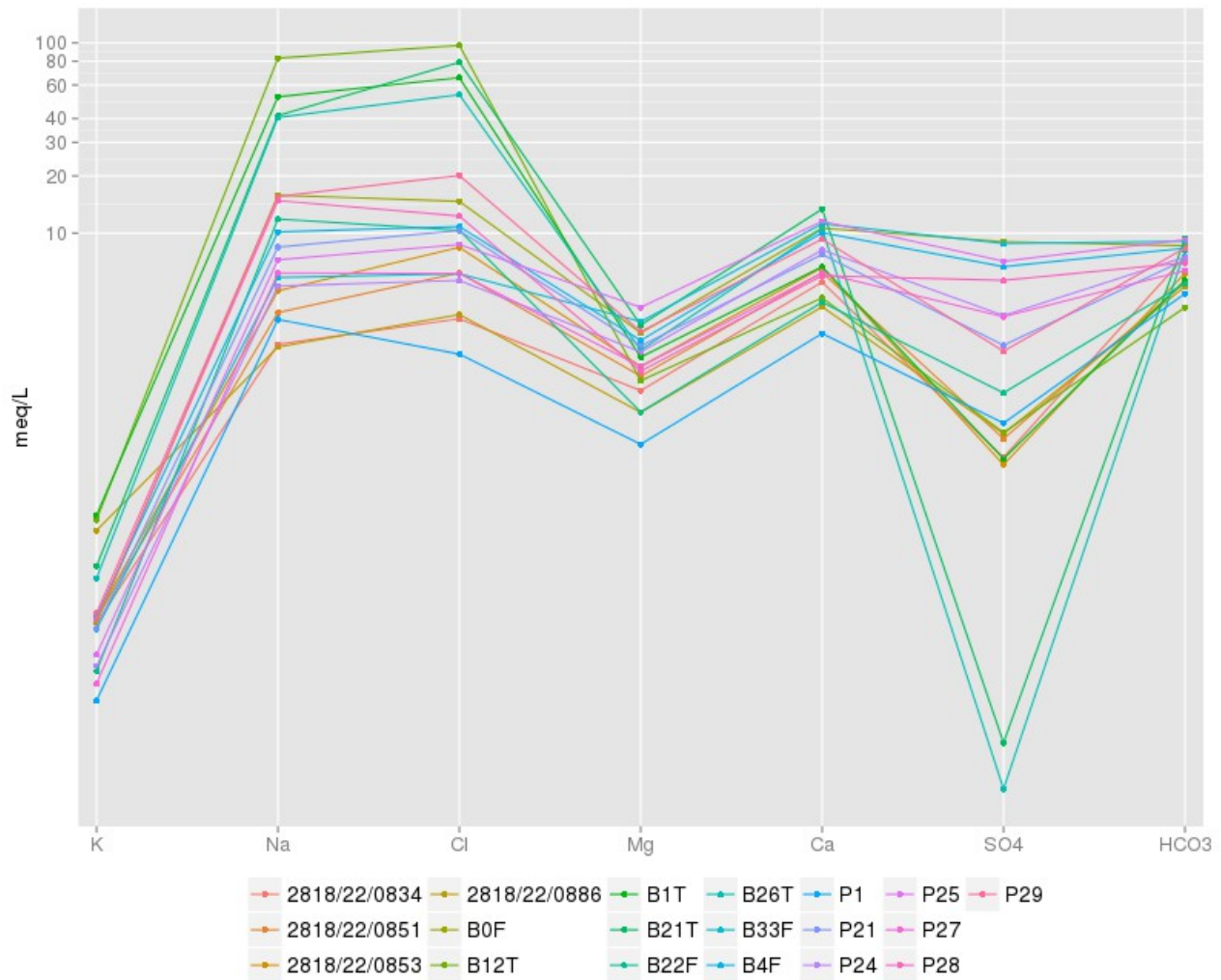


Fig 28 - Schoeller diagram

The plot shows that there are some piezometers with high chlorine and sodium concentrations (B12T, B1T, B26T and B21T) while others show low sulfate concentrations (B21T and B26T).

6 Data interpretation

The comparison of the historical series and the values collected during the 2013 summer sampling campaign might allow to understand particular chemical behavior and trends. It is not easy to figure out if a possible contamination hails from the leaching of the landfill material: surrounding environmental conditions are quite difficult to assess but statistical and graphical method might help to evaluate and identify the contamination source.

6.1 Groundwater types

As described in section 5.5.1, Piper diagrams are a very useful tool for the categorization of groundwater types. The following classification is based on the criteria provided by Kumar.

6.1.1 Group 1: Ca – HCO₃

This group consist of 3 piezometers (2818/22/0834, 2818/22/0886 and P1) which are located at the northern and eastern border of the Seehausen area (Piper diagram is available in Attach 1).

These piezometers, beside their high Ca and HCO₃ content, are characterized by low Cl and Na concentrations. The poor Cl concentration can be due to the fact that the piezometers are shallows (P1 is the deepest with a depth of 13.50 meters, see Attach 1) and so they might not be influenced by the deep and salty water of the bottom aquifer. Historical data are available only for P1 and they show that for electrical conductivity, chlorine and sulfate content, except for the time interval 2007-2009, values are quite stable (see Fig 29). P1 is located at the eastern border of the landfill and its physical-chemical parameters could be influenced also by the mix with other waters coming from the eastern part of Seehausen (see Fig 22 for the flow direction): it is very difficult to proof this fact without further analysis.



Fig 29 - P1 physical-chemical trends

Otherwise, piezometers 2818/22/0853 and 2818/22/0886 are very close to the river (northern side of Seehausen): nevertheless, the river has a visible effect only on the physical component (pressure and consequently on water table height) and not on the chemistry of the groundwater. Actually, the plot of electrical conductivity (Fig 30) provided by the data logger installed in 2818/22/0853 (1 month of measurements) shows that there are not significant changes of this value during time.

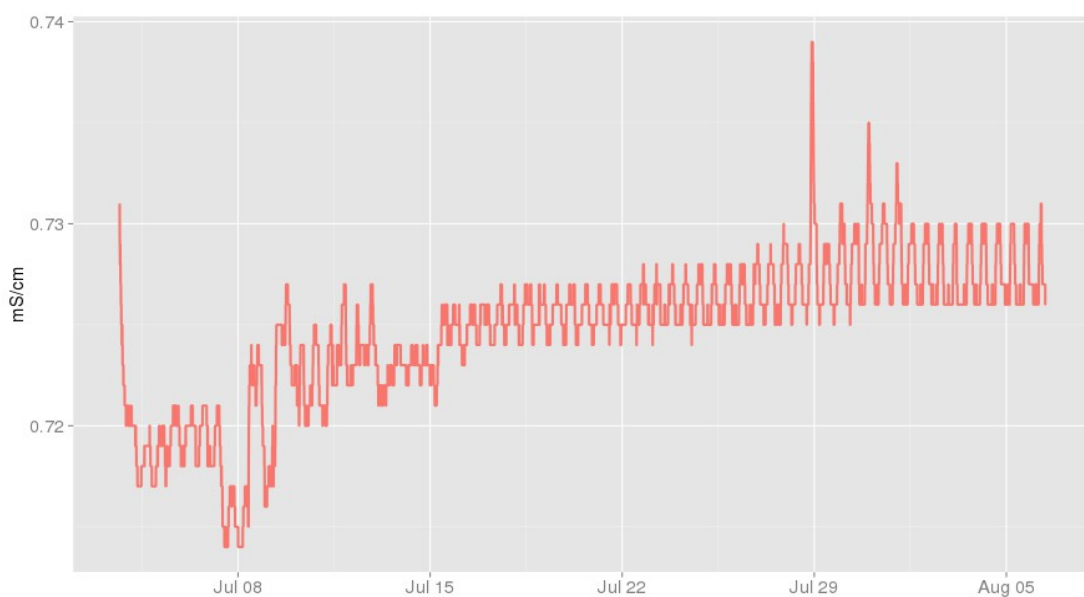


Fig 30 - Electrical conductivity in 2818/22/0853

Piper diagram for this group is available in Attach 1.

6.1.2 Group 2: Na – Cl

This category includes 8 piezometers: the great majority are deep ones (see Piper diagram in Attach 12 for the list of piezometers). In chapter 3.5 it has been explained that the whole area is interested by ancient deep channel partially filled with deep salt structures. The high Cl and Na concentrations are probably due to the leaching from water of these geological features. Plotting Cl versus the Na concentrations (in mmol/L) it is possible to see that the half of the piezometers stand exactly on the salt-dissolution line ($\text{Na} = \text{Cl}$) and the other half has a higher Cl concentration (see Fig 31). This higher Cl concentrations might be due to the cation exchange capacity that reduces the Na concentration in solution: Na is absorbed on the sediments and so its concentration lowers.

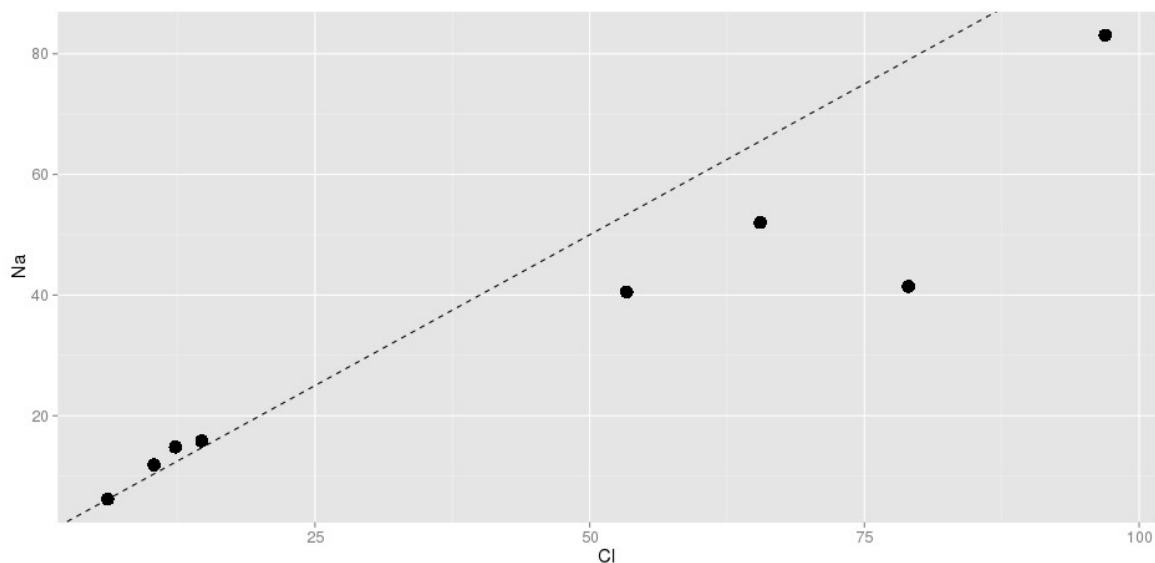


Fig 31 - Na vs Cl (mmol/L)

All the piezometers are located inside the landfill area (drying fields and sediment landfill). Some piezometers have really high concentration of Na and Cl that covers almost the 100% of the respectively cation and anion content. Moreover in this group there are the highest electrical conductivity values of all the piezometers (maximum measured is in B12T with 9700 $\mu\text{S}/\text{cm}$) and the lowest of SO_4 (minimum in B25T with 0.57 mg/L). With these other two parameters one has the chance to classify these waters as “very salted”.

6.1.3 Group 3: Ca – Mg – Cl

This group includes 8 piezometers, 7 shallows and only 1 deep (see Attach 13 for the list of piezometers), that are located in the middle of the landfill (see map in Attach 14). In this group it is possible to find the highest SO_4 values (except for B0F of group 2): in 3 piezometers the SO_4 concentrations exceed 300 mg/L. SO_4 concentrations does not seem related with the electrical conductivity and Cl values and so the source of SO_4 might be difficult to explain.

Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) might be a source of SO_4 , and plotting the Ca versus SO_4 concentrations in mmol/L it is possible to notice that most of the piezometers remains on the line $\text{Ca} = 2(\text{SO}_4)$; that is that the content of Ca is doubled compared with SO_4 (see Fig 32).

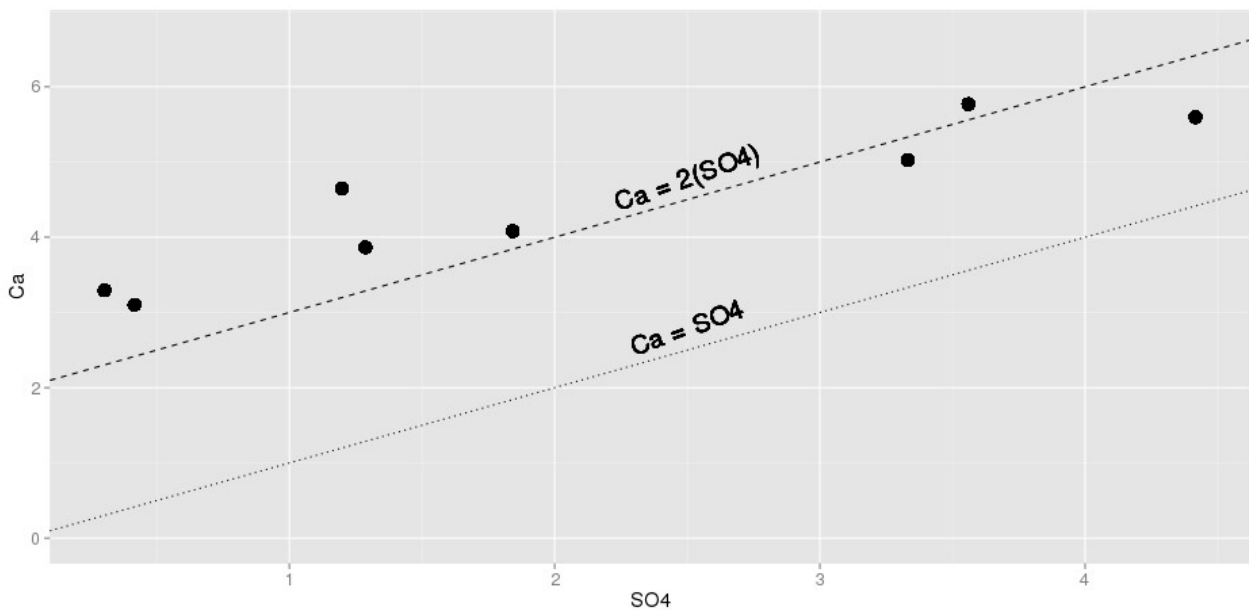


Fig 32 - SO_4 versus Ca in mmol/L

The higher Ca concentrations mean that there should be another source of Ca or perhaps Ca is released by the aquifer due to cation exchange properties or by the leaching of geological structures like limestone.

The map in Attach 14 shows all the piezometers categorized according to the Piper group of belonging spread in the territory. It is now simpler to see that there seems to be a spatial pattern of water types: moving from south to north groundwater losses Cl and Na and

becomes richer in other ions (Mg, SO_4 and Ca).

However, Piper categories don't care about the depth of the piezometers. Given that, it is useful to see water types groups depending both on Piper's categories and filter depth. The following plot is a kind of contingency table that summarize Na, Cl, EC and SO_4 values for all the piezometers:

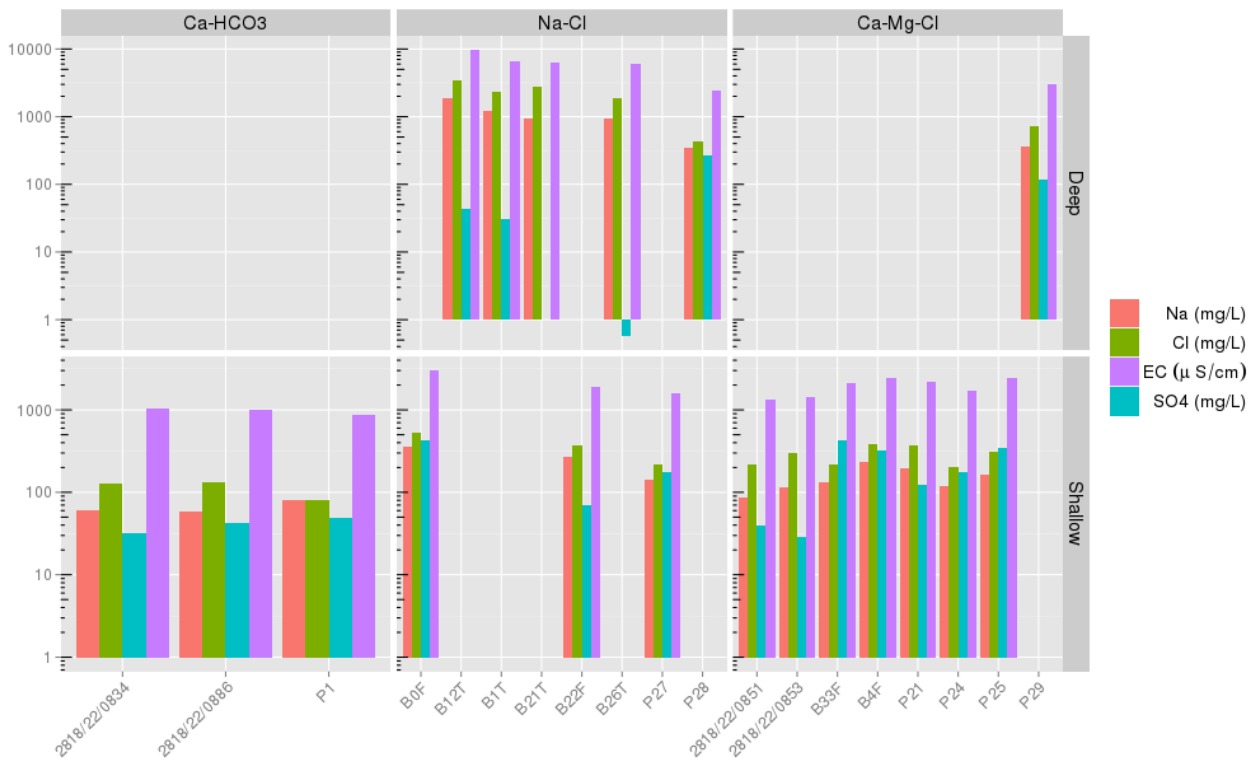


Fig 33 - Piper category versus depth for Na, Cl and EC

At first blush, looking at the scale, one can see that deep and shallow piezometers belong to two different worlds. In particular, EC values differ by almost an order of magnitude and SO_4 values of deep piezometers are very low compared to those of shallow ones. Statistical tests have been run in order to prove this separation (see next sections).

6.2 Study of the parameters

6.2.1 Correlation matrix

The following correlation matrix (see Table 8) shows the correlation between the parameters of the current sampling campaign (2013). Some variables are strongly

correlated with others: first of all it is possible to notice the very strong correlation between Cl and Na. The interpretation is that the source of Cl is very likely the same for Na, so leaching of salt structures. Another interesting correlation is those of Br with Cl and Na and the explanation is probably the same of above: salt structures leaching. Indeed Hem (Hem, 1985) points out that Br has mostly the same chemical behavior of Cl and it can be found in evaporites and brines.

Electrical conductivity is strongly correlated with all the three previous ions: this means that this physical parameters is mostly influenced by them.

Other strong correlations are between Mg and Ca and between Ca and HCO_3 . The first one could be due to the similar chemical behavior of Mg and Ca: both have +2 valence and are the major constituents of limestone (Mg is a kind of impurity) and dolomites. Ca and HCO_3 correlation is probably related with carbonate rocks leaching: these are the most common source of HCO_3 in groundwaters (Hem, 1985).

	Mn	Ca	Fe	Mg	Na	Cl	SO4	Br	HCO3	$\delta^2\text{H}$	$\delta^{18}\text{O}$	T	O	pH	EC
K	-0.44	-0.12	-0.54	-0.12	0.75	0.74	-0.39	0.67	-0.35	-0.84	-0.66	0.32	0.17	0.70	0.72
Mn		0.32	0.79	0.43	-0.68	-0.65	0.57	-0.58	0.46	0.44	0.20	0.30	-0.09	-0.75	-0.61
Ca			0.39	0.93	0.07	0.19	0.46	0.28	0.92	-0.14	0.12	-0.36	-0.25	-0.15	0.22
Fe				0.49	-0.57	-0.54	0.64	-0.44	0.60	0.51	0.34	0.18	0.00	-0.67	-0.50
Mg					0.05	0.12	0.58	0.24	0.86	-0.06	0.13	-0.32	-0.15	-0.16	0.19
Na						0.97	-0.31	0.95	-0.21	-0.73	-0.34	-0.20	0.30	0.87	0.99
Cl							-0.38	0.98	-0.10	-0.77	-0.32	-0.24	0.20	0.77	0.98
SO4								-0.29	0.55	0.46	0.32	0.06	0.18	-0.28	-0.25
Br									-0.01	-0.71	-0.26	-0.30	0.18	0.74	0.98
HCO3										0.08	0.18	-0.23	-0.25	-0.35	-0.06
$\delta^2\text{H}$											0.63	-0.03	-0.10	-0.60	-0.74
$\delta^{18}\text{O}$												-0.41	-0.05	-0.28	-0.32
T													0.34	-0.15	-0.25
O														0.22	0.24
pH															0.83

Table 8 - Correlation matrix of sampled piezometers (2013)

6.2.2 Cluster analysis and Multi-dimensional-scaling

Depending on which variable have been considered in the calculation of the distance matrix (euclidean distance used), clusters are quite different (see Fig 34).

In the first case (cations, upper-left corner) all cations, except Li, have been used to calculate the distance matrix. It is possible to recognize 4 groups with no apparently spatial

dependence and just a poor depth correlation.

In the second cluster (physical, upper-right corner) the variables EC, pH, T and O₂ have been used in the calculation of the distance matrix and there is possible to identify just two main groups. This means that physical parameters alone are not quite good to separate piezometers.

In the third case (anions, bottom-left corner), Cl, SO₄, HCO₃ and Br have been used as variables. As for the cation cluster, it is possible to recognize 3 main group, but in this case there is a more evident depth correlation: the first group (B21T, B26T, B12T and B1T) includes all deep piezometers. Spatial correlation is not so evident at all.

In the last cluster (all, bottom-right corner) all the variables have been used together. Here it is possible to identify 3 groups: also in this case the first group is made up by the same 4 deep piezometers of the anions cluster and a spatial correlation is not so clear.

