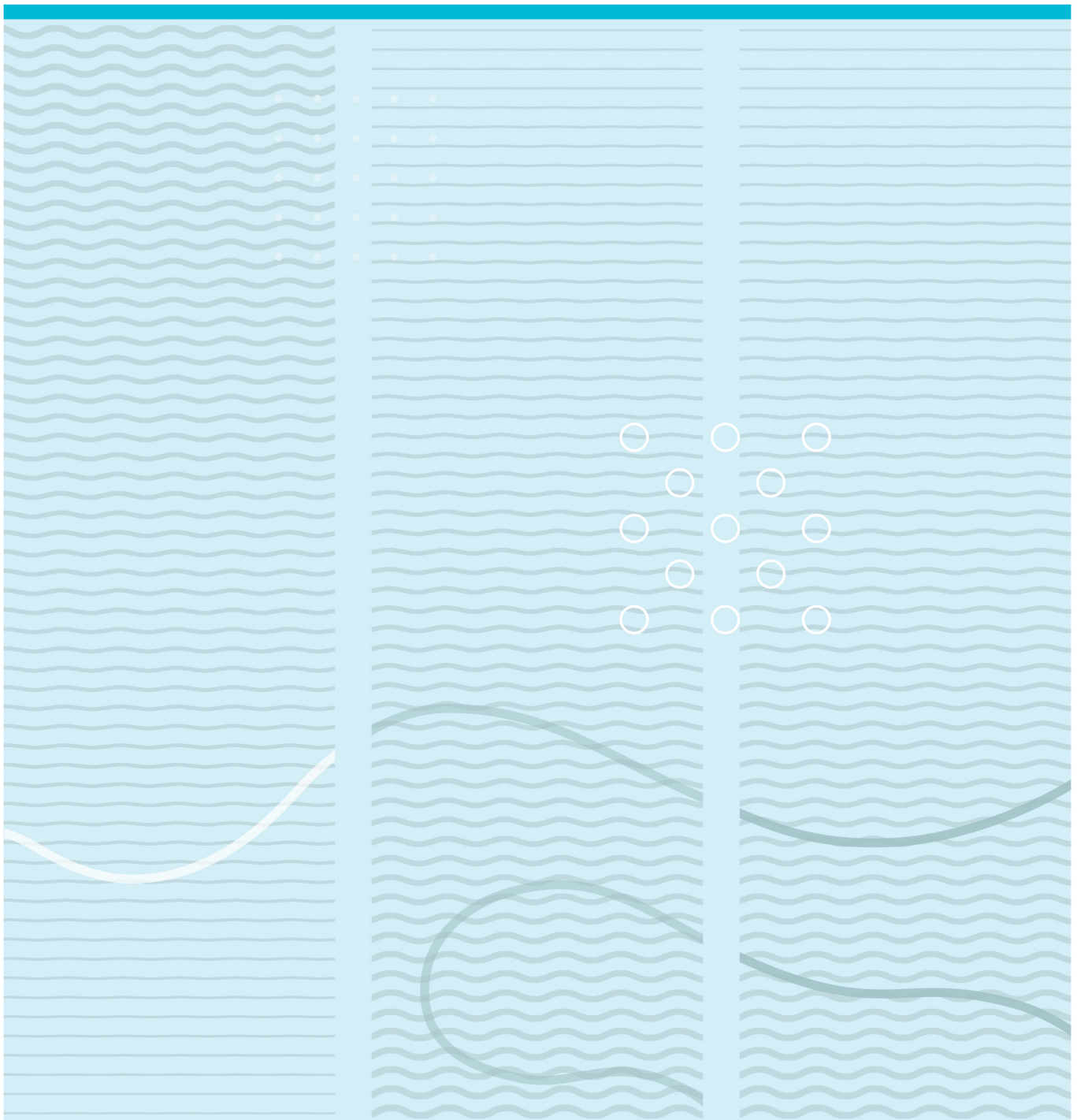HSN

Daniel Abiriga

Groundwater contamination from an old municipal landfill at Revdalen, Norway

Groundwater quality, redox conditions and feasibility of natural attenuation as a remedy

This thesis is worth 60 study points

Abstract

Negative environmental impacts of landfill operations have led to establishment of stringent legislation on dumping of wastes in landfills. Emphases have been put on integration of various disciplines where experts from engineering, geology, hydrology and chemistry collaborate to ensure construction of landfills that pose less risks to the environment. Revdalen landfill has neither liners nor leachate collection system, reflecting luck of interdisciplinary collaboration in its construction, which must have been due to lack of adequate information in the year of its construction (1974). This is a report on a 23-year study of groundwater chemistry of the aquifer polluted by leachate emanating from Revdalen Landfill. The study aimed to characterise the organic and inorganic compositions of the groundwater, identify the processes governing natural attenuations, and further examine effects of landfill age, landfill closure and season on the groundwater quality.

Groundwater samples were taken twice a year from wells established using Waterloo Multilevel Groundwater Monitoring System and separate multilevel sampling wells. The samples were analysed for several chemical parameters. Results showed substantial input of mainly inorganic pollutants from the landfill. Seasonal dynamics on groundwater quality has indicated slightly higher concentrations of pollutants in dry season (autumn) than in wet season (spring). The results further demonstrated that, closing the landfill was followed by decrease in concentrations of contaminants in groundwater. Generally, concentrations of all the parameters were found to be on the verge of attaining the natural background level as the age of the landfill approached 21 years. The seasonal variations could be due to dilution in wet season and concentration effect in dry season, whereas that of landfill closure could partly be due to initiation of reducing condition that immobilised pollutants, and in part due to controlled infiltration of precipitation that would otherwise lead to wash out of pollutants. The decrease in concentrations of pollutants with age was probably a result of landfill stabilisation, when most of the contaminants would have been leached out. The redox conditions responsible for attenuation processes have been identified in the order of increasing distance from the landfill as; sulphate reducing, iron reducing, manganese reducing, nitrate reducing and finally aerobic condition. The feasibility of the aquifer acting as a treatment plant for the pollutants was very substantial, thus eliminating any serious environmental risk associated with the emanating leachate.

Key words: *Landfill, Leachate, Aquifer, Groundwater, Attenuation, Redox, Monitoring.*

Acronyms and Abbreviations used in the Text

Anammox	Anaerobic ammonium oxidation
BDL	Below Detection Limit
BOD	Biochemical Oxygen Demand
BPEO	Best Practicable Environmental Option
COD	Chemical Oxygen Demand
DNA	Deoxyribonucleic Acid
DNRA	Dissimilatory Nitrate Reduction to Ammonia
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
EC	Electrical Conductivity
EU	European Union
m.a.s.l	Metres Above Sea Level
MLS	Multilevel Sampler
MSW	Municipal Solid Waste
NEA	Norwegian Environment Agency
NVOC	Non Volatile Organic Compounds
PAH	Polycyclic Aromatic Hydrocarbons
PCB	Polychlorinated Biphenyls
PTFE	Polytetrafluoroethylene
TOC	Total Organic Carbon
Tot-N	Total Nitrogen
Tot-P	Total Phosphorous
TVA	Total Volatile Acids
USEPA	United States Environmental Protection Agency
USN	University College of Southeast Norway
VFA	Volatile Fatty Acids
VOA	Volatile Organic Acids
VOC	Volatile Organic Compounds
XOC	Xenobiotic Organic Compounds

Contents

Foreword

This dissertation constitutes up to 50% of the overall 120 study points in MSc. Environmental Science. It presents a report from a monitoring programme established at Revdalen Landfill, which is the historic landfill site in Bø municipality. Up to early 90's, landfill was the most plausible cost effective waste management strategy in Norway. Far be it from this rather a primitive practice, a clear picture of how waste is managed in Norway today places landfill as the last alternative, with total ban on damping biodegradable waste into landfill. This dissertation presents a report on "groundwater chemistry" of a contaminated aquifer at Revdalen Landfill. Knowledge of chemistry, hydrogeology and biology is required to understand the work presented herein.

Bø, May 2017
Daniel Abiriga

1 Introduction

1.1 Background

Revdalen Landfill was established in 1974 by Bø municipal authority and closed in 1997. During its active years, the landfill received huge volume of wastes from Bø and Sauherad municipalities. As a consequence of the landfill operation, contamination of groundwater by leachate generated from the landfill has been reported (Klempe et al., 1992). In particular, the deterioration in water quality of a private well located close to R4 (see section 2.2). This led to intervention by experts from the municipality, and the geotechnical team of University College of Southeast Norway (USN), to establish monitoring wells for periodical assessment of the groundwater quality in the contaminated aquifer. The monitoring programme started in 1992, when the landfill was still operational and continued even after its closure in 1997, until today.

1.1.1 Statement of the problem

Revdalen Landfill has neither been equipped with liners nor leachate collection system. This therefore endangered the groundwater and surface water in the surrounding area, exacerbated by the sedimentology of the landfill area, which provided an insignificant retardation to the leachate that drained from the waste. The less retarded leachate drained through a sub-glacial channel and ended up in the aquifer as a plume (Klempe et al., 1992). The landfill was located in the watershed area that recharged the aquifer. Thus, there was a continuous transport of plumes in the aquifer. This hampered with the legitimate utilisation of this geological resource for drinking water, due to presence of potentially pathogenic microbes and toxic chemicals in landfill leachate. Therefore, the result of the study should satisfactorily ascertain if the landfill was still producing toxic leachate after 23 years of monitoring, and also examine the feasibility of natural attenuation as a remedy to the problem. This would enable stakeholders and policy makers on natural resource management to make informed decisions, about the possible reclamation and subsequent utilisation of this groundwater resource in the area.

1.1.2 Aim of the study

The study aimed to characterise the chemical compositions of the contaminated groundwater, using a database generated for 23 years of observations. Specific objectives were to

characterise the organic and inorganic pollutants in the groundwater, examine effects of landfill closure, age and season on groundwater quality, and identify the natural attenuation processes.

1.2 Literature review

1.2.1 Landfills

We live in a world characterised by a continuous rise in human population, with a resultant associated increase in waste generation. This inextricable relationship is corroborated by data for Norway (NEA, 2016) and for United States (US-EPA, 2012) among others. These wastes, which include household waste, building and construction waste, chemical and hazardous waste, sludge and ash (Bjerg et al., 2003, Östman et al., 2006) would need to be efficiently disposed off. Landfilling has for long been the major disposal method for both domestic and industrial wastes (Reinhard et al., 1984). However, improper landfill management may pose serious environmental threats through emission of gas, liquid and solid, causing a constant deterioration in environmental quality (Cossu, 2013, Peng, 2013). Negative environmental impacts due to release of toxic substances, such as additives from wastes, have led to the ban or restriction on the use of some chemicals (Eggen et al., 2010). Due to the shortcomings associated with landfill operations, the European Union (EU) waste management strategy emphasises strict observance of waste management hierarchy that places landfill as the least desirable option (Williams, 2013) (Figure 1-1). The overall idea is to generate less waste at industrial level, while maintaining high quality of goods (McDougall et al., 2008). The principle of Best Practicable Environmental Option (BPEO) has been developed to ensure careful investigation of different alternative options to give the best environmental outcome, in terms of emissions to land, air and water at an acceptable cost, albeit the best practicable technique may not necessarily be the cheapest (Williams, 2013).
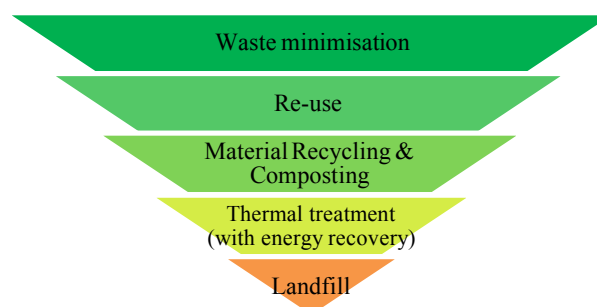

Figure 1-1: *The hierarchy of waste management [Source; McDougall et al. (2008), and Williams (2013)].*

1.2.2 Landfill leachate

One of the leading pollution problems caused by the Municipal Solid Waste (MSW) landfill is landfill leachate (Bhalla et al., 2013). The term "leachate" describes the liquid that percolates through the dumped waste, which is formed from rainwater, snowmelt, natural humidity and inherent water content of wastes, or intrusion of groundwater (Bhalla et al., 2013, Peng, 2013). This leach both soluble and insoluble organic and inorganic products originating from the body of the waste, extracted by physical and chemical, as well as hydrolytic and fermentative processes (Lema et al., 1988, Slack et al., 2005, Bhalla et al., 2013, Peng, 2013). These processes transfer pollutants from the waste material into percolating liquid (Han et al., 2014). The leachate is, therefore, considered to be polluted due to its contact with deposited waste (Øygard et al., 2004). As a result, there is a serious threat to public health due to environmental pollution caused by the leachate (Bhalla et al., 2013).