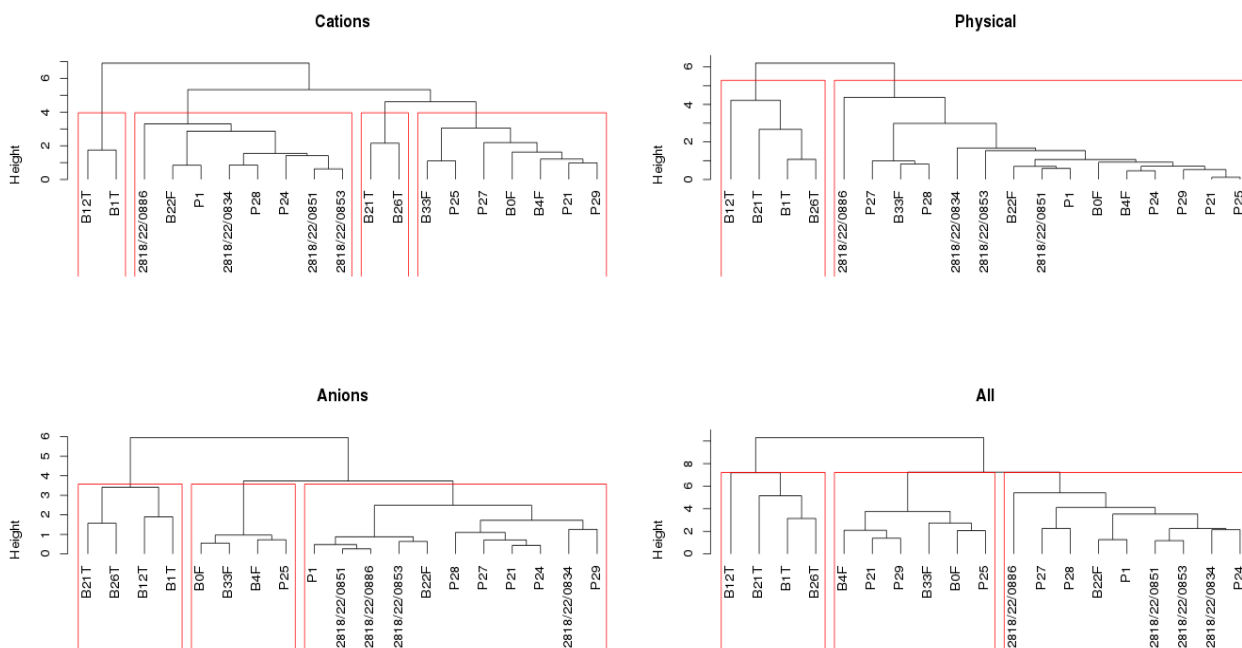


Fig 34 - Cluster analysis

Multi-dimensional-scaling has been used in the same way as cluster analysis, that is that 4 plots have been created depending on the same variables distinction (anions, cations, physical-parameters and all variables together). The only difference is that all cations and anions have been used, no exceptions (see Fig 35).

In the following plots it is possible to see more clearly the distinction of the deep piezometers among all the others and a spatial correlation is even more difficult to see. Deep piezometers group is clearly noticeable in all 4 plots, no matter which variables have been used to perform the calculation.

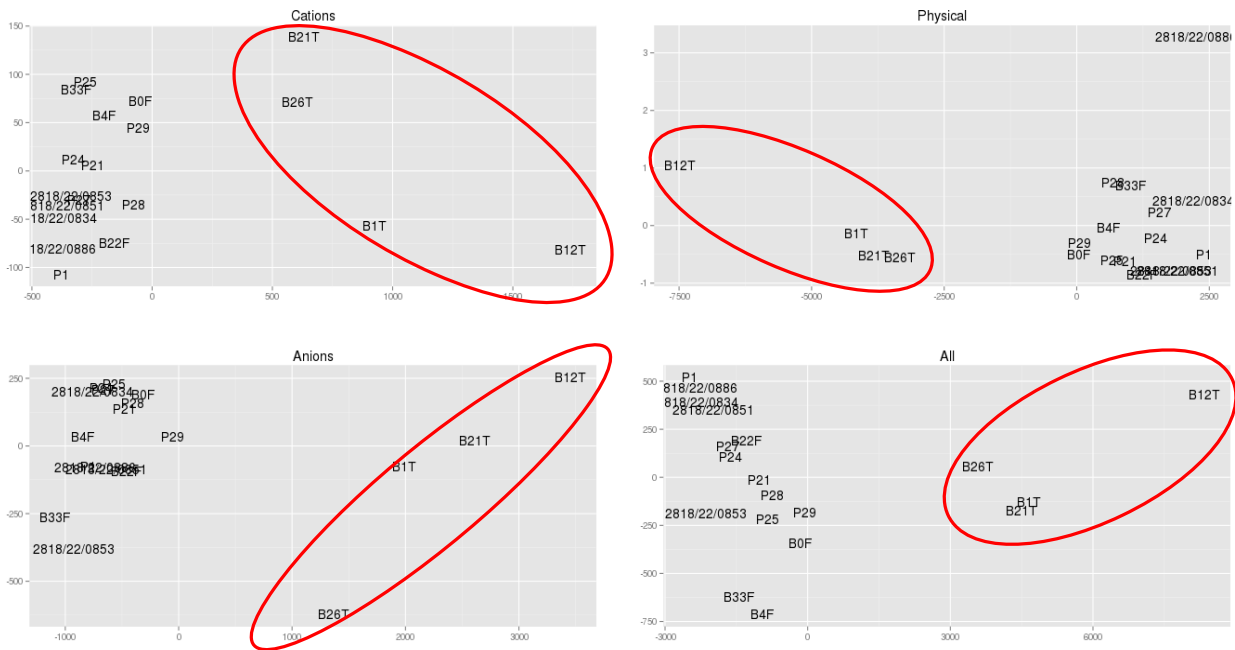


Fig 35 - Multi-Dimensional-Scaling

This two multivariate graphical techniques show that the groups depending on the piezometers position (see Section 5.4) is useful to have a general idea of the area and the territory, but it is only a theoretical grouping not supported by physical-chemical parameters. So, the upstream piezometers should not be considered as “blanks”.

While cluster analysis and MDS are just a graphical way to see the data and their differences, with the wilcoxon test one can statistically assert that samples belongs to different populations (Reimann et al. 2011). Wilcoxon-test is a non-parametric test: so it is not necessary that data follows a normal distribution. R software returns p-values for wilcoxon-test: if the p-value is bigger then the significance level (usually 0.05) than one has to reject the null-hypothesis (that samples come from the same population) and has to accept the alternative-hypothesis (that samples belong to different populations).

Results of the test confirm what seen with the graphical methods: trying to separate

piezometers depending on position (upstream versus downstream) gives a p-value next to 1 while the separation depending on Depth give a p-value smaller than 0.05. In other words, these results demonstrate that dividing piezometers according to their position is useless. Otherwise, the filter installation depth shows that there is a clear separation between the upper and the lower aquifer.

6.3 Concentration maps

It has been possible to compare the shallow piezometer concentrations of Cl and SO₄ of 1993 (Ortlam, Sauer, 1993) and those of 2013. Concentration maps of 1993 were made using more piezometers then those of 2013, however the comparison is very useful to understand the shallow pattern of this two elements.

In the last 20 years Cl concentration didn't vary much in the shallow aquifer: the two following maps show this fact. Using the same interpolation color scale one can immediately see the background pattern and the variation:

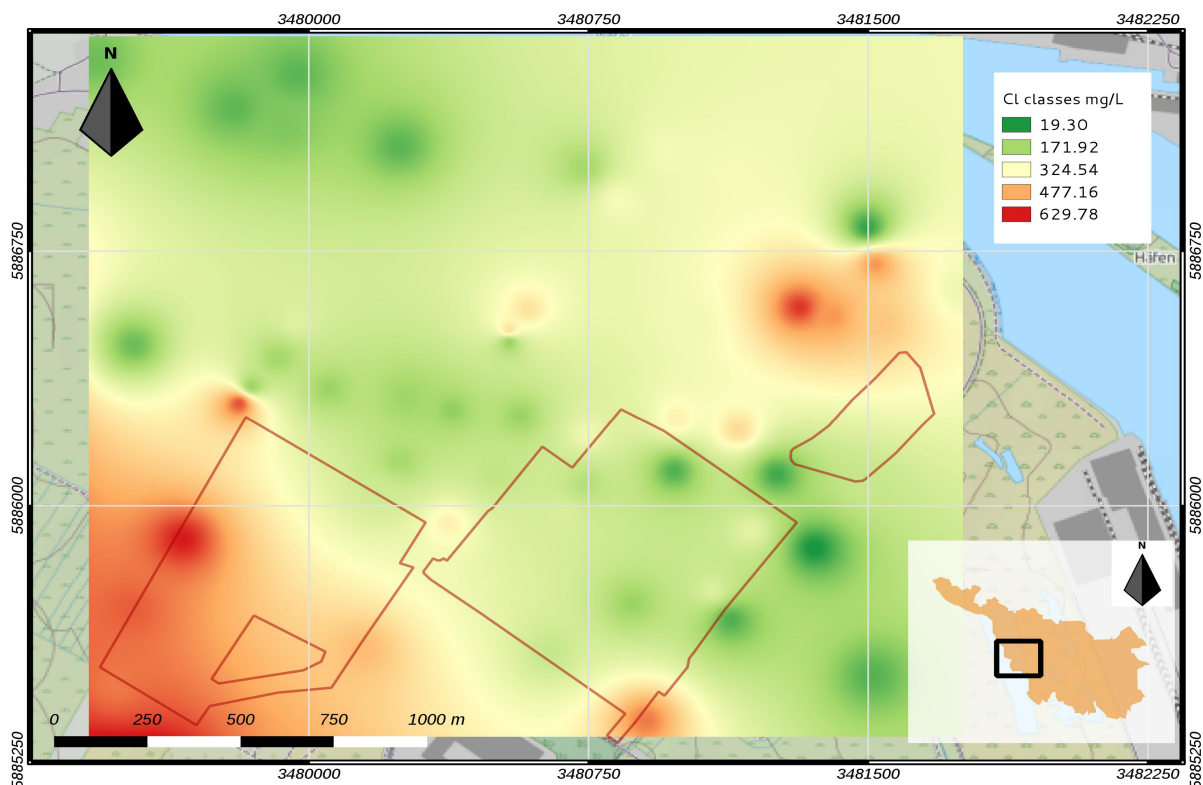


Fig 36 - Cl concentration map of 1993 (adapted from Ortlam, Sauer, 1993) of shallow aquifer

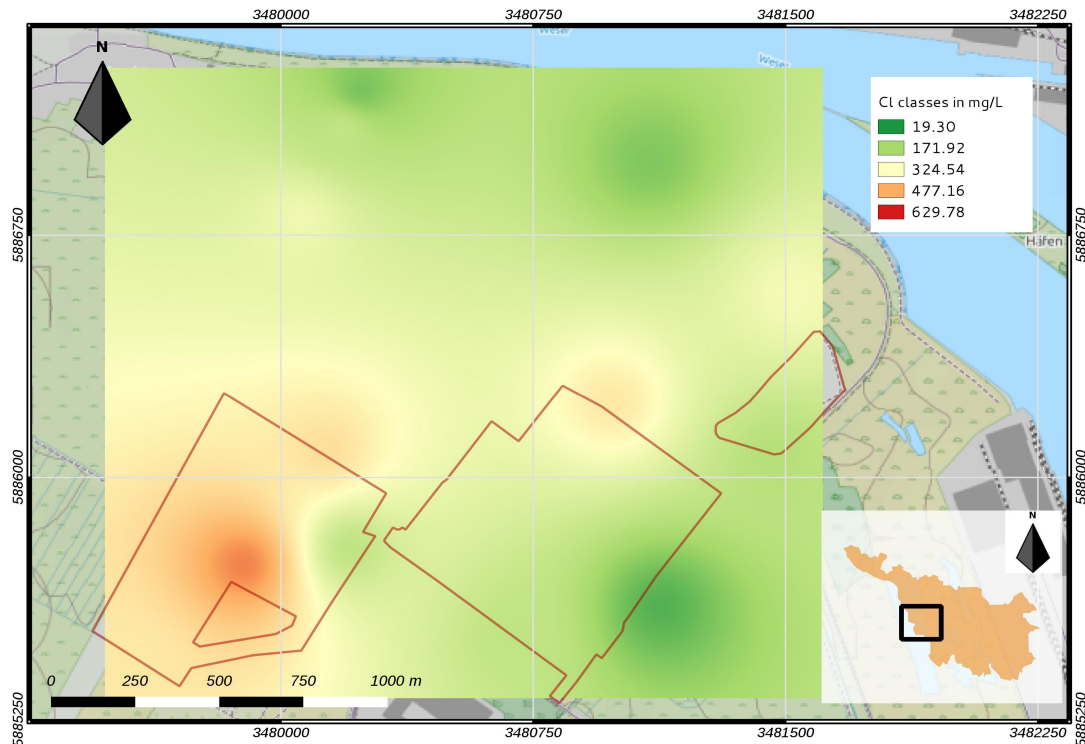


Fig 37 - Cl concentration map of 2013 of shallow piezometers

Besides the image resolution difference (as said, map of 1993 is the result of a larger number of piezometers), Cl pattern is not so different: the south-western part of the territory has the greatest values that follow the north-east direction.

The same comparison has been made for SO_4 . The following two images show the comparison:

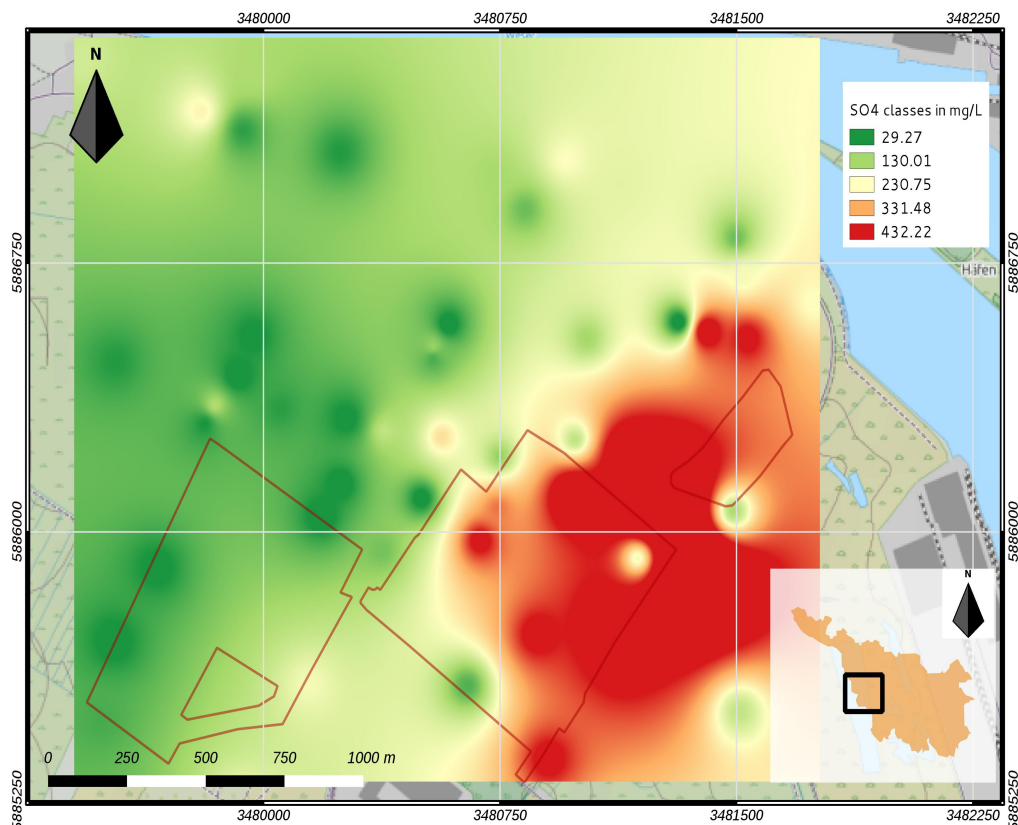


Fig 38 - SO_4 concentration map of 1993 (adapted from Ortlam, Sauer, 1993) of shallow aquifer

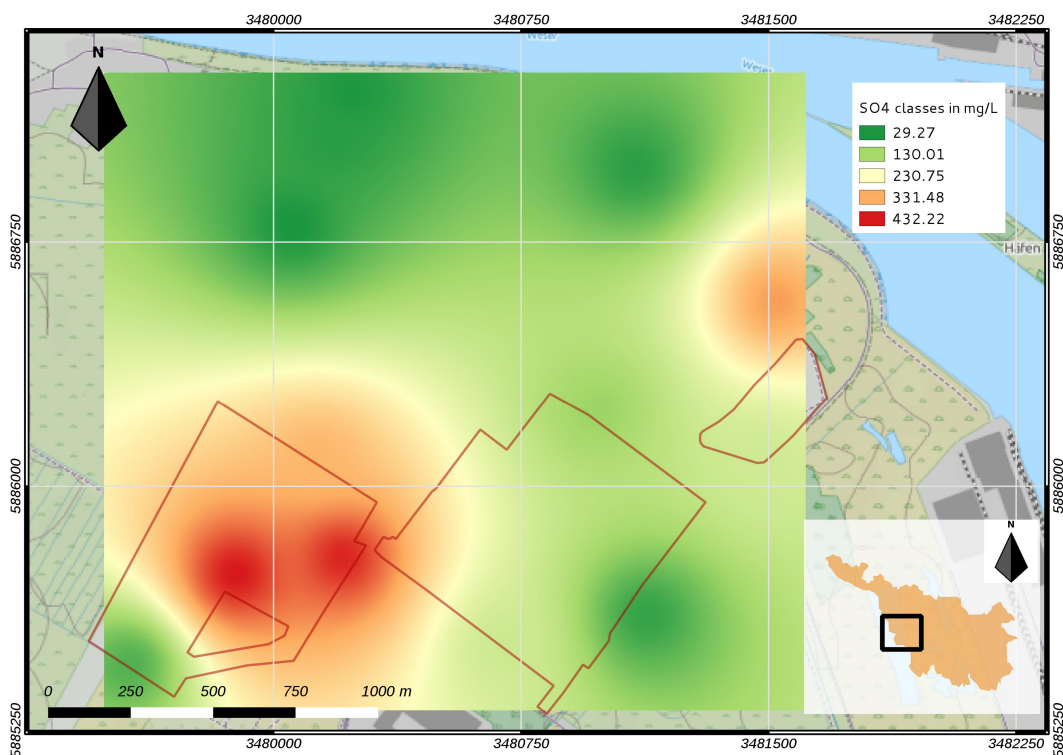


Fig 39 - SO_4 concentration map of 2013 of shallow piezometers

The comparison between these two maps shows that sulfates have moved from east to west, exactly where the sediments landfill is today located. It is possible that in 1993 some raw material for the landfill construction caused an infiltration of SO_4 into the shallow aquifer: this could explain the limited contamination source. So, once the landfill has been constructed, contamination source stops.

It is also possible that there is not correlation between the two sulfate sources. Given that the two maps refer to punctual events (1993 and 2013) it might be that what happened in 1993 moves away and then something different is related to what the map of 2013 shows. Anyway, more difficult to explain are the high SO_4 concentrations located at the end of the sediments landfill. It is not simple to assert that this increase is caused by the landfill, however something happens and is still happening in the shallow aquifer.

This hypothesis is confirmed by analyzing time trends of the piezometers. Focusing on piezometers located directly at the end of the sediments landfill (where the SO_4 concentrations in Fig 1 are higher) and plotting the SO_4 concentrations from 1996 to 2011 it is possible to see an increasing trend of SO_4 :

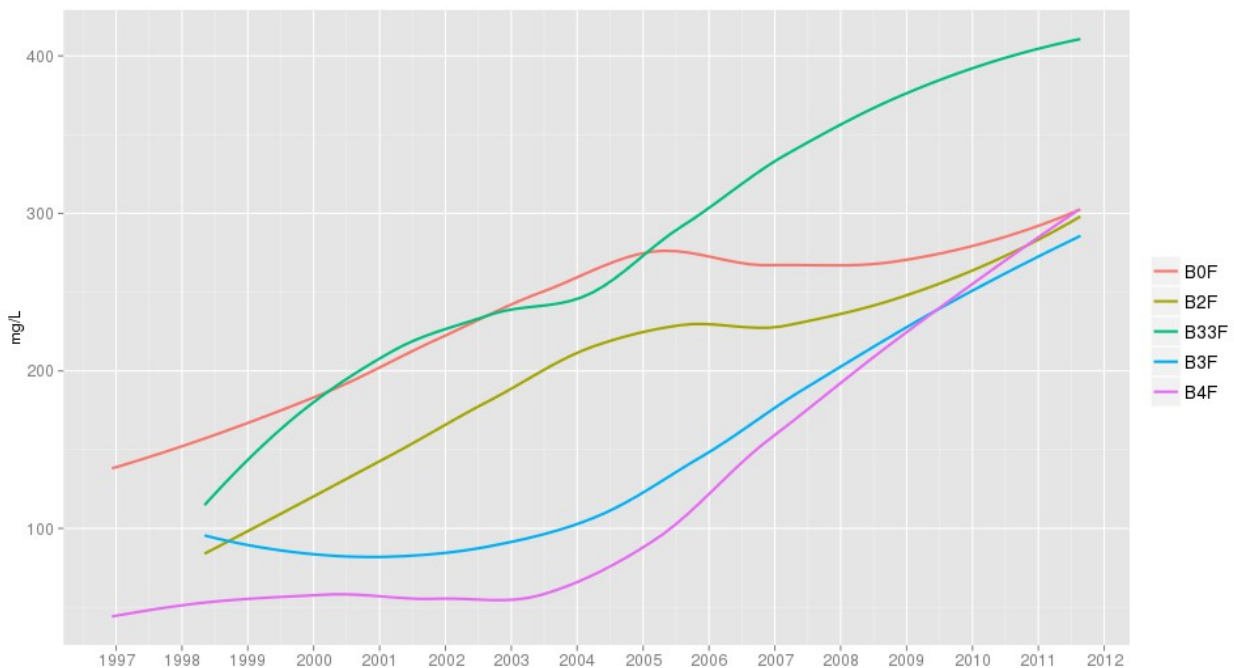


Fig 40 - SO_4 time trends

As Fig 40 shows, in these piezometers the SO_4 concentration is growing during the last years and, even if in some piezometer the effect is retarded, mostly all of them converge

on the same value (around 300 mg/L).

Strange behavior of SO_4 are noticeable also in piezometers P27 and P28 located at the beginning of the drying fields. It is important to remember that P28, even if is categorized as a deep piezometers, has a quite long filter. Given that, P28 chemical values could reflect more a mix of different water types rather than only the deep aquifer. Nevertheless, especially in P27, SO_4 and Cl appears very fluctuating as shown in Fig 41.