The major potential environmental impacts related to landfill leachate are pollution of groundwater and surface water (Kjeldsen and Christophersen, 2001, Kjeldsen et al., 2002, Słomczyńska and Słomczyński, 2004), since many of the thousands of landfills, active or abandoned, have been operated with little regard for the dangers of groundwater contamination (Reinhard et al., 1984). This is particularly true, because historically, landfill site selection was based on close proximity to waste production and the availability of large pits, which were usually the result of either quarrying or gravel, sand or brick–clay extraction, rather than on geological criteria of site suitability (Hamer, 2003). Those that were built lacked engineered liners and leachate collection systems (Kjeldsen et al., 2002). This has led to serious contamination of groundwater reservoirs, especially where the bottom of the depressions is below the water table, or if the earth material separating the dump from the aquifer is primarily silt, sand, or other relatively permeable material (Zanoni, 1972).

The potential for generating strongly contaminated leachate from landfill waste is very substantial (Bjerg et al., 2003). As a result, groundwater contamination cases are registered both in old uncontrolled and modern (engineered with liners and drainage system) landfills, partly due to the life span of barriers; frequently proving their efficiency to be shorter than the duration of impacts (Cossu, 2013), and partly due to inadequate design, construction, and maintenance, resulting in the leakage of leachate (Bjerg et al., 2003). The resultant groundwater pollution plume in the leachate-affected aquifer may last for decades to centuries (Bjerg et al.,

2003, Bjerg et al., 2011, Cozzarelli et al., 2011, Bhalla et al., 2013). Therefore, waste dumps with no measures to control leachate entrance into the groundwater may constitute a source of groundwater contamination long after dumping has ceased (Bjerg et al., 2003).

1.2.3 Leachate variability

Leachate composition and characteristics vary significantly among landfills, depending on a number of factors such as waste composition (which depends on the standard of living of the surrounding population), precipitation rate, site hydrology, compaction, waste age, landfill technology and sampling procedures (Lema et al., 1988, Christensen et al., 2001, Kjeldsen et al., 2002, Bjerg et al., 2003). Leachate production is generally greater whenever the waste is less compacted, since the degree of compaction affects the filtration rate (Lema et al., 1988). Moisture content has most consistently been shown to affect the rate of refuse decomposition. It is generally accepted that refuse buried in arid climates decomposes more slowly than refuse buried in regions that receive > 50-100 cm of annual infiltration into the waste (Kjeldsen et al., 2002). As a first approximation, the quantity of leachate produced may be regarded as proportional to the volume of water percolating through the landfill waste – which is the difference between precipitation and surface runoff (Tatsi and Zouboulis, 2002). Therefore, a first line of pollution prevention strategy is to limit the amount of water entering the landfill.

As a result of variable leachate composition, leachate treatment methods have not been unified so far (Kulikowska and Klimiuk, 2008). A leachate treatment plant designed to handle average leachate quality only, would in practice be occasionally overloaded. Therefore, an ideal treatment plant should be designed taking into account the worst-case scenario (Tatsi and Zouboulis, 2002).

1.2.4 Chemical nature of landfill leachate

Pollutants in MSW landfill leachate can be divided into four groups (Kjeldsen et al., 2002). The first component is the Dissolved organic matter, quantified as Chemical Oxygen Demand (COD) or Total Organic Carbon (TOC), Volatile Fatty Acids (VFAs) and more refractory compounds, such as fulvic-like and humic-like compounds (Kjeldsen et al., 2002). The Dissolved Organic Carbon (DOC) originates from the organic waste in the landfill and is a product of the anaerobic degradation processes in the landfill (Christensen et al., 1998). Analysis showed that the organic matter in the leachate are present as free VFAs, fulvic-like

material, humic carbohydrate-like complex and hydrophilic fraction in the order of decreasing amount (Chian and DeWalle, 1977). Isolation and subsequent quantification of the humic acids, fulvic acids and the hydrophilic fraction by Christensen et al. (1998) confirmed the pattern described by Chian and DeWalle (1977).

Inorganic macrocomponents forms yet another group of chemical contaminants in landfill leachate. The term macrocomponents has been used to refer to inorganic constituents present at elevated concentrations such as calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), ammonium (NH_4^+), iron (Fe^{2+}), manganese (Mn^{2+}), chloride (Cl^-), sulphate (SO_4^{2-}) and hydrogen carbonate (HCO_3^-) (Christensen et al., 2001, Kjeldsen et al., 2002).

Heavy metals such as cadmium (Cd^{2+}), chromium (Cr^{3+}), copper (Cu^{2+}), lead (Pb^{2+}), nickel (Ni^{2+}) and zinc (Zn^{2+}) (Kjeldsen et al., 2002), and Xenobiotic Organic Compounds (XOCs) form the third and fourth group of pollutants respectively. The XOCs may originate from household or industrial chemicals. They are present in relatively low concentrations (Kjeldsen et al., 2002), usually in the order of micrograms per litre (µg/L) and in many cases the concentrations are below detection limit (BDL) (Reinhart and Grosh, 1998, Öman and Junestedt, 2008). Despite the fact that most of these compounds are present at trace levels in the environment, harmful effects to the ecosystem and to the food web cannot be excluded (Eggen et al., 2010). Many of these XOCs can be hazardous in low doses and negative effects are often caused by a cocktail and synergistic effects (Öman and Junestedt, 2008). Therefore, detection is often more important than the reported concentration (Reinhart and Grosh, 1998). These compounds include among others, a variety of aromatic hydrocarbons, phenols, chlorinated aliphatics, pesticides, and plasticisers (Kjeldsen et al., 2002). Elaborate list of these compounds is to be found elsewhere (Kjeldsen et al., 2002, Slack et al., 2005, Eggen et al., 2010). Thus municipal landfill leachate may represent a significant source for legacy, new and emerging chemicals in groundwater (Eggen et al., 2010). Numerous XOCs are detectable, but they only account for a few percent of the organic matter in the leachate (Ruegge et al., 1995). The XOCs and heavy metals fractions are generally classified as hazardous substances in leachate, since some are carcinogenic, teratogenic, mutagenic, corrosive and flammable, while others are persistent and bio-accumulate (Slack et al., 2005).

Other possible pollutants in landfill leachate are borate, sulphide (S^{2-}), arsenate, selenate, barium, lithium, mercury (Hg^{2+}) and cobalt. Nevertheless, this group of pollutants are found in very low concentrations and are said to be only of secondary importance (Kjeldsen et al., 2002).

In general, municipal landfills generate strongly anaerobic leachate with high contents of DOC, salts, NH_4^+, organic compounds and metals released from the waste (Bjerg et al., 2003) (Table 1-1). Detection of NH_4^+, Cl^-, COD, SO_4^{2-}, Fe^{2+}, Mn^{2+} and some heavy metals are used as the main indicators of groundwater pollution from landfill leachate (Cossu, 2013, Han et al., 2014). Metals are often precipitated within the landfill and are thus infrequently found at high concentrations in leachate, with the exception of Fe^{2+} (Reinhart and Grosh, 1998).

Table 1-1: *General chemical compositions of landfill leachate, XOCs excluded (values are in mg/L, unless otherwise stated)*

Parameter	Range
pH	4.5-9
Electrical conductivity (μScm^{-1})	2500-35000
Total Solids	2000-60000
Organic matter	
Total Organic Carbon	30-29000
Biological Oxygen Demand	20-57000
Chemical Oxygen Demand	140-152000
BOD_5/COD	0.02-0.80
Organic nitrogen	14-2500
Inorganic macrocomponents	
Total phosphorous	0.1-23
Chloride	150-4500
Sulphate	8-7750
Hydrogen bicarbonate	610-7320
Sodium	70-7700
Potassium	50-3700
Ammonium-N	50-2200
Calcium	10-7200
Magnesium	30-15000
Iron	3-5500
Manganese	0.03-1400
Silica	4-70
Heavy metals	
Arsenic	0.01-1
Cadmium	0.0001-0.4
Chromium	0.02-1.5
Cobalt	0.005-1.5
Copper	0.005-10
Lead	0.001-5
Mercury	0.00005-0.16
Nickel	0.015-13
Zinc	0.03-1000

Adapted from Kjeldsen et al. (2002)

1.2.5 Phases of landfill Stabilisation

An understandably remarkable factor that is decisive on the quality of leachate emanating from a landfill is the stage of a landfill stabilisation, which represents the age of the landfill. Under favourable conditions, landfills behave like large-scale anaerobic reactors (Kulikowska and Klimiuk, 2008), with majorly four key phases (Figure 1-2). Transition through the phases is reflected by significant changes in leachate and gas quality (Reinhart and Grosh, 1998).

The first phase, which is normally short, is characterised by degradation of organic matter (Bhalla et al., 2013) by aerobic microorganisms that degrade the organic materials to carbon dioxide (CO_2), water (H_2O) and partially degraded residual organics, producing considerable heat (Reinhart and Grosh, 1998). The aerobic phase in a landfill lasts only a few days because oxygen (O_2) is not replenished once the waste is covered (Kjeldsen et al., 2002). Depletion of the available O_2 leads to a transition from aerobic to anaerobic degradation processes, represented by phase II with no remarkable reactions involved (Karthikeyan and Joseph, 2006).

What supersedes phase II is the third phase, in which the process of decomposition becomes anaerobic (Eliassen, 1942). This supports fermentation reactions (Kjeldsen et al., 2002). The phase is dominated by hydrolytic, fermentative and acetogenic bacteria (composed of strict and facultative anaerobes), yielding substantial amounts of soluble organic acids such as VFAs, amino acids, other low molecular weight compounds and gases like hydrogen (H_2) and CO_2 (Kjeldsen et al., 2002, Kulikowska and Klimiuk, 2008, Bhalla et al., 2013). Concomitant with episodes of organic acids from fermentation processes, a decrease in pH values is often observed and increased metal mobilisation resulting in a chemically aggressive leachate (Reinhart and Grosh, 1998, Kjeldsen et al., 2002).

In the Fourth phase, methane-forming consortia utilise intermediate acids as carbon sources, producing methane (CH_4) and CO_2 as by-products (Reinhart and Grosh, 1998). Later, when the fermentation products are converted effectively to CH_4 and CO_2, the pH increases and the degradability of the organic carbon in the leachate decreases (Bjerg et al., 2003), due to their conversion into CH_4 and CO_2 (Bhalla et al., 2013). The greater portion of the organic matter in the leachate becomes dominated by refractory compounds such as humic and fulvic-like fractions (Kulikowska and Klimiuk, 2008), whence the rate of CH_4 production is dependent on the rate of cellulose and hemicellulose hydrolysis (Kjeldsen et al., 2002). Also, SO_4^{2-} and nitrate (NO_3^-) are reduced to S^{2-} and NH_4^+, respectively. Sulphide causes considerable metal precipitation (Reinhart and Grosh, 1998). Most S^{2-} compounds have relatively low solubility, and they will, to a larger extent be immobilised within the landfill (Øygard et al., 2004). This occurs four to ten years after landfill closure (Reinhart and Grosh, 1998). The pH values become elevated, being controlled primarily by the HCO_3^- buffering system and also due to decrease in the concentration of ionisable organic acids, which are utilised as energy source (Reinhart and Grosh, 1998).