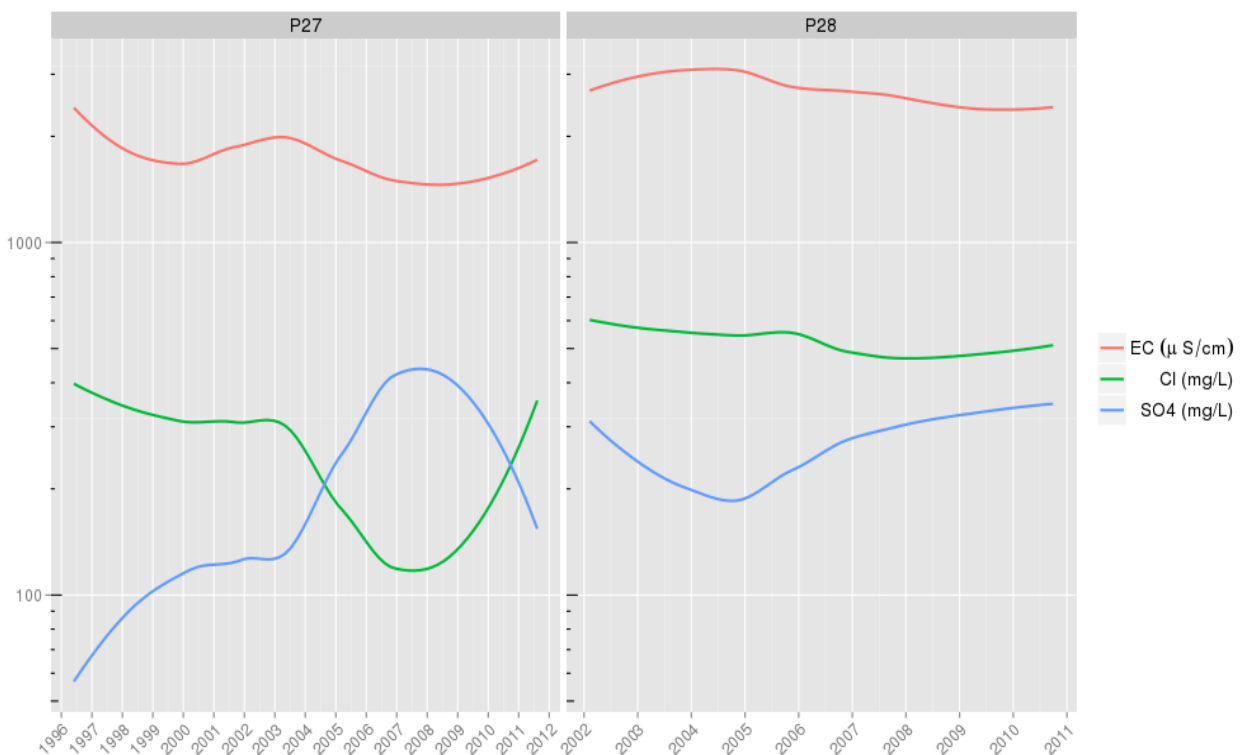


Fig 41 - EC, Cl and SO_4 time trends in P27 and P28

In particular in P27, SO_4 trend seems to be opposite to those of Cl. Furthermore it seems that none of these two variable influence EC value. This very strange behavior of both SO_4 and Cl is very difficult to interpret: it is possible that from 2004 to 2010 (more or less the time interval of the fluctuations) water coming from outside the landfill, rich in SO_4 and poor in Cl, changed the ions concentration of the aquifer. However, no similar trends has been noticed in other nearby piezometers (P1, P21, P29), so probably there is another source of contamination.

EC, Cl and SO_4 time trends for all piezometers are available in Attach 15.

6.4 Comparison between sediments leaching water and piezometers

Sediments leaching water data refers to the water coming from the drying fields, in particular this data concern an area nearby piezometers P1, P27, P28 and B33F.

Many chemical variables have been collected during a quite wide time interval (from 1996 to 2005): comparison between Cl and SO₄ of the sediments leaching water and the historical data of the piezometers can help to see if there is some correlation.

Fig 42 shows the comparison of SO₄ between leaching water values and the 4 piezometers: it is possible to see that leached water has always larger values than piezometers ones and a small similar trend can be noticed in B33F and P27 while in the other 2 piezometers trends are quite different.

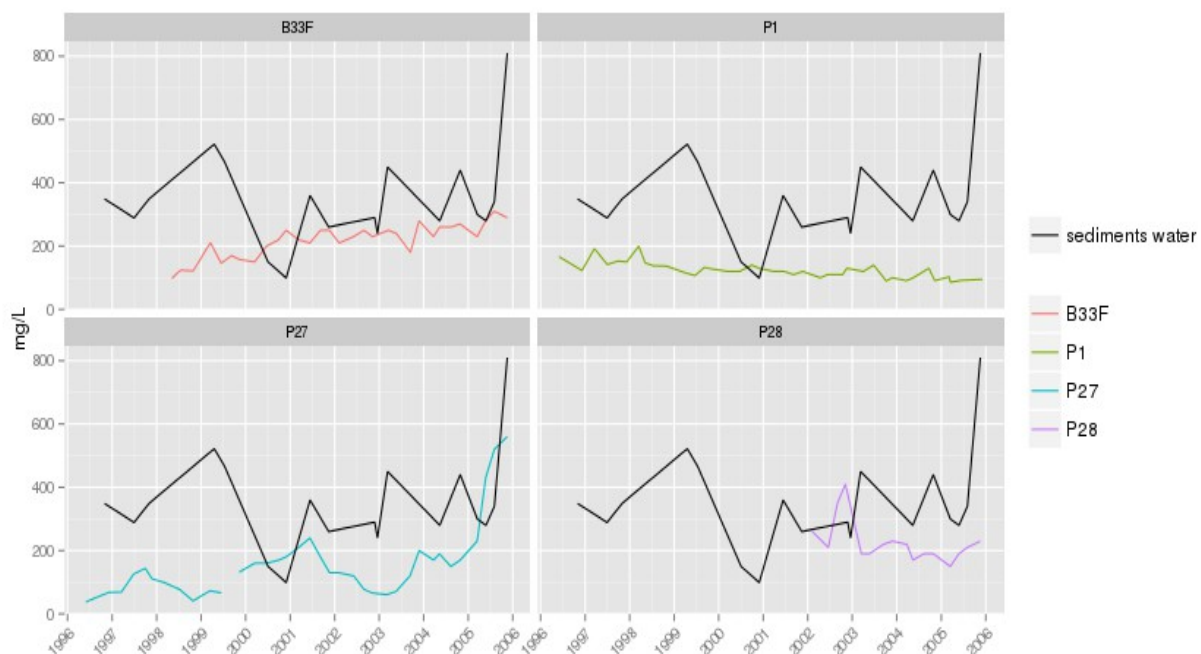


Fig 42 - Sediments leaching water comparison for SO₄

Besides P28 (deep piezometer but with a long filter) the other 3 piezometers are shallow, but P1 doesn't seem to be influenced so if there were a contamination, it affects the central area of the entire landfill.

Similarly, Fig 43 shows the comparison of Cl between sediments leaching water and piezometers values. Unlike SO₄ trends, it seems that no correlation is present: absolute

values differ pretty much and while Cl trends in piezometers are stable in time, those of sediments leaching water have a fluctuating behavior.

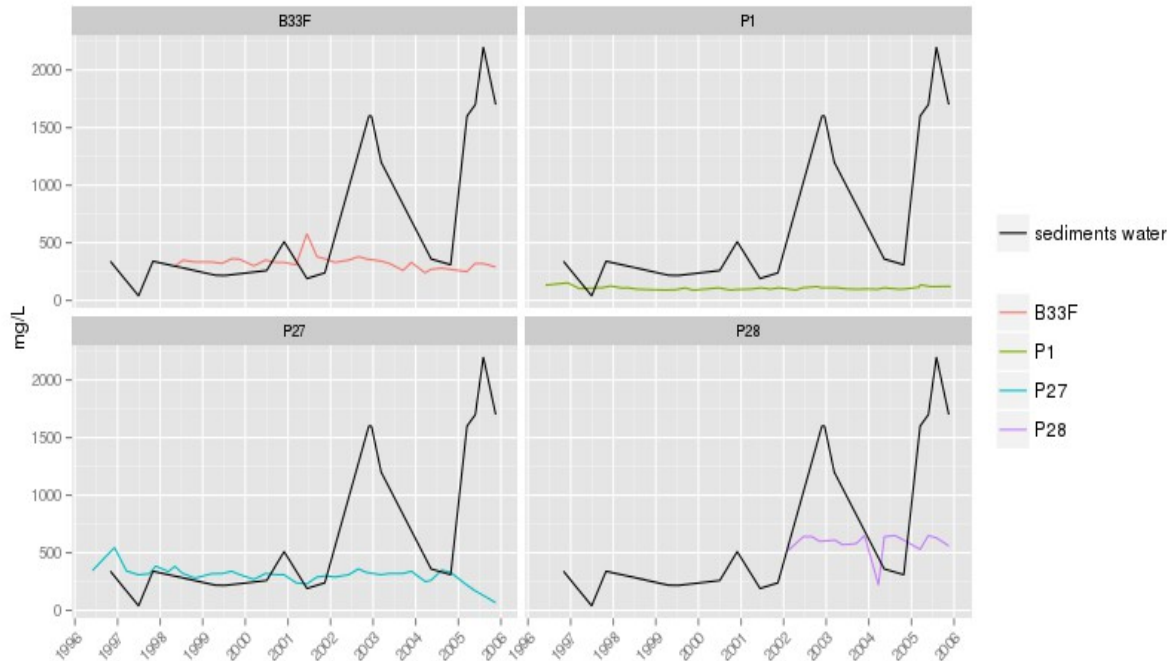


Fig 43 - Sediments leaching water comparison for Cl

6.5 Ions ratio

Groundwater salinization may result from numerous natural or anthropic processes like inflow of sea water (in coastal aquifer), mix of saline water with fresh water as a result of salty minerals leaching or industrial wastes.

According to Vengosh (Vengosh, 1994) and Stober (Stober, 2000) studying ions ratios is useful to understand the source of the salty water or at least to have an idea of the processes that are taking place.

Both authors suggest ranges in which one can find a specific water category depending of the ions content in the water. Three main ratios have been analyzed with current data: Cl/Br and Na/Cl.

Following tables summarize piezometers value with color scale depending on the classes:

<i>ID</i>	<i>Cl/Br</i>	<i>Na/Cl</i>	<i>Depth</i>
2818/22/0834	1416.56	0.74	Shallow
2818/22/0851	1703.00	0.62	Shallow
2818/22/0853	2588.06	0.59	Shallow
2818/22/0886	3313.70	0.68	Shallow
B0F	1161.75	1.08	Shallow
B12T	2021.72	0.86	Deep
B1T	2060.98	0.79	Deep
B21T	1985.19	0.52	Deep
B22F	1292.00	1.14	Shallow
B26T	2030.24	0.76	Deep
B33F	788.75	0.96	Shallow
B4F	1966.92	0.94	Shallow
P1	1320.29	1.52	Shallow
P21	1113.42	0.82	Shallow
P24	617.44	0.93	Shallow
P25	773.11	0.83	Shallow
P27	845.52	1.01	Shallow
P28	3071.54	1.20	Deep
P29	1485.41	0.78	Deep

<i>Indicator</i>	<i>Sea water</i>	<i>Brackish water</i>	<i>Deep salt structure presence</i>	<i>Rain water</i>	<i>"Natural water"</i>
Cl/Br	288*	50 – 150**	500 – 3000**	17*	286**
Na/Cl	0.86**	1**	~1**	---	>1*

* Stober & Bucher 2000

** Vengosh & Rosenthal 1993

Fig 44 - Molar ratios

As one can see, all Cl/Br values belong to the *Deep salt structure presence*. This fact confirm what said before, that is that aquifer can be seriously influenced by salt structures leaching. However, all the piezometers belong to this class both shallows and deeps and what is odd is that the highest value is found in a shallow piezometer.

Na/Cl values are more spread into the classes: some affinity with salt structures found with the Cl/Br ratio is confirmed, but other behavior can also be discovered.

7 Conclusions

During this master thesis, it has been studied the hydrogeochemical situation of the groundwater in the Seehasen landfill (Bremen). Aim of this study has been to describe the geochemical pattern of the shallow and deep aquifers and to study a possible impact of the landfill into the groundwater.

The Seehausen landfill is a large and dynamic territory while the natural geological underground is influenced by many natural conditions. It is never simple to split up anthropic impacts and natural ones and, at the same time, it is not simple to identify the possible contamination sources.

What emerges in this study is that the separation of piezometers in downstream and upstream categories in order to use upstream ones as a possible “blank” is not adequate: these piezometers have to be treated as the other ones and the categorization is purely informative.

Otherwise, shallow and deep piezometers are completely separated. Deep piezometers have an ions concentration much higher than shallow ones and this fact is very likely linked to the leaching of the deep salt structures. Deep and shallow aquifer can be linked in small areas and this may cause an uprising of salty waters. However, a possible impact of the landfill in the aquifer can only be seen in the shallow aquifer.

Historical data show that there are growing sulfate trends in the sediments landfill area: the fact that this growing trends don't involve other parameters, especially electrical conductivity and chlorine, could be due to a possible sediments leaching into the aquifer. Furthermore, the growing trends in all the involved piezometers converge around the same value: it is possible that sulfate rich water climb up, but it is unlikely that this fact is spread in a quite large area.

Moreover, the comparison between sulfate interpolation maps shows that its concentration has moved from outside the landfill area to the sediments landfill in the last years.

It seems that there are no particular problems related in the drying fields area, unless for one piezometer (P27) that shows strange sulfate behavior. It is not possible to understand the reason of this problem, further analysis has to be done in order to understand the fluctuation of this value.

The less strange behavior of the nearby piezometer (P28) is probably due to the long filter installation. Its chemical values reflect more likely a shallow-deep water mix rather than only one single part of the aquifer. Nevertheless, its values are not so fluctuating like those of P27.

To better understand the hydrogeochemical setting of this area, deep oriented samplings have to be considered. This way one can see if the problem is related to the leaching of a particular aquifer or if the problem involve the whole section.

A good idea would be to extend the number of piezometers even outside the landfill area, especially to the southern part. As said, a clear distinction according to the position of the piezometers has not been possible to find, so other piezometers could help to find natural (and surely not landfill influenced) groundwater conditions. Anyway, this impossibility to separate piezometers could be a signal of non effect, that is, the aquifer is rather homogeneous.

Chemical sampling and analysis of sediments located in the sediments landfill could be useful for a further comparison with groundwater values: this could help to understand if the sulfate in groundwater is the result of a slow leaching of them.

At last, the employment of specific tracers (chlorine isotopes for example, see Zhang, 2007) could aid to comprehend the source of particular elements.

In conclusion, it is not possible to assert that the Seehausen landfill has an impact on the groundwaters, but at the same time it seems that the landfill has some strong influences on the shallow aquifer in the western part of the territory.

Further analysis and studies have to be done in order to better understand geochemical pattern that are modifying the chemical content of the shallow aquifer.

Maybe the current monitoring concept of the Seehausen landfill has to be reviewed: after 20 years of data collection (groundwater, incoming dredged sediments, chemistry about sediments) it should be possible to see if the landfill has an impact on the groundwaters or most generally on the local environment.

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Attaches

Attach 1 - Piezometer information

ID	Pipe elevation (+m MSL)⁽¹⁾	Filter (-m ground level)		Depth (-m pipe)	Depth description⁽²⁾	Position⁽³⁾
		beginning	end			
2818/22/0834	5.21	10.10	12.10	12.10	S	D
2818/22/0851	1.72	10.00	12.00	13.00	S	D
2818/22/0853	1.82	10.00	12.00	13.00	S	D
2818/22/0886	3.17	3.00	6.00	7.00	S	D
B0F	1.36	4.80	11.80	14.00	S	D
B12T	4.58	38.00	42.00	42.00	D	D
B1T	2.19	23.80	44.80	45.00	D	D
B21T	4.16	31.50	36.50	37.00	D	U
B22F	4.28	6.00	11.00	12.00	S	U
B26T	3.37	17.00	22.00	24.00	D	U
B2F	4.61	9.00	15.00	15.00	S	D
B33F	2.97	9.00	15.00	15.00	S	D
B3F	4.58	8.20	12.20	13.00	S	D
B4F	1.92	6.50	16.50	17.00	S	D
B7F	4.79	11.00	16.00	16.00	S	D
P1	5.85	-	-	13.50	S	U
P21	6.30	7.40	11.40	12.00	S	D
P24	3.01	7.00	9.00	10.00	S	D
P25	4.74	9.00	11.00	12.00	S	D
P27	9.57	10.10	14.10	15.00	S	U
P28	8.73	9.00	29.00	29.00	D	U
P29	8.85	9.50	48.50	48.50	D	D

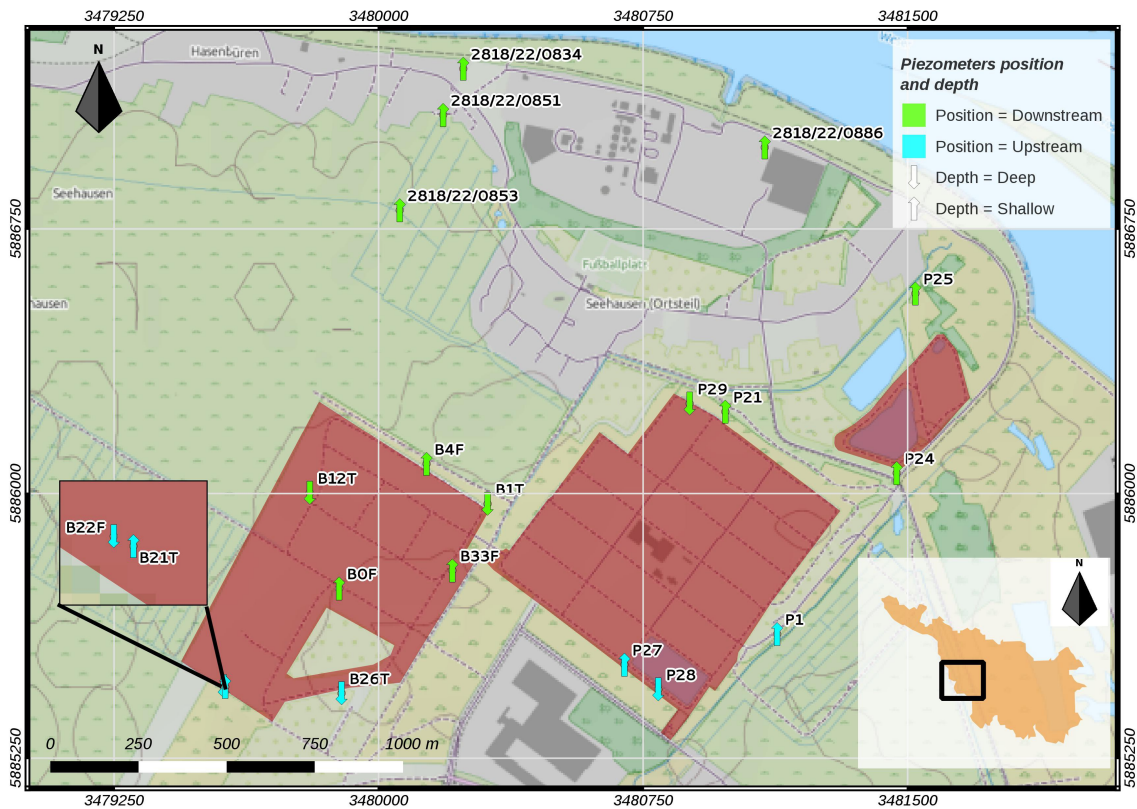
Attach 1 - Piezometer information

⁽¹⁾ MSL = middle sea level

⁽²⁾ Shortcut referring to the depth of the piezometer: S for shallow (pipe filter is < 20 meters under the ground level) and D for deep (pipe filter > 20 meters under ground level)

⁽³⁾ Shortcut for describing the position of the piezometer according to the flow direction and the landfill location: U is upstream and D is downstream.

Attach 2 - Piezometers according to position and depth

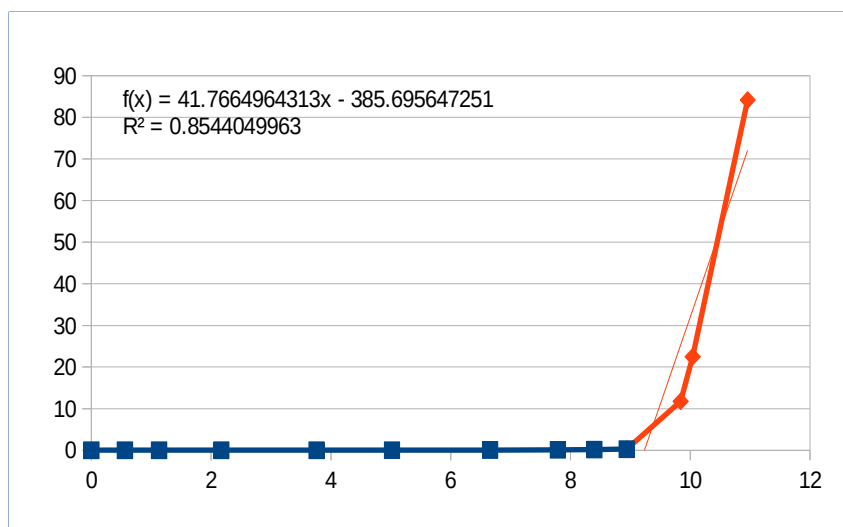


Attach 2 - Piezometers according to position and depth

Attach 3 - Gran Titration spreadsheet template

Sample: P27

VHCL		V0+VHCL	pH	$10^{-\text{pH}(V_0+V_{\text{HCL}})} \times 1000$
ml	L	ml	-	$\mu\text{mol H}^+$
0.00	0,00	100	6.78	0.0166
0.56	0.0006	100.56	6.77	0.0171
1.13	0.0011	101.13	6.73	0.0188
2.17	0.0022	102.17	6.65	0.0229
3.76	0.0038	103.76	6.52	0.0313
5.02	0.0050	105.02	6.40	0.0418
6.66	0.0067	106.66	6.22	0.0643
7.79	0.0078	107.79	6.00	0.1078
8.40	0.0084	108.4	5.82	0.1641
8.94	0.0089	108.94	5.59	0.2800
9.84	0.0098	109.84	3.97	11.7696
10.04	0.0100	110.04	3.69	22.4673
10.96	0.0110	110.96	3.12	84.1718



Equation of the line	$y=mx+q$	$y=41.77x + 385.70$
Point at $y=0$ [mL]	$y=0 \rightarrow x=m/q$	$x=385.70 / 41.77$
Alkalinity [mmol/L]	$A=V_{\text{HCl}} / V_0$	$A=9.2233 / 1000$