During the final stage of landfill stabilisation, nutrients and available substrate become limiting, and the biological activity shifts to relative dormancy (Reinhart and Grosh, 1998). Gas production dramatically drops and leachate strength remains steady at much lower concentrations (Reinhart and Grosh, 1998). The rate of O_2 diffusion into the landfill may exceed the rate of microbial O_2 depletion, thus over time, the anaerobic landfill is hypothesised to become an aerobic ecosystem (Kjeldsen et al., 2002). Under aerobic conditions, additional refuse oxidation will occur, as some of the lignocellulosic substrate is more degradable under aerobic conditions relative to anaerobic conditions (Kjeldsen et al., 2002). A decrease in pH is expected in part due to the CO_2 phase, and also in part due to the oxidation of metal S^{2-}, resulting in production of SO_4^{2-} ions, which further decrease the pH and increase the amount of free metal ions (Mårtensson et al., 1999, Kjeldsen et al., 2002).
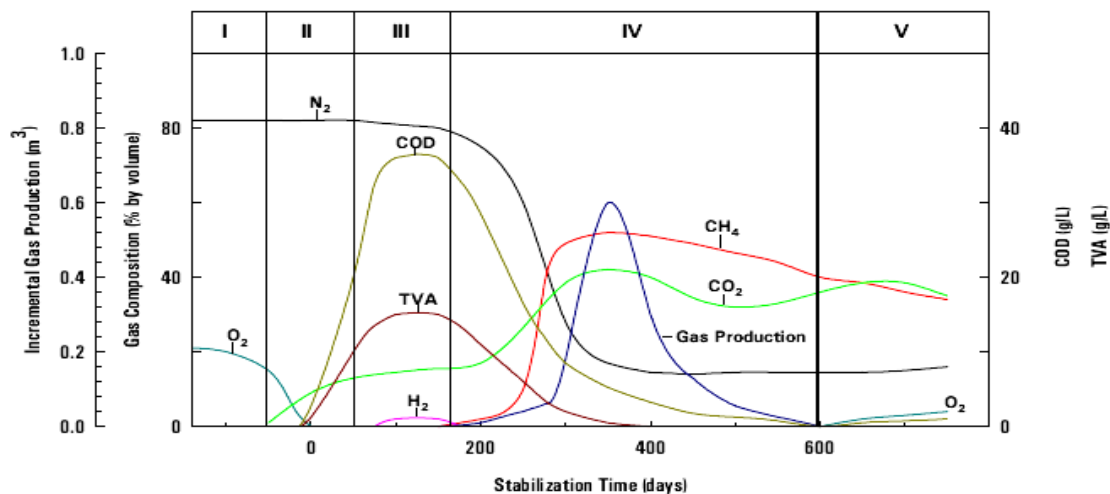

Figure 1-2: *Changes in concentrations of selected parameters during the phases of landfill stabilisation [Source; Karthikeyan and Joseph (2006)].*

1.2.6 Leachate plume redox zones

The redox zones are believed to constitute an important chemical framework for the attenuation processes in the plume (Bjerg et al., 1995). Chemical analyses for the levels of redox-sensitive species herein referring to CH_4, S^{2-}, Fe^{2+}, Mn^{2+}, NH_4^+, NO_3^- and O_2 in the groundwater samples are used to assign redox status of the aquifer (Lyngkilde and Christensen, 1992, Bjerg et al., 1995). A typical redox zone of a plume (Figure 1-3) follows the sequence from the outer edge: aerobic, denitrifying, manganese reducing, iron reducing, sulphate reducing and finally, under strictly anaerobic conditions, methanogenic conditions develop in the core closest to the landfill (Bjerg et al., 2011). A trend towards reducing conditions is established in accordance with shifting of electron acceptors from O_2 to NO_3^- and SO_4^{2-} (Reinhart and Grosh, 1998). The

criteria used to assign the redox status of an aquifer are provided elsewhere (Lyngkilde and Christensen, 1992). Diverse microbial communities including methanogens, sulphate reducers, iron reducers, manganese reducers and denitrifiers have been identified in leachate plumes, and are believed to be responsible for the redox processes (Ludvigsen et al., 1998, Christensen et al., 2001). Microbial analysis of groundwater is thus utmost importance if their influence to the cause and effect of redox processes is to be understood (Freeze and Cherry, 1979). These microorganisms, which are fundamental to the development and maintenance of redox zones in environmental systems, according to Fetter (1993), may occur as a biofilm on the surfaces of the aquifer materials. Variations in geology and geochemistry may affect the microbial redox processes and the redox conditions in the plume, due to changes in flow conditions and availability of substrates, nutrients or electron acceptors (Ludvigsen et al., 1998).

The fate of reactive contaminants in a plume-affected aquifer depends on the sustainability of biogeochemical processes affecting contaminant transport (Cozzarelli et al., 2011). Seasonal dynamics, such as temporal groundwater level fluctuations may have a great influence on the migration of the plume beneath the landfill, by controlling vertical hydraulic gradients and fluxes (Han et al., 2014). This can cause an unexpected spreading pattern despite of homogeneous aquifer conditions (Bjerg et al., 2003), leading to distortion of redox zones.
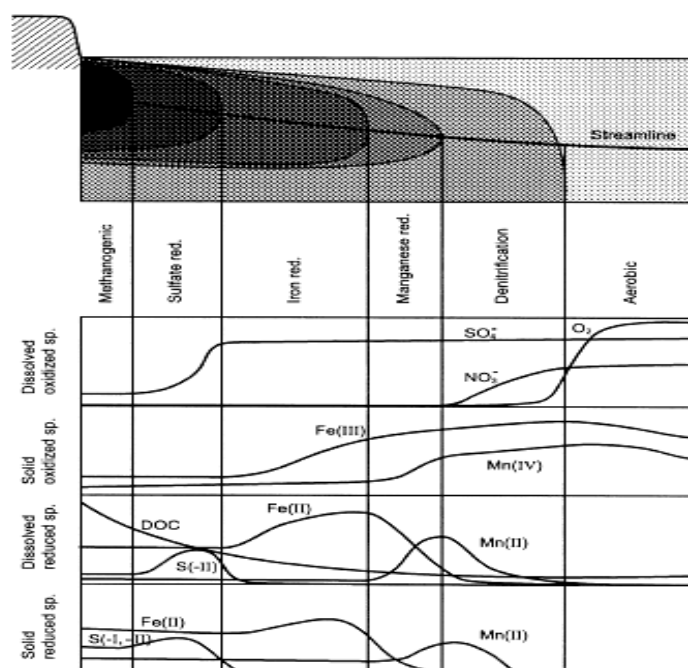

Figure 1-3: Schematic redox zonation in an originally aerobic aquifer downstream from a landfill, and the distribution of redox-sensitive species [Source; Christensen et al. (2001)].

1.2.7 Importance of leachate quality analysis

Knowledge of leachate composition and quantity is necessary in assessing the risk to groundwater resources, while the availability of electron acceptors such as iron oxides or dissolved SO_4^{2-} are important for evaluating the efficacy and sustainability of natural attenuation as a remedy for leachate plumes (Bjerg et al., 2003, Słomczyńska and Słomczyński, 2004, Slack et al., 2005). These would provide an understanding about the potentially harmful constituents in the leachate and the significance of attenuating factors, which according to Reinhard et al. (1984) are key in seeking to mitigate the problem. Natural attenuation here refers to natural processes that reduce the concentrations of dissolved contaminants in leachate plume. These processes include dilution, sorption, cation exchange, precipitation, redox reaction and degradation processes (Christensen et al., 2001, Statom et al., 2004). Attenuation processes in leachate plumes may, for many contaminants provide significant natural remediation, limiting the effects of the leachate on the groundwater to an area usually not exceeding 1000 m from the landfill (Christensen et al., 2001). To evaluate an aquifer's capacity for natural attenuation of groundwater contamination from landfill leachate, the chemical characteristics of the leachate need to be defined from initial generation to some point in the future (Statom et al., 2004). By so doing, factors such as variations in site geography, climate, waste composition, landfill volume and moisture content do not complicate the analysis of the influence of landfill age on leachate chemistry (Statom et al., 2004). Understanding the complex environments developing in leachate plumes is fundamental for developing cost-effective remediation strategies (Bjerg et al., 2003).

2 Material and Methods

2.1 Site description

2.1.1 Revdalen Landfill

Revdalen Landfill is one of the several historic landfill sites in Norway. Being historic here means that the landfill has neither leachate collection system nor liners. It is to be found about 3.5 km North of Bø town, located on a glaciofluvial outwash at coordinates 59º25'58.26"N (Latitude) and 9º06'1.53"E (Longitude). The maximum depth of the landfill is about 8 m, and covers a total area of 30,137.2 m^2. The landfill had four cells, denoted by the years of activity as 1974-1980, 1981-1986, 1987-1996, and 1974-1996 (Figure 2-1C). Cell marked "1974-1996" operated for the entire duration of waste emplacement (1974-1996) because it was specifically demarcated to hold wastewater treatment sludge. According to workers at the site, the landfill has received all kinds of wastes, ranging from household waste, industrial waste, chemical waste, sludge, ash, to building, demolition and construction waste. After the waste emplacement ceased, the landfill was covered with a layer of clay of about 40 – 50 cm thick. The clay layer was then overlaid with a mixture of sand (50%), sludge (30%) and bark (20%). Later on, Norway spruce *(Picea abies)* and black alder (*Alnus glutinosa*) were planted on the cover.

2.1.2 Revdalen Aquifer

The contaminated aquifer under investigation is situated just beneath the landfill, about 20 m below the ground surface. It has a length of 1.7 km, a thickness of 5 m and a width of 70 m. Based on calculations, Klempe (2015) found the volume of the aquifer to be 254,000 m^3. This aquifer is recharged mostly by runoff from a small watershed (Klempe, 2015) (Figure 2-2). It is a confined aquifer covered by a moraine complex of ridges and till plains. The aquifer matrix is characterised by an unconsolidated quaternary glaciofluvial deposit, comprising of medium to high permeability sand and gravel of thickness between 5 and 8 m. The groundwater flow velocity is 1.3 m per day and mean residence time of 2½ years. The storage coefficient is 10^{-4} (Klempe, 2015). Data from the piezometers indicated fluctuations in the water table. This seasonal variation makes the aquifer sometimes phreatic in its upper layer in R1 which is an artesian well. Groundwater level fluctuations in R4 cause changes in status from artesian well to flowing artesian well, especially in spring seasons. The direction of the groundwater flows

is mainly southwest wards, discharging at huge seepage faces at Gåra rivulet and Helland, both located at the fringe of the aquifer (Figure 2-2). In the immediate vicinity of the landfill are delta deposit and exposed bedrock (Figure 2-1D).
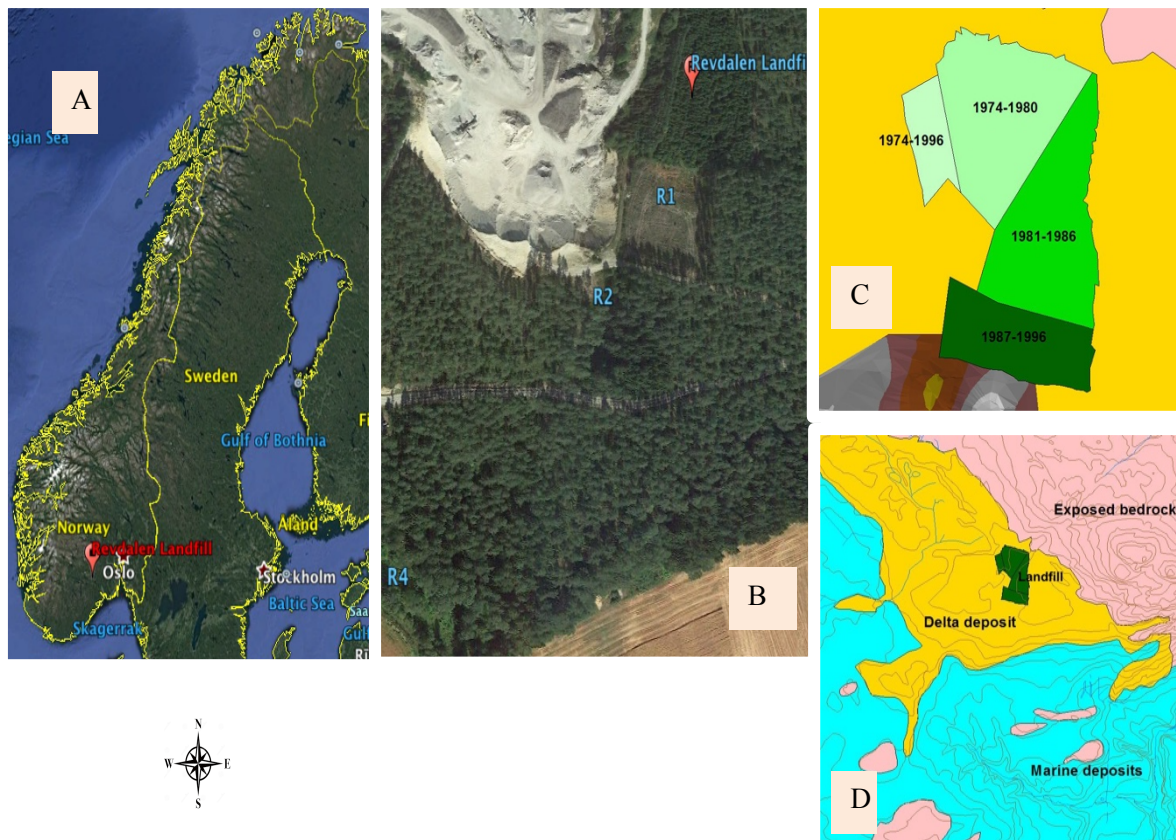

Figure 2-1: *Study area located in southeast Norway (A). An aerial photo of Revdalen Landfill with the monitoring wells (B), on the left of the landfill is the quarry and sand/gravel mining (B) [courtesy of Google Earth]. The landfill cells shown by years of waste emplacement (C), and the sedimentology around the landfill (D) [Source; Klempe and Kvålseth (2006)].*

2.2 Sampling wells

Monitoring wells R1 and R2, located downgradient of the landfill have each, been equipped with multilevel sampler (MLS), established using Waterloo Multilevel Groundwater Monitoring System. R1 was equipped with 5 MLS (R1-1, R1-2, R1-3, R1-4 and R1-5), while R2 was equipped with 4 MSL (R2-1, R2-2, R2-3 and R2-4). R4 consisted of 3 MLS (R4-1, R4-2 and R4-3), but are typically 3 separate wells drilled at different depths. In addition to these monitoring wells, well R0 was used to determine the background level for the parameters included in the monitoring programme. Details of the monitoring wells are presented in Figure 2-3 and Table 2-1. Due to the nature of aquifer formation at Revdalen, technical challenges have been encountered during drilling and consequently, establishment of dense monitoring network at the site has been impossible. It is for this reason that well numbered 3 (Figure 2-3)

was not fully developed to become functional. Christensen et al. (2001) linked the lack of reports from this kinds of geological formations to such technical complications and huge demands for economic resources in undertaking the study.
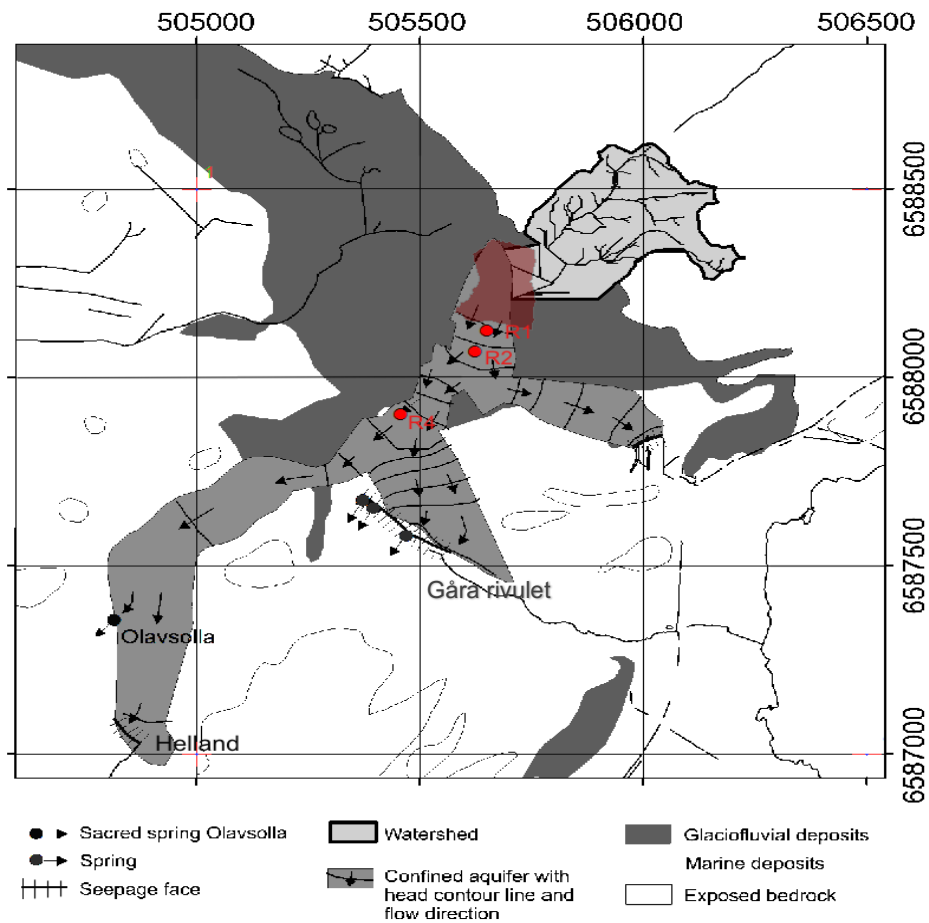

Figure 2-2: *Watershed recharging the aquifer from the landfill site and the flow pattern through the monitoring wells out to the seepage faces at Helland and Gåra rivulet. The brown mark is the landfill, while the red marks R1, R2 and R4 are the monitoring wells [Source; modified from Klempe (2015)].*
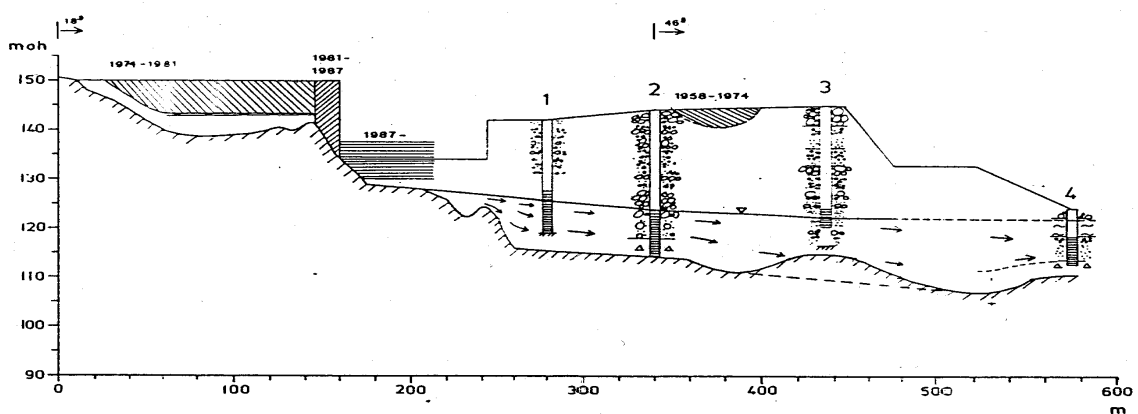

Figure 2-3: *A cross section of the landfill cells, aquifer and monitoring wells. Numbers 1, 2, 3 and 4 represent wells R1, R2, R3 and R4 respectively [Source; Klempe et al. (1992)].*

Table 2-1: *Sampling wells and depths of their corresponding multilevels. R4-2 is the deepest of all the levels. The sampling levels were recorded as metres above sea level (m.a.s.l).*

		Sampling level (m.a.s.l)				
WELL	Distance from the landfill (m)	X-1	X-2	X-3	X-4	X-5
R1	26.48	126.07	125.01	123.95	122.89	121.94
R2	87.83	121.94	120.84	118.94	117.84	-
R4	323.64	118.00	114.42	116.75	-	-

X takes the form of R1, R2 and R4 for each corresponding wells.

2.3 Sampling procedure and chemical analysis

Sampling at R1 and R2 were performed by N_2 pressure through Teflon (Polytetrafluoroethylene [PTFE]) tubes lowered into the well, while that at R4 was performed by suction pump. In order to obtain representative samples, water volume equivalent to twice the fill capacity of the pipes was emptied. Electrical conductivity and temperature were determined *in-situ*, using WTW LF320 conductivity meter. In addition, pH was also measured in the field, using WTW pH 330i. Dissolved Oxygen (DO) was determined by Winkler method using Mettler DL25 Titrator. The samples were immediately preserved with 15.32M concentrated nitric acid and transported to USN laboratories. They were then sent to ALcontrol Laboratories in Skien for analyses of K^+, Na^+, NH_4^+-N, Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}, Cd^{2+}, Cr^{3+}, Cu^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, Hg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, NO_3^--N, NO_2^-, Tot-N, Tot-P, TOC, PCB_7 and PAH_{16}.

Groundwater samples were taken twice a year. One immediately after snow melt in spring, hereafter referred to as "wet season". The second sampling was performed in autumn, when the groundwater level drops following a period of at least one month without precipitation, hereafter referred to as "dry season". The groundwater level follow-up was achieved by monitoring the groundwater level from a nearby well established by Norwegian Groundwater Network for monitoring the groundwater quality in the area.

2.4 Data analysis and statistics

The monitoring programme generated a huge set of data that have been stored in Access database. The database was retrieved and then analysed using statistical software packages in Excel worksheet and Minitab. Excel worksheet was used for basic statistical analyses such as mean, minimum and maximum values, counts, graphs, and regressions. Minitab was used to

construct longitudinal cross sections for redox sensitive species. Person's correlations (r) with *P*-value for some selected parameters were also calculated using Minitab. Akima's polynomial interpolation method was used to the construct longitudinal cross sectional graphics, that aided in visualisation of the distribution of redox indicator species in the aquifer. The mesh size for interpolating surface was automatically generated by the computer.

For the purposes of future reclamation of the groundwater resource, the values of the parameters were compared to that of Norwegian drinking water standards. Measurement from R0 was used as the reference level.

3 Results

3.1 Background concentration

The unpolluted aquifer was aerobic, with a moderately acidic pH (5.0). The electrical conductivity was low. Concentrations of Zn^{2+}, Pb^{2+}, Cu^{2+}, SO_4^{2-} and TOC were however, slightly high, albeit below the Norwegian drinking water standards. All the concentrations of other parameters showed low levels (Table 3-1).

3.2 Physical parameters

From the quantitative information presented in Table 3-1, the pH of the polluted groundwater ranged from weakly acidic (6.3) to weakly alkaline (7.8). The electrical conductivity was very high compared to the background level. Low level of DO was measured in the aquifer. Detailed description of O_2 variation to be found under redox species and seasonal variation. Groundwater temperature was found to vary with seasons, where measurements done in wet season showed lower values than those in dry season (data not shown).

3.3 Inorganic macrocomponents and heavy metals

The major pollutant in this study has been HCO_3^- (Table 3-1). Concentrations of Mn^{2+}, SO_4^{2-}, NH_4^+-N, NO_3^--N, Tot-N and TOC were lower than those of K^+, Na^+, Ca^{2+}, Mg^{2+}, Fe^{2+} and Cl^-. Nevertheless, they constituted a moderate pollution problem, although their concentrations were above the background level. Nitrite and Tot-P were present at very low concentrations.