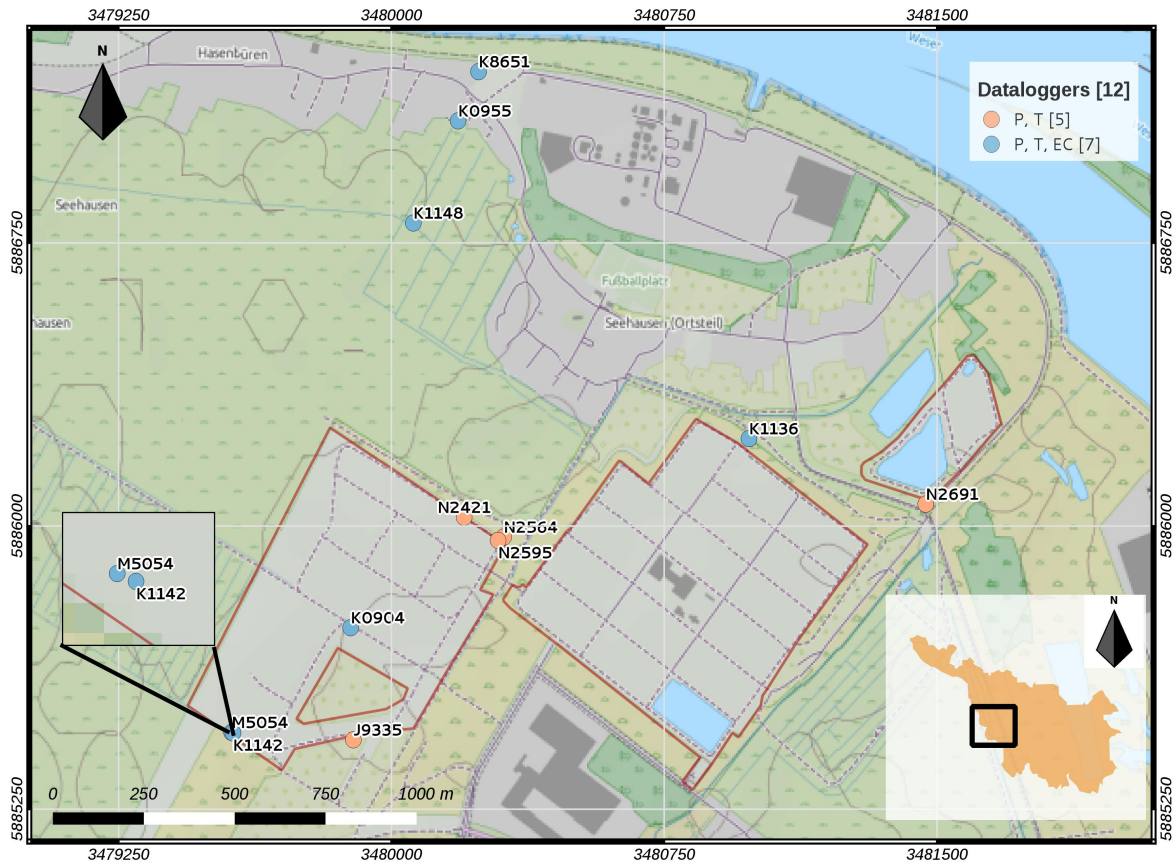
Attach 3 - Gran Titration spreadsheet template

Attach 4 - Data loggers

piezometer ID	datalogger ID	depth logger (m under water table)	parameters measured	days of measure	number of values collected
2818/22/0834	K8651	2.00	P, T, EC	34	9706
2818/22/0853	K1148	1.75	P, T, EC	34	9722
2818/22/0851	K0955	1.75	P, T, EC	34	9721
P21	K1136	2.20	P, T, EC	34	9764
B21T	M5054	1.30	P, T, EC	34	9783
B22F	K1142	0.90	P, T, EC	34	9783
B0F	K0904	1.75	P, T, EC	34	9791
B1T	N2564	1.00	P, T	34	4871
P24	N2691	1.00	P, T	34	4865
B3F	N2421	1.40	P, T	34	4885
B2F	N2595	1.50	P, T	34	4886
B26T	J9335	1.00	P, T	34	4892

Attach 4 - Data loggers

Attach 5 - Map of the data loggers



Attach 5 - Map of the data loggers

Attach 6 - Results of the analysis 1

Piezometer ID			2818/22/0834	2818/22/0851	2818/22/0853	2818/22/0886	B4F	B3F	B7F
Piezometer position and depth*			SD	SD	SD	SD	SD	SD	SD
Date of sampling			13/08/13	13/08/13	13/08/13	13/08/13	11/06/13	11/06/13	11/06/13
Anions	Cl	mg/L	125.7	219.12	298.55	132.32	383.98		
	SO4		31.83	39.93	29.15	42.36	320.1		
	F		0.3	0.2		0.04			
	Br		0.2	0.29	0.26	0.09	0.44		
	NO3			0.1	0.07	0.08			
	HCO3		458.82	335.38	375.17	319.78	507.86		
Cations	K	mg/L	3.5	3.7	3.81	10.8	3.85		
	Na		65	92.5	118.1	63.3	238.7		
	Mg		18.67	21.49	23.62	14.81	32.18		
	Ca		126	139.9	146.7	93.7	218.1		
	Mn		7.17	9.58	7.16	10.62	13.77		
	Fe		30.24	12.14	14.79	33.48	40.46		
	Li								
Isotopes	δ2H	‰	-52.7	-51.03	-51.76	-52.71	-49.47		
	δ18O		-7.58	-7.08	-7.41	-8.35	-6.91		
Field parameters	T	°C	11.80	10.70	10.70	14.40	11.30	11.30	12.10
	O	mg/L	0.32	0.16	0.17	0.22	0.03	0.03	0.89
	pH		6.81	6.78	6.49	6.72	6.84	6.84	6.88
	EC	µS/cm	1046.67	1315.00	1418.00	997.33	2470.00	2470.00	3190.00
	Water table	m above msl	0.49	0.53	0.66	0.43	0.99	0.99	0.92
	color		transparent	transparent	transparent	yellow	transparent	transparent	transparent
	odor		smellless	smellless	smellless	smellless	smellless	smellless	smellless
	turbidity		clear	clear	clear	strong	clear	clear	clear

Attach 6 - Results of the analysis 1

* SD refers to shallow and downstream

** elevation of the piezometer based on the last year measure because it has been damaged and its elevation has not been updated to the new reconstruction

Attach 7 - Results of the analysis 2

Piezometer ID			B33F	B2F	P21	P24	P25	B12T	B1T	P29
Piezometer position and depth*			SD	SD	SD	SD	SD	DD	DD	DD
Date of sampling			12/06/13	11/06/13	12/06/13	12/06/13	12/06/13	12/06/13	11/06/13	12/06/13
Anions	Cl	mg/L	216.97		365.56	199.98	308.71	3435.49	2322.61	711.77
	SO4		424.19		123.67	176.99	342	43.05	31.32	115.15
	F				0.2	0.17	0.17	0.28	0.13	0.18
	Br		0.62		0.74	0.73	0.9	3.83	2.54	1.08
	NO3		0.06							
	HCO3		552.2935		441.36	456.76	563.27	248.09	344.68	508.72
Cations	K	mg/L	3.3		3.32	2.1	2.4	11.49	12.71	3.98
	Na		137.5		194.8	124.3	170.7	1403.9	1015.6	346.1
	Mg		40.31		30.54	28.38	47.56	19.28	26.52	36.28
	Ca		244.1		172.1	178.8	252.3	94.2	145.1	209.4
	Mn		14.05		10.89	8.24	11.4	0.08	0.17	10.74
	Fe		48.98		45.54	27.1	43.76	0.61	2.63	52.34
	Li							0.06	0.04	
Isotopes	δ2H	‰	-48.66		-48.28	-47.03	-47.57	-56.59	-58.32	-51.81
	δ18O		-6.32		-7.21	-6.71	-7.19	-7.78	-7.41	-7.1
Field parameters	T	°C	11.90	12.30	10.80	11.20	10.80	11.50	10.80	11.00
	O	mg/L	0.64	0.82	0.06	0.09	0.04	0.93	0.15	0.16
	pH		6.76	6.86	6.74	6.77	6.73	7.68	7.69	6.72
	EC	μS/cm	2096.00	2310.00	2201.70	1685.60	2416.70	9700.00	6726.00	2962.00
	Water table	m above msl	0.99	0.93	0.97	0.88	0.98	0.74	0.9	0.95
	color		soft grey	soft grey	transparent	transparent	transparent	transparent	transparent	transparent
	odor		smellless	smellless	smellless	smellless	smellless	smellless	smellless	smellless
	turbidity		clear	clear	clear	clear	clear	clear	clear	clear

Attach 7 - Results of the analysis 2

* **SD** refers to shallow and downstream, **DD** refers to deep and downstream

Attach 8 - Results of the analysis 3

Piezometer ID			P1	P27	B0F	B22F	P28	B21T	B26T
Piezometer position and depth*			SU	SU	SU	SU	DU	DU	DU
Date of sampling			11/06/13	12/06/13	11/06/13	11/06/13	12/06/13	11/06/13	11/06/13
Anions	Cl	mg/L	82.01	217.58	520.6	366.87	436.09	2800.9	1891.63
	SO4		48.16	174.84	432.88	69.45	271.27	1.01	0.57
	F		0.31	0.21	0.17	0.26	0.23	0.04	0.21
	Br		0.14	0.58	1.01	0.64	0.32	3.18	2.1
	NO3		0.07			0.03			0.02
	HCO3		293.12	387.50	523.51	331.56	425.81	571.23	492.15
Cations	K	mg/L	1.35	1.66	3.6	1.93	0.21	7	6.15
	Na		85.9	145	360.4	279.7	8944.99	851.1	819.8
	Mg		10.9	24.38	35.14	14.93	1123.07	37.18	26.95
	Ca		67.3	137.4	231.8	99.4	356.39	290.1	230.9
	Mn		2.62	10.19	7.11	3.13		4.43	0.5
	Fe		27.32	47.98	42.43	21.06		28.31	6.72
	Li								
Isotopes	δ2H	‰	-46.33	-48.9	-50.63	-44.57	-47.86	-55.32	-55.4
	δ18O		-6.16	-6.88	-7.44	-6.76	-7.17	-7.02	-7.73
Field parameters	T	°C	11.00	11.50	10.80	10.60	11.90	10.50	10.50
	O	mg/L	0.11	0.83	0.23	0.09	0.81	0.11	0.11
	pH		6.91	6.68	6.88	6.97	6.94	6.84	7.38
	EC	μS/cm	867.00	1618.30	2972.30	1916.00	2410.00	6441.30	6002.50
	Water table	m above msl	0.99	1.08	0.92**	1.06	1.05	0.94	1.12
	color		transparent	soft grey	transparent	transparent	transparent	transparent	transparent
	odor		smellless	smellless	smellless	lightly rotten	smellless	smellless	smellless
	turbidity		clear	clear	clear	clear	clear	clear	clear

Attach 8 - Results of the analysis 3

* **SU** refers to shallow and upstream and **DU** refers to deep and upstream

Attach 9 - Anions calibration summary

Sample	Dilution MES : MilliQ	Type	F ⁻	Cl ⁻	NO ₂ ⁻	Br	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻
			mg/L						
Standard 1	1:1	S	5.07	298.47	5.10	5.11	29.90	5.08	299.93
		M	5.07	298.44	5.10	5.11	29.85	5.08	299.40
Standard 2	1:2	S	2.53	149.08	2.55	2.55	14.93	2.54	149.81
		M	2.53	149.03	2.55	2.55	14.92	2.55	149.59
Standard 3	1:4	S	1.27	74.90	1.28	1.28	7.50	1.27	75.27
		M	1.27	74.89	1.28	1.28	7.50	1.27	75.14
Standard 4	1:8	S	0.63	37.17	0.64	0.64	3.72	0.63	37.35
		M	0.63	37.16	0.64	0.64	3.72	0.63	37.31
Standard 5	1:16	S	0.32	18.69	0.32	0.32	1.87	0.32	18.78
		M	0.32	18.69	0.32	0.32	1.87	0.32	18.78
Standard 6	1:32	S	0.16	9.40	0.16	0.16	0.94	0.16	9.45
		M	0.16	9.40	0.16	0.16	0.94	0.16	9.45
Standard 7	1:64	S	0.08	4.59	0.08	0.08	0.46	0.08	4.61
		M	0.08	4.59	0.08	0.08	0.46	0.08	4.61
CRM SW (CRM)		S	-	19000.00	-	65.00	-	-	2895.52
		M	-	19728.00	-	65.01	-	-	2968.32
K15 (CRM)		S	1.29	20167.85	-	67.00	-	-	2712.00
		M	1.30	19354.00	-	67.68	-	-	2603.77
Detection limits			-	<2	<0.3	<0.3	<0.44	<0.3	<0.5