The heavy metals quantified in this study included Cd^{2+}, Cr^{3+}, Cu^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+} and Hg^{2+}. Episodes of high Zn^{2+}, Pb^{2+} and on rare occasions Cu^{2+} were identified. Concentrations of heavy metals such as Cd^{2+}, Cr^{3+} and Hg^{2+} in the groundwater samples were at times BDL. In some instances, the levels of Cd^{2+}, Cr^{3+} and Hg^{2+} surpassed the background concentrations, but remained below the Norwegian drinking water standards. Ni^{2+} have never been detected in the groundwater samples.

Table 3-1: *Descriptive statistics for the groundwater chemistry of the leachate-affected aquifer, compared with the background value and the Norwegian drinking water standards. (All units are in mg/L, unless indicated)*

Parameter	N	Mean value	StDev	Min	Max	Background value	Norwegian drinking water standards
Temp/℃	72	7.5	1.9	3.7	10.8	5.2	
pH	176	6.9	0.6	5.2	8.4	5.0	6.5 – 9.5
E.C (µS/cm)	175	431	264	33	1331	25	2500
Oxygen	116	1.31	1.24	0.00	8.70	2.17	
Potassium$^\sigma$	119	29.9	17.6	3.7	106.0	0.2	
Sodium	185	20.6	18.6	2.9	109.3	1.6	200
Calcium$^\sigma$	119	33.7	16.3	12.7	81.7	1.3	
Magnesium$^\sigma$	118	8.6	5.4	0.0	32.7	0.3	
Ammonium-N	189	8.0	8.1	0.0	35.0	0.3	0.5
Iron	192	16.3	19.8	0.0	90.8	0.1	0.2
Manganese$^\sigma$	119	4.60	3.66	0.68	35.00	0.03	0.05
Chloride	193	32.1	25.4	2.1	122.7	2.3	250
Bicarbonate$^\sigma$	114	203.0	122.4	41.9	569.3	2.5	
Sulphate	174	8.3	10.2	0.2	117.8	4.9	250
Nitrite	5	0.01	0.01	0.00	0.01	0.00	0.5
Nitrate-N	190	1.39	1.88	0.00	15.75	0.05	50
Tot-N$^\sigma$	118	13.5	10.2	2.6	62.5	0.3	
Tot-P	11	0.02	0.01	0.00	0.04	0.01	
TOC	189	9.2	6.0	0.0	38.2	7.9	
Zinc (µg/L)	94	267.9	757.0	0.0	4371.0	15.1	
Lead (µg/L)	192	8.6	62.7	0.0	852.0	2.8	10
Copper (µg/L)	73	16.4	41.8	0.0	258.0	3.0	2000
Cadmium (µg/L)	77	0.2	1.2	0.0	9.5	0.2	5
Chromium (µg/L)	65	1.0	4.8	0.0	37.0	0.1	50
Mercury (ng/L)	37	2.8	12.1	0.0	72.5	0.0	1000
Nickel (µg/L)							20
∑PAH16 (µg/L)	0,391						
∑PCB7 (ng/L)	<7.0						

$^\sigma$Parameters analysed from 1992 to 2003. As such, the descriptive statistics of these parameters are relatively higher than it would be if they were analysed for the entire monitoring period of 23 years.

N = ∑ (n*3); n = number of sampling performed per year; 3 = represents the 3 monitoring wells.

NB: *For the purpose of data management and statistical analysis, values below detection limit for both heavy metals and XOC (PCB$_7$ and PAH$_{16}$) were treated as zero.*

3.4 Xenobiotic Organic Carbon

PCB_7 and PAH_{16} were the only XOCs that have been included in the monitoring programme. All the PCB congeners included in the study were BDL, while 13 of the PAH_{16} congeners were detected, even though at lower concentrations (Figure 3-1). Pyrene had the highest concentration, while Naphthalene and Dibenzo[a,h]anthracene were not detected.
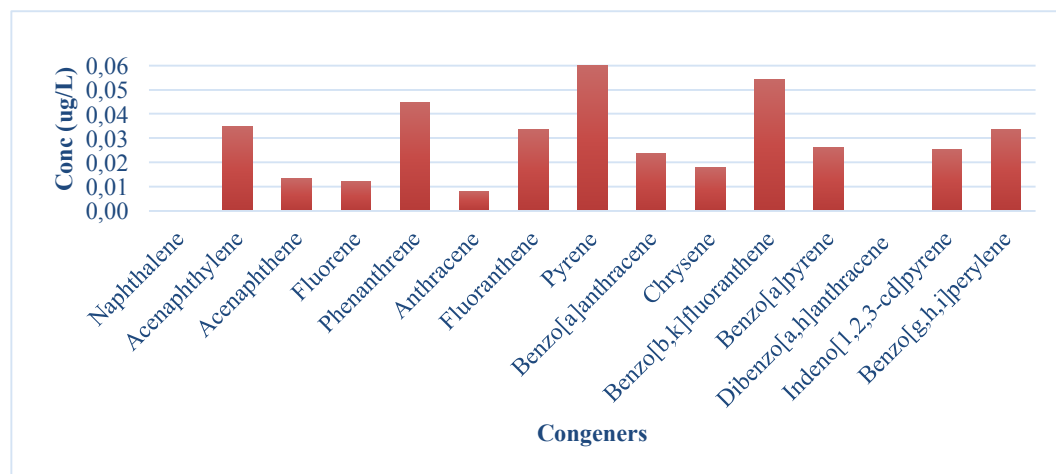

Figure 3-1: *13 of the 16 PAHs that have been detected in the leachate-affected groundwater.*

3.5 Effect of landfill age on the groundwater quality

Annual presentation of the groundwater quality data has shown a decrease in concentrations of pollutants with age of the landfill (Figure 3-2). Closing the landfill was followed by a remarkable decrease in the concentrations of most parameters. An exception to the observed trend of decrease in concentration with age of the landfill were O_2, NO_3^--N and SO_4^{2-} concentrations, which on the contrary increased with time. Concentration of NO_3^- increased and fluctuated at a slightly higher value above the background level, although typically low levels of NO_3^--N have been quantified in this study, the highest being 15.75 mgN/L. Unlike NO_3^--N, SO_4^{2-} concentration was first above the background level, but showed decrease after landfill closure, and fluctuated somewhat around the natural level before showing an increase above the background concentration from 2008. Oxygen followed such similar trend as SO_4^{2-}. The pH varied within a narrow range (Figure 3-2). In general, concentrations of most pollutants decreased near the background level as the age of the landfill approached 21 years.
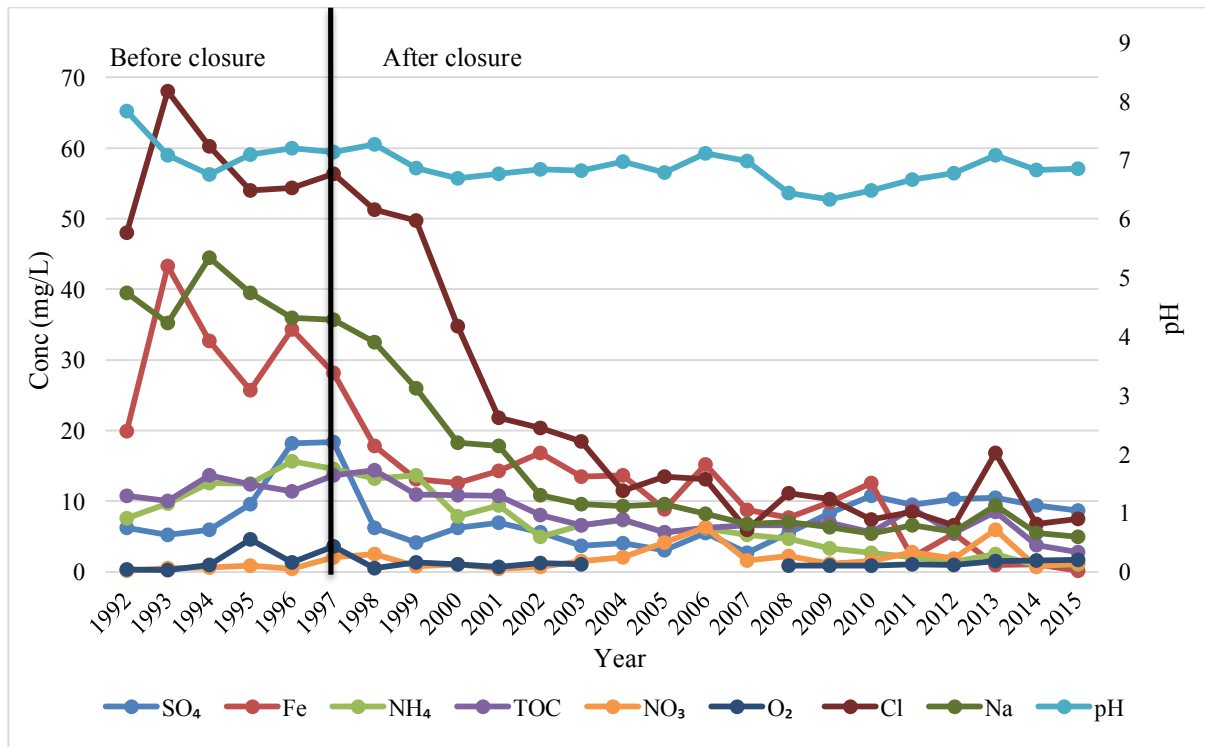
Figure 3-2: *Overall annual mean values, showing variation in the concentrations of some selected contaminants with years of monitoring. Before closure referred to the years of monitoring when the landfill was active, while after closure was used to refer to years of monitoring after the landfill was closed. The black line denotes the year of landfill closure.*

3.6 Season dynamics on the groundwater quality

Generally, concentrations of the monitored parameters were higher in dry season than in wet season, e.g. for SO_4^{2-} (Figure 3-3). Oxygen was an exception to this, it showed higher values in wet season than in dry season as depicted in Figure 3-3.
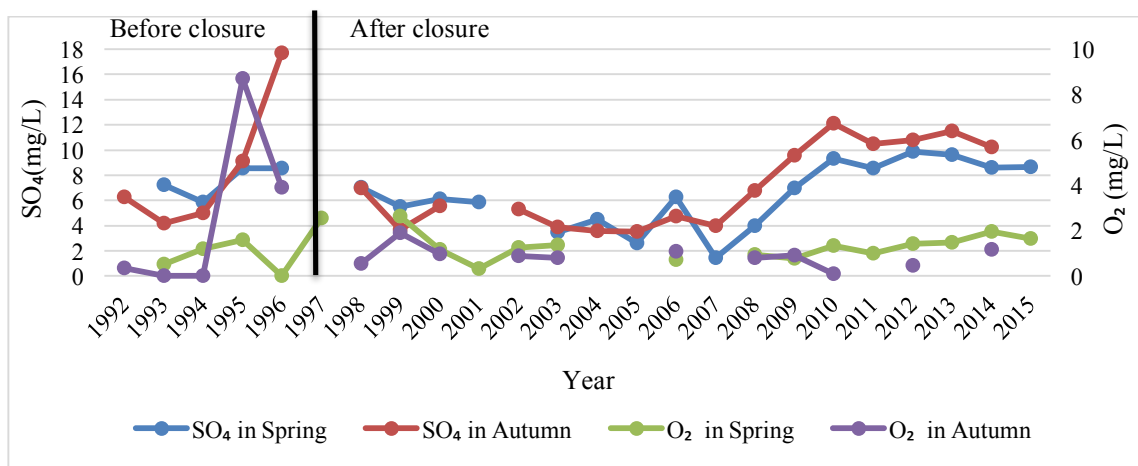
Figure 3-3: *Annual mean values of SO_4^{2-} and O_2 concentrations in wet and dry periods. See figure 3-2 for explanations on before closure, after closure and the black line.*

Seasonal variation in the concentrations of NO_3^--N and NH_4^+-N followed an irregular pattern, characterised by overlaps in concentrations of the pollutants in the two seasons, although, there has been biasness for values to be higher in dry season than in wet season (Figure 3-4). Concentrations of either pollutants varied antagonistically to each other.
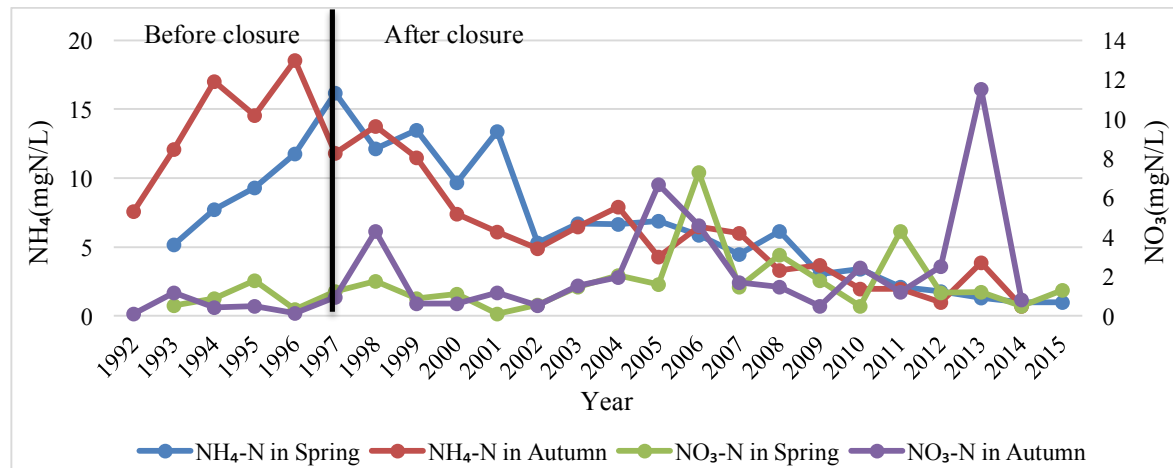

Figure 3-4: *Annual mean values of NH_4^+-N and NO_3^--N concentrations in wet and dry seasons. See figure 3-2 for explanations on before closure, after closure and the black line.*

Iron and TOC have also shown higher concentrations in dry season than in wet season. However, there were occasions when the values in wet season overlapped with that of dry season (Figure 3-5).
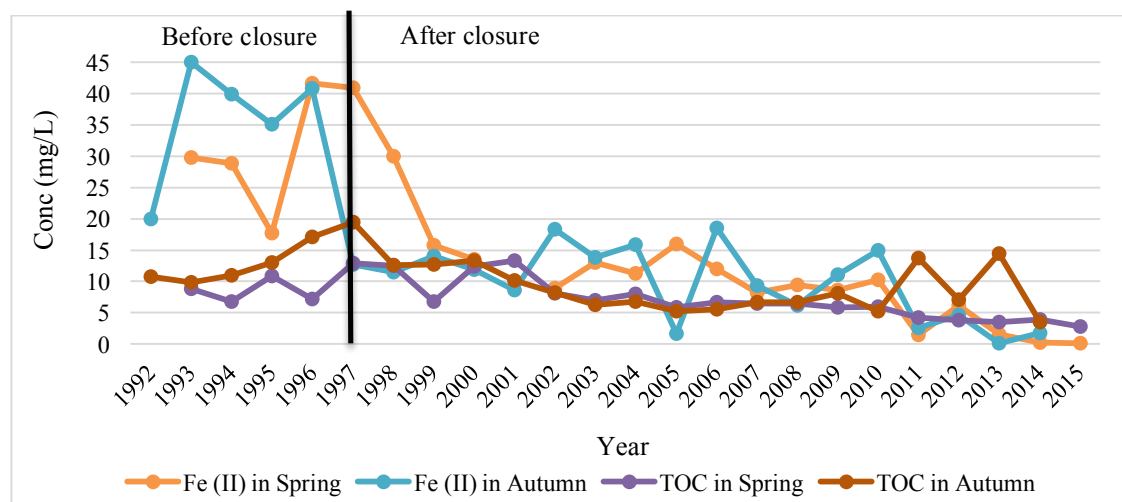

Figure 3-5: *Annual mean values of Fe^{2+} and TOC concentrations in wet and dry seasons. See figure 3-2 for explanations on before closure, after closure and the black line.*

3.7 Distribution of redox sensitive species

The distribution of O_2 across the aquifer was in the order R1 < R2 < R4. Complete absence of O_2 was sometimes observed at R1. From 2011, there was an overall increase in the O_2 concentration right from R1 to R4, but the value in R2 dropped lower than that in R1 and R4 from 2013 (Figure 3-6).
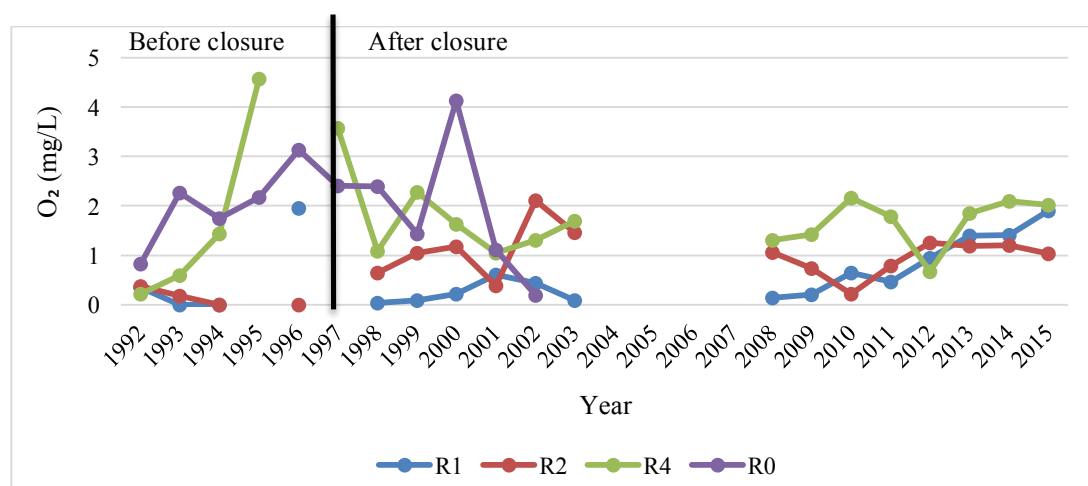

Figure 3-6: *Annual mean values of O_2 concentrations in R1, R2 and R4, compared with the background level from R0. See figure 3-2 for explanations on before closure, after closure and the black line.*

Multilevel sampling illustrated by the longitudinal cross section (Figure 3-7) for the month of June 1999 showed increase in O_2 concentration with increasing distance from the landfill, in accordance with the annual mean value for each well (Figure 3-6).
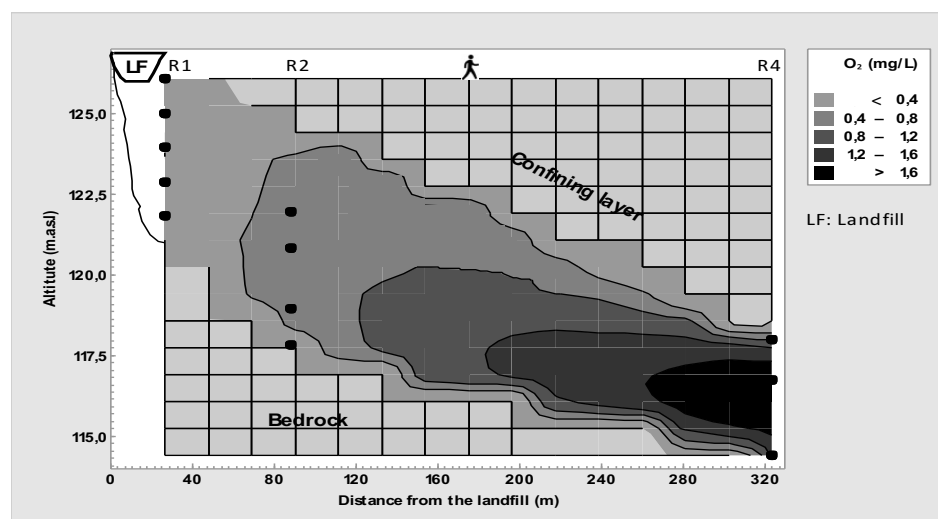

Figure 3-7: *Contours of O_2 concentrations from MLS in the leachate-polluted Revdalen Aquifer downgradient of the landfill in June 1999. The vertical black dots denote the sampling points in R1, R2 and R4.*

The distribution of SO_4^{2-} as a function of distance from the landfill had less distinctiveness compared to those of Fe^{2+}, Mn^{2+} and NO_3^--N. Between 2002-2007, SO_4^{2-} concentration in R1 dropped below the background level, while R2 and R4 had values close to the background level. Although lately, there has been an overall increase in SO_4^{2-} concentration above the background level in all the wells (Figure 3-8).
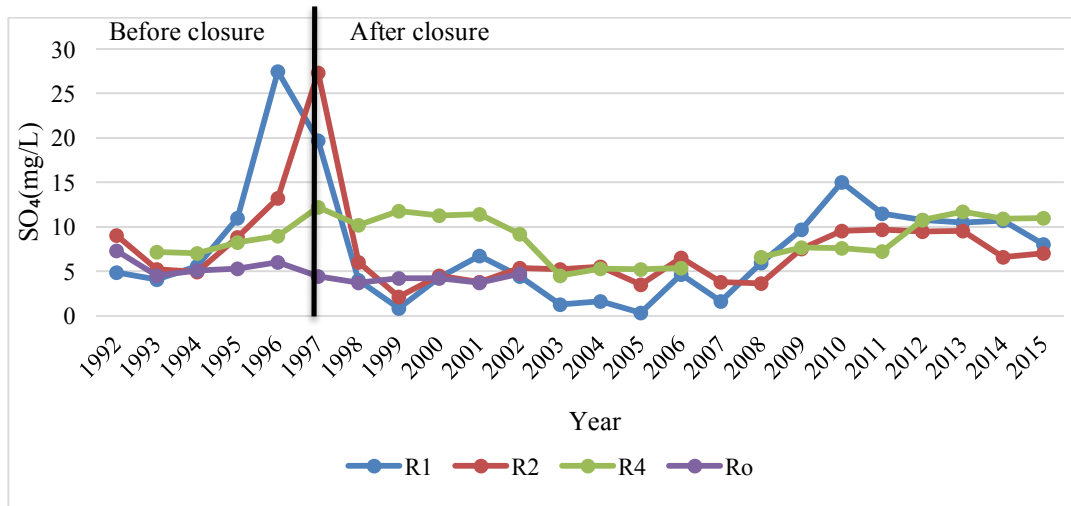

Figure 3-8: *Annual mean values of SO_4^{2-} concentrations in R1, R2 and R4, compared with the natural level in R0. See figure 3-2 for explanations on before closure, after closure and the black line.*

Distribution of SO_4^{2-} from the MLS in the aquifer took the form of an increase with distance from the landfill, a pattern that resembles that of O_2 as illustrated by data for June 1999 (Figure 3-9). Highest concentration was measured in R4.
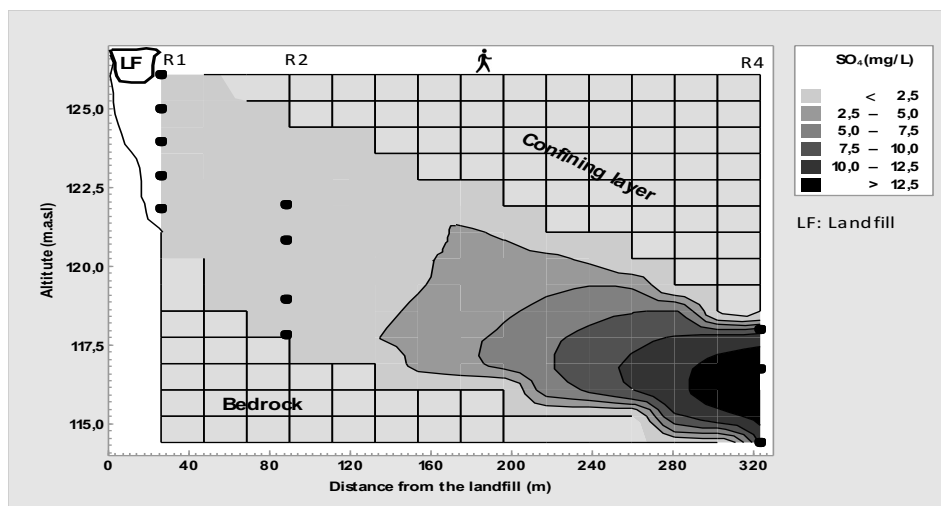