MES → Multielementstandart

S → Standard

M → Measured

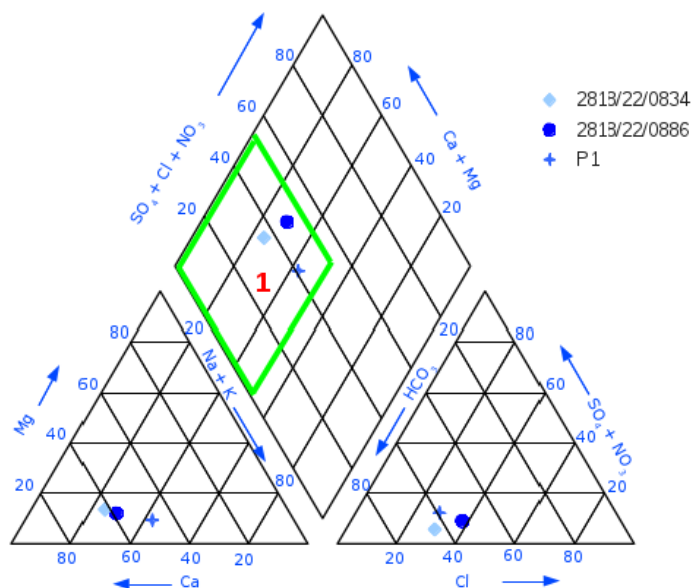
Attach 9 - Anions calibration summary

Attach 10 - Cations calibration summary

Element	Corr. Coef.	Detection limits (mg/L)
Na	0.999964	<0.25
Li	0.99994	<0.5
Be	0.999946	<0.1
Mg	0.99992	<0.5
K	0.999804	<0.5
Ca	0.999313	<0.25
Al	0.999891	<0.5
Fe	0.99994	<0.5
Mn	0.999877	<0.1
Ni	0.999899	<0.5

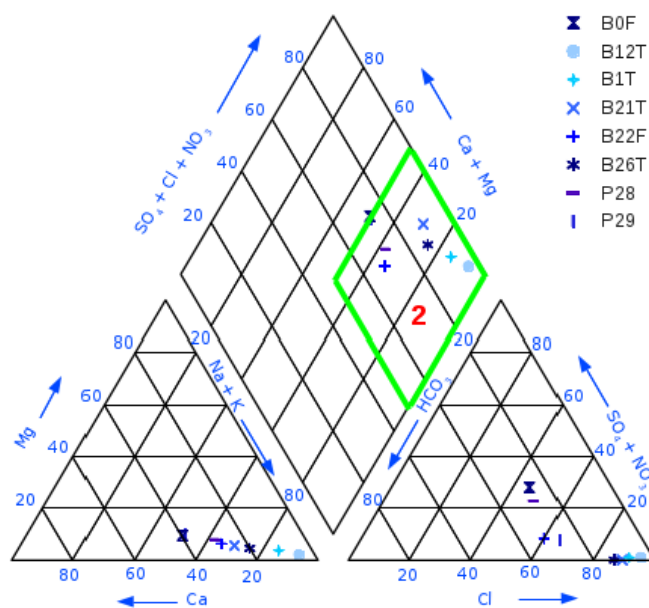
Attach 10 - Cations calibration summary

Attach 11 - Piper diagram - group 1



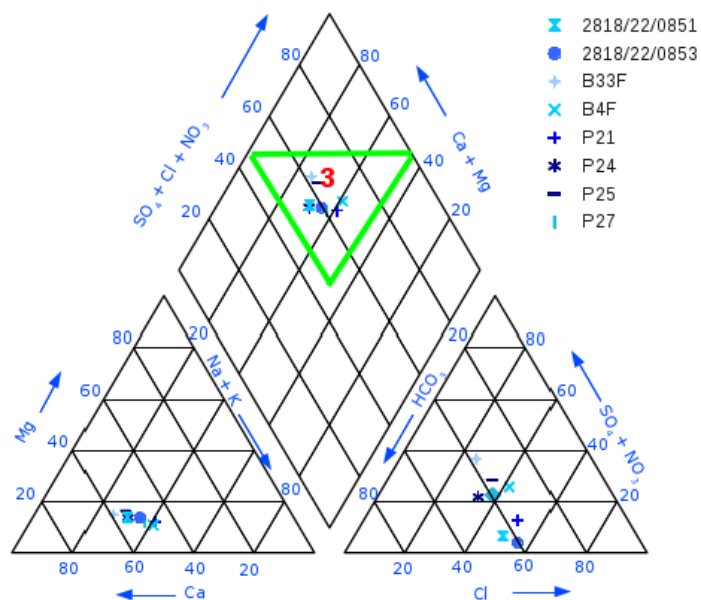
Attach 11 - Piper diagram - group 1

Attach 12 - Piper diagram - group 2



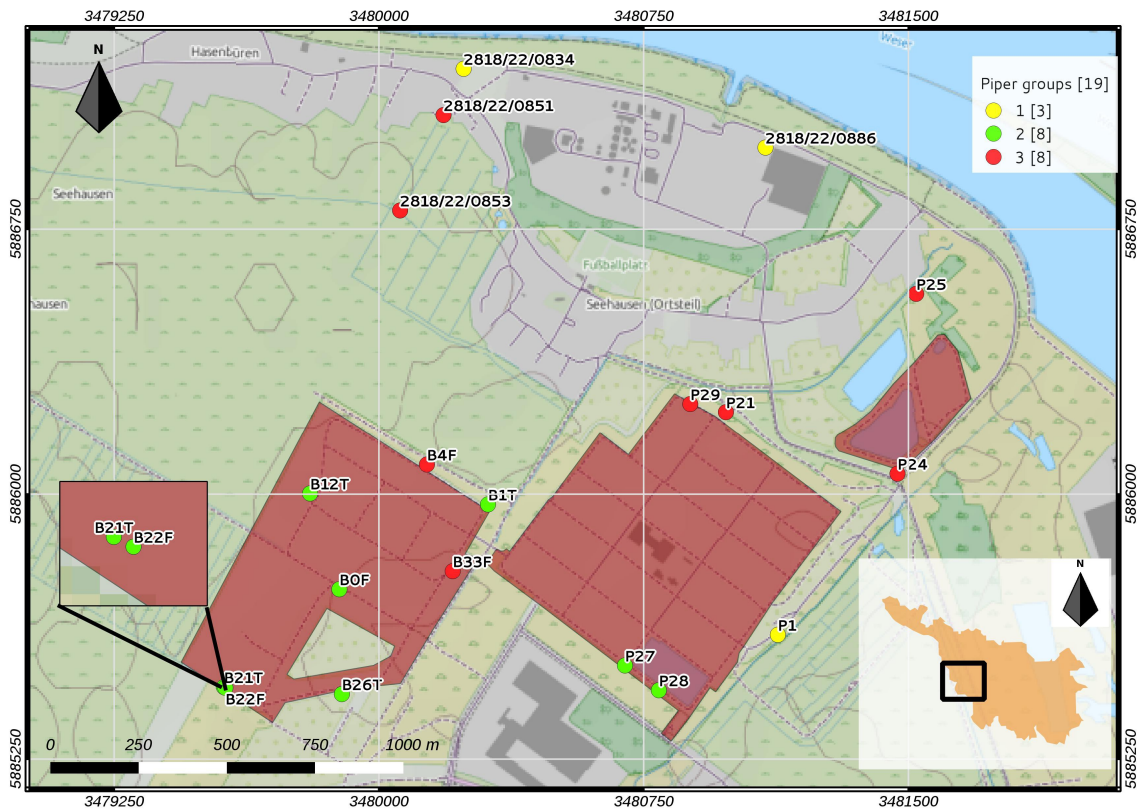
Attach 12 - Piper diagram - group 2

Attach 1 - Piezometer information



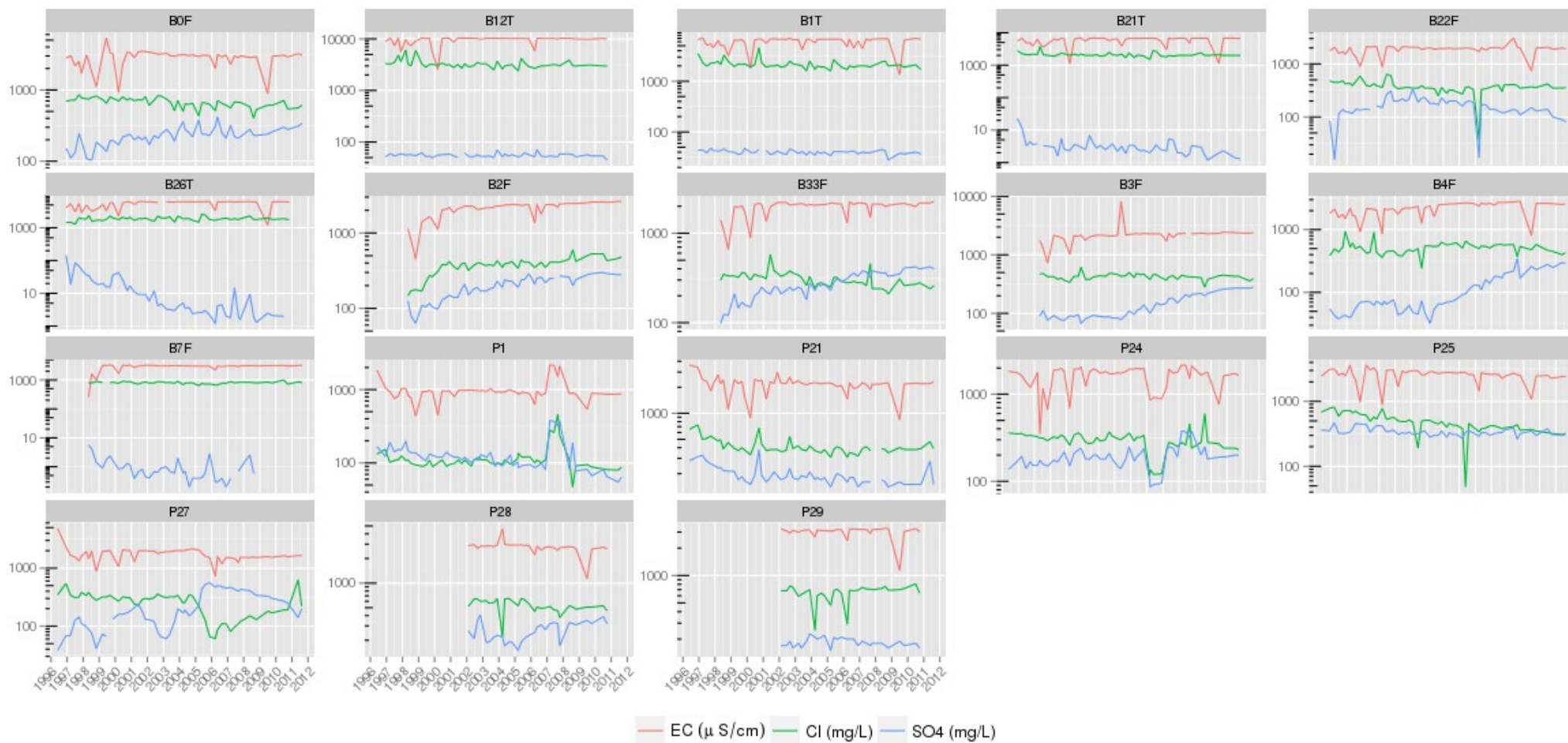
Attach 13 - Piper diagram - group 3

Attach 14 - Piezometer according to Piper categories



Attach 14 - Piezometer according to Piper categories

Attach 15 - EC, Cl and SO₄ time trend in all piezometers



Attach 15 - EC, Cl and SO₄ time trend in all piezometers