Figure 3-9: *Contours of SO_4^{2-} concentrations from the MLS in the leachate-polluted Revdalen Aquifer downgradient of the landfill in June 1999. The vertical black dots denote the sampling points in R1, R2 and R4.*

Nitrate-N distribution along the aquifer was in the order R1 < R2 < R4 prior to the landfill closure. After the landfill closure, the pattern R1 < R4 < R2 was rather predominantly evidenced (Figure 3-10). In most of the cases, there was a complete absence and/or nearly zero value of NO_3^--N at R1, but data from 2010 has shown that, the entire aquifer contained a plume of NO_3^--N as shown by the data from R1, R2 and R4 in Figure 3-10.
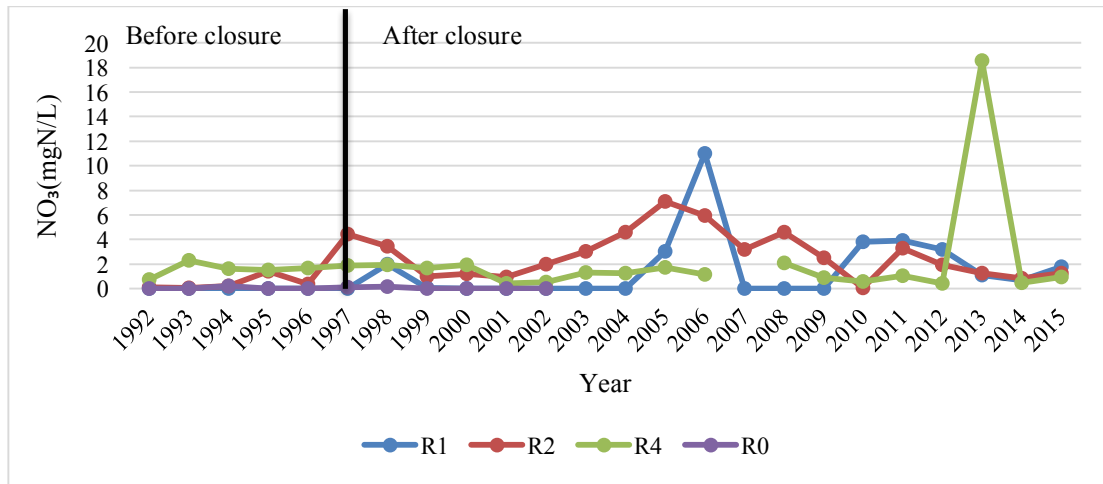

Figure 3-10: *Annual mean values of NO_3^--N concentrations in R1, R2 and R4, compared with the natural background level from R0. See figure 3-2 for explanations on before closure, after closure and the black line.*

Data from the MLS for the month of June 1999 has shown the trend R1 < R2 < R4, a trend similar to those of O_2 and SO_4^{2-}. Higher NO_3^--N concentrations have been found at R4-1 and R4-2 (Figure 3-11).
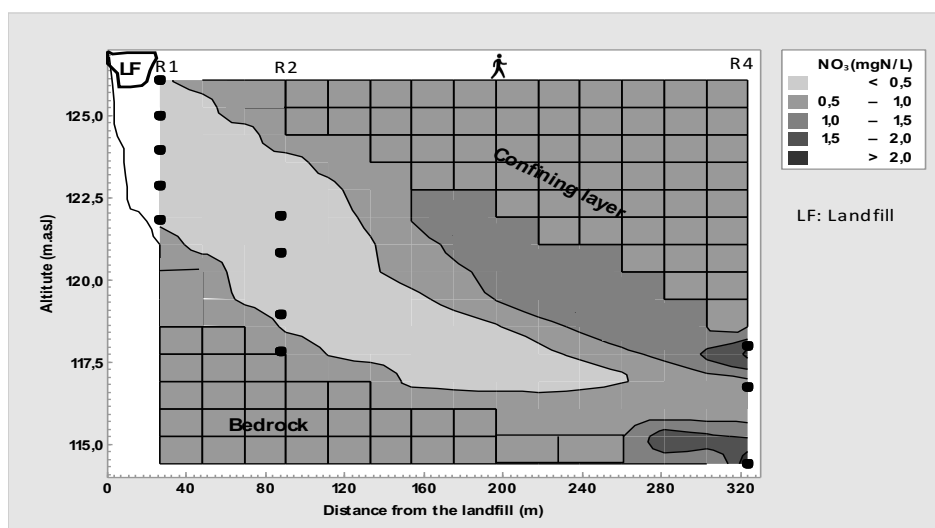

Figure 3-11: *Contours of NO_3^--N concentrations from MLS in the leachate-polluted Revdalen Aquifer downgradient of the landfill in June 1999. The vertical black dots denote the sampling points in R1, R2 and R4.*

The variation in the concentration of NH_4^+-N with distance from the landfill was very distinct, next to that of Fe^{2+}. The variation in NH_4^+-N observed in the wells was in the order R1 > R2 > R4. From 2002, the pattern changed to R1 > R4 > R2, which in turn shifted to R4 > R2 > R1 in 2010. By this time, the values in R1 and R2 were near background level, and that in R4 dropped to less than 5 mgN/L (Figure 3-12).

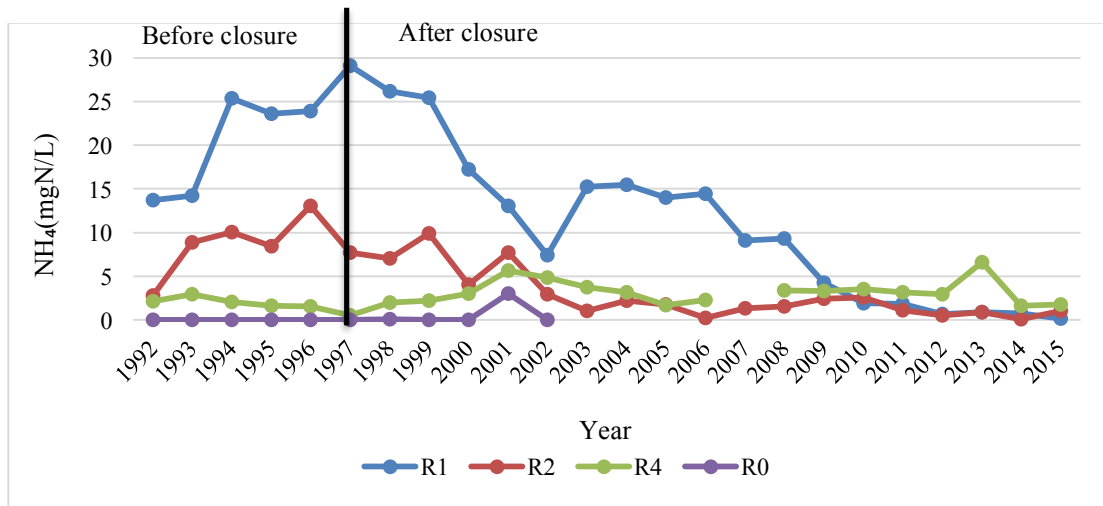**Figure 3-12:** *Annual mean values of NH_4^+-N concentrations in R1, R2 and R4, compared with the background concentration at R0. See figure 3-2 for explanations on before closure, after closure and the black line.*

Results from the MLS for the month of June 1999 (Figure 3-13) agreed to the pattern of R1 > R2 > R4 for NH_4^+-N distribution. The result further showed that, NH_4^+-N entered the groundwater from R1-4 and R1-5.
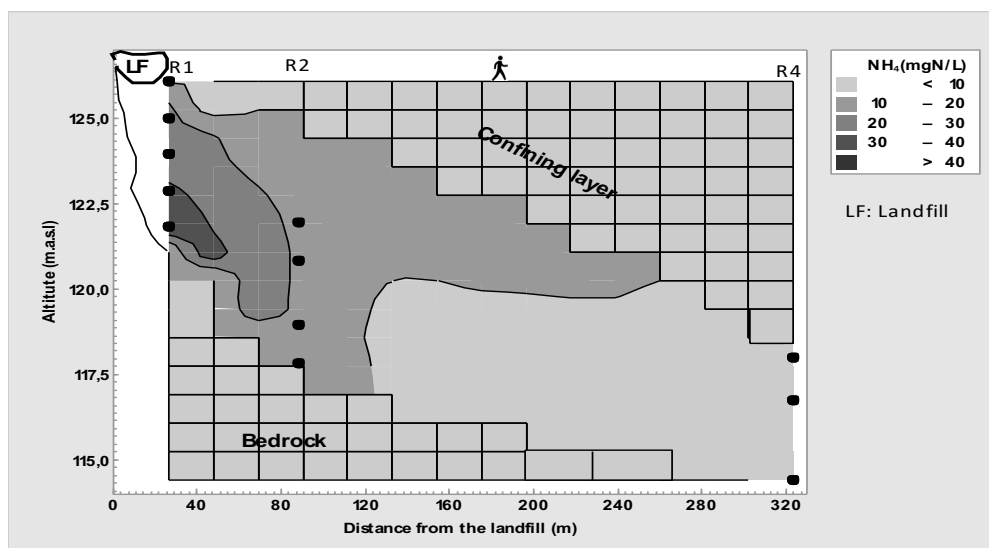

Figure 3-13: *Contours of NH_4^+-N concentrations from the MLS in the leachate-polluted Revdalen Aquifer downgradient of the landfill in June 1999. The vertical black dots denote the sampling points in R1, R2 and R4.*

The effect of distance on the Fe^{2+} content in the leachate-affected aquifer was very substantial (Figure 3-14). The order of occurrence in Fe^{2+} in the wells was in the order R1 > R2 > R4. From 2009, R2 had the highest level of Fe^{2+}, while that in R1 dropped significantly from 2010, to a value very close to natural background level. Measurement in R4 remained near background level throughout the study period. During the period 2013-2015, values in all the sampling wells dropped very close to the natural background level.
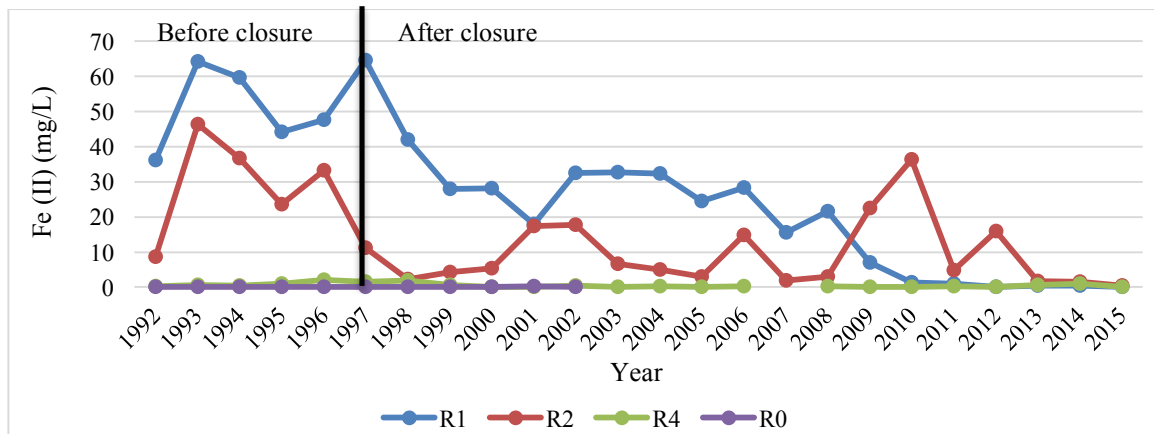

Figure 3-14: *Annual mean values of Fe^{2+} concentration in R1, R2 and R4, compared with the natural concentration from R0. See figure 3-2 for explanations on before closure, after closure and the black line.*

Analysis from the MLS in June 1999 (Figure 3-15) showed decrease in the order of R1 > R2 > R4, consistent with Fe^{2+} distribution before 2009 (Figure 3-14). The data further indicated that, a plume of Fe^{2+} intruded into the aquifer from the deepest level (R1-5).
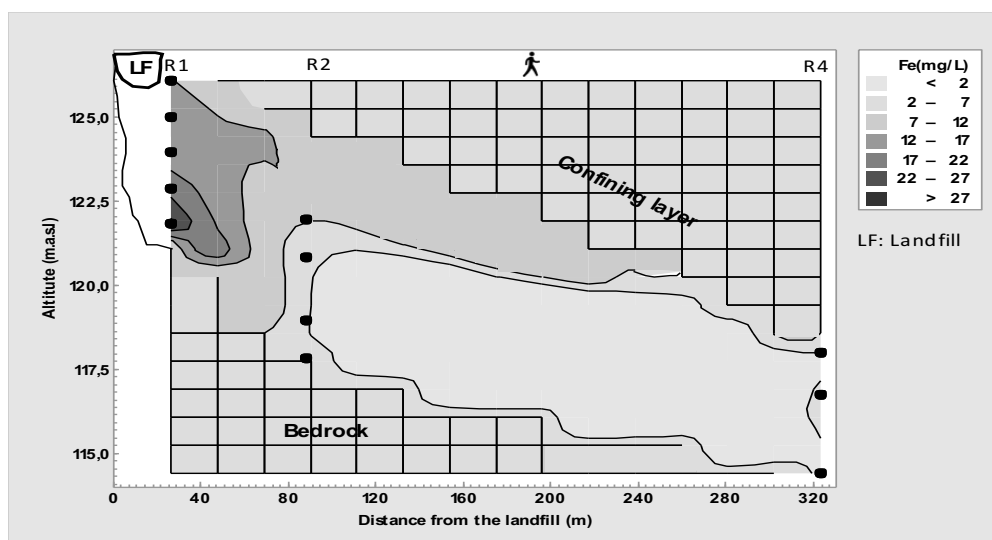

Figure 3-15: *Contours of Fe^{2+} concentrations from the MLS in the leachate-polluted Revdalen Aquifer downgradient of the landfill in June 1999. The vertical black dots denote the sampling levels in R1, R2 and R4.*

Results have indicated high Mn^{2+} concentrations in R1. Values in R2 and R4 overlapped each other, but there was a tendency of Mn^{2+} concentration being higher in R4 than in R2 (Figure 3-16). The values were well above the natural background concentration and the Norwegian drinking water standards. Generally, Mn^{2+} concentration in this study remained low.
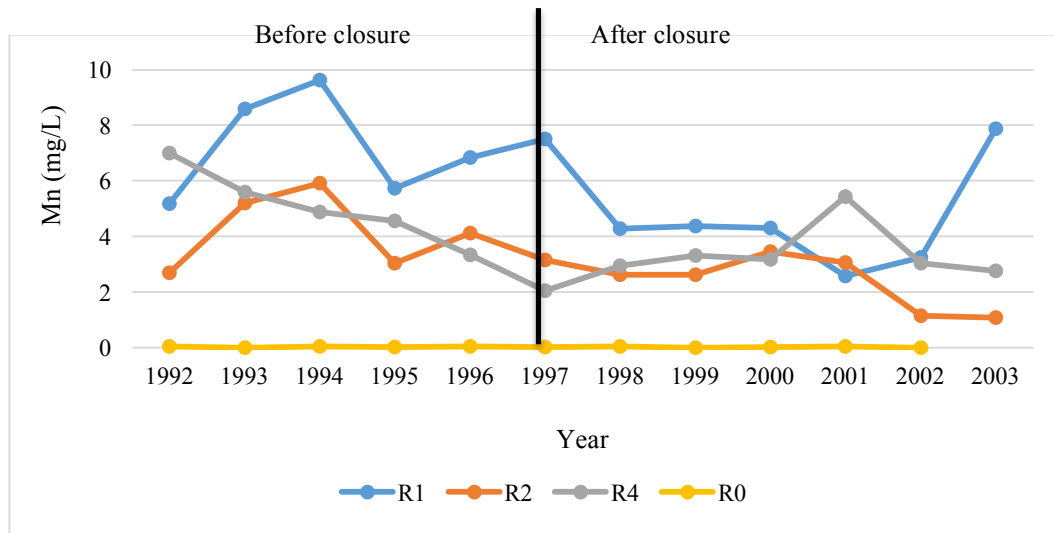

Figure 3-16: *Annual mean values of Mn^{2+} concentration in R1, R2 and R4, compared with the background concentration from R0. See figure 3-2 for explanations on before closure, after closure and the black line.*

Contours of Mn^{2+} for the month of June 1999 has shown a pattern of R1 < R2 < R4, with the highest measurement obtained at R4-3 (Figure 3-17).
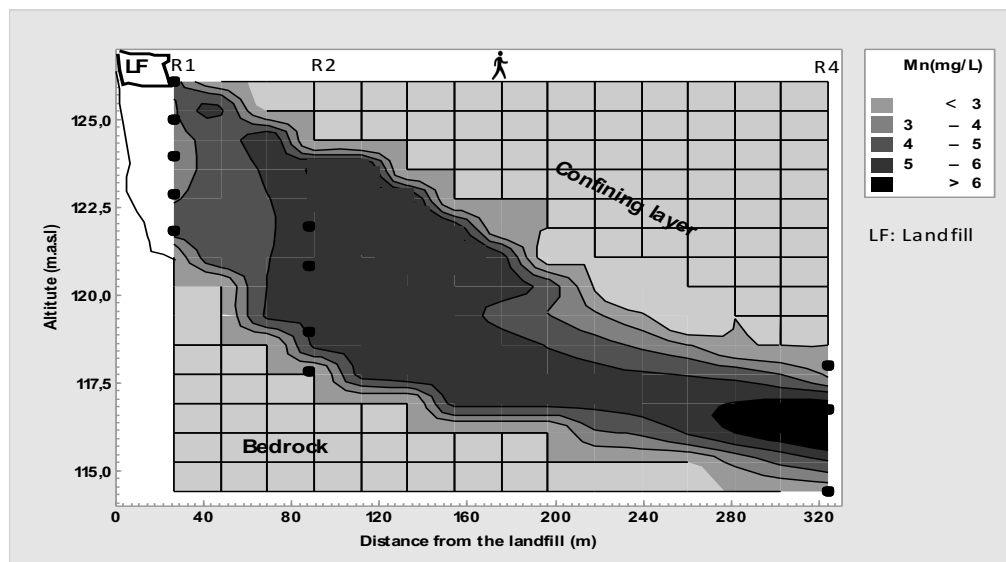

Figure 3-17: *Contours of Mn^{2+} concentrations from the MLS in the leachate-polluted Revdalen Aquifer downgradient of the landfill in June 1999. The vertical black dots denote the sampling levels in R1, R2 and R4.*

The fluctuation in pH between R1 and R2 occurred so, within a narrow range, with pH value at R2 being only slightly above that in R1. Measurement in R4, however, showed a weakly acidic pH, which varied by about a unit above the background pH value of ~ 5 (Figure 3-18).
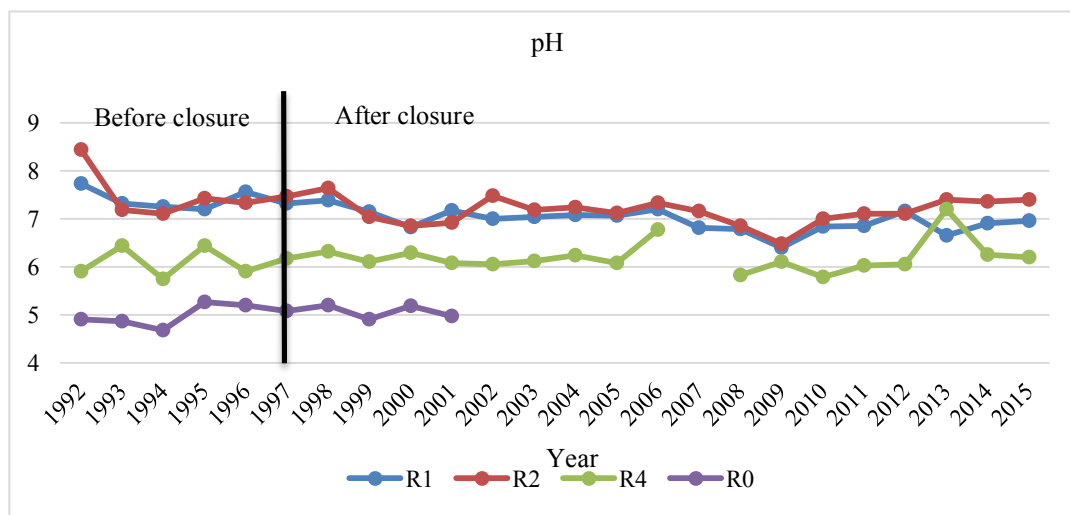
Figure 3-18: *Annual mean values of pH in R1, R2 and R4, compared with the background pH value from R0. See figure 3-2 for explanations on before closure, after closure and the black line.*

The observed variation in pH was compared to that of the HCO_3^-, as illustrated by the multilevel sampling data for June 1999 (Figure 3-19), where a decrease in level of HCO_3^- with distance from the landfill was identified.

Figure 3-19: *Contours of HCO_3 concentrations from the MLS in the leachate-polluted Revdalen Aquifer downgradient of the landfill in June 1999. The black dots denote sampling points in R1, R2 and R4.*

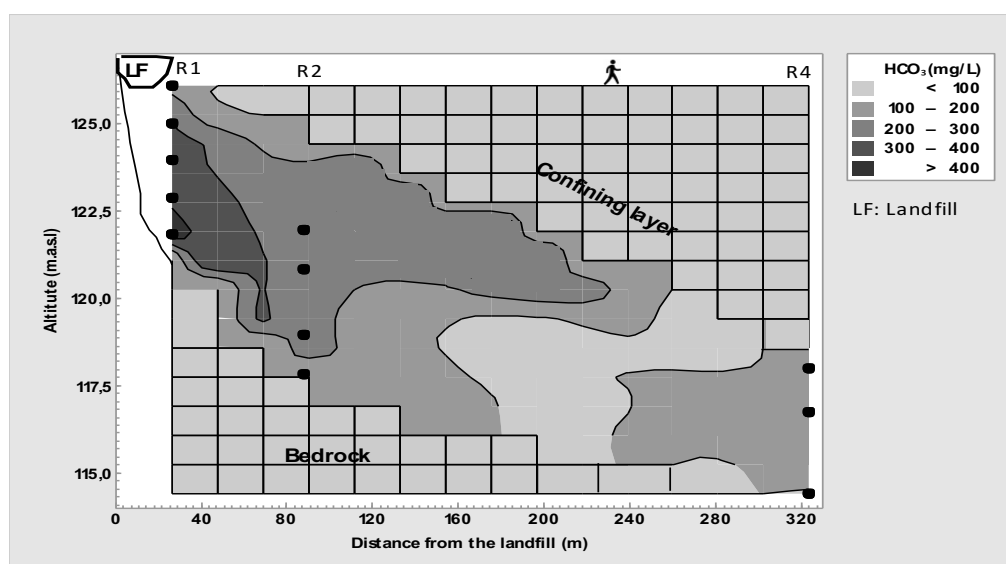Weak positive correlations have been found between; O_2 and SO_4^{2-}, and O_2 and NO_3^-. On the other hand, NH_4^+ and Fe^{2+} showed negative correlations with O_2 (Figure 3-20). More regressions and detailed Pearson's correlation (r) with *P*-value for the groundwater chemistry are provided in Annex A and B.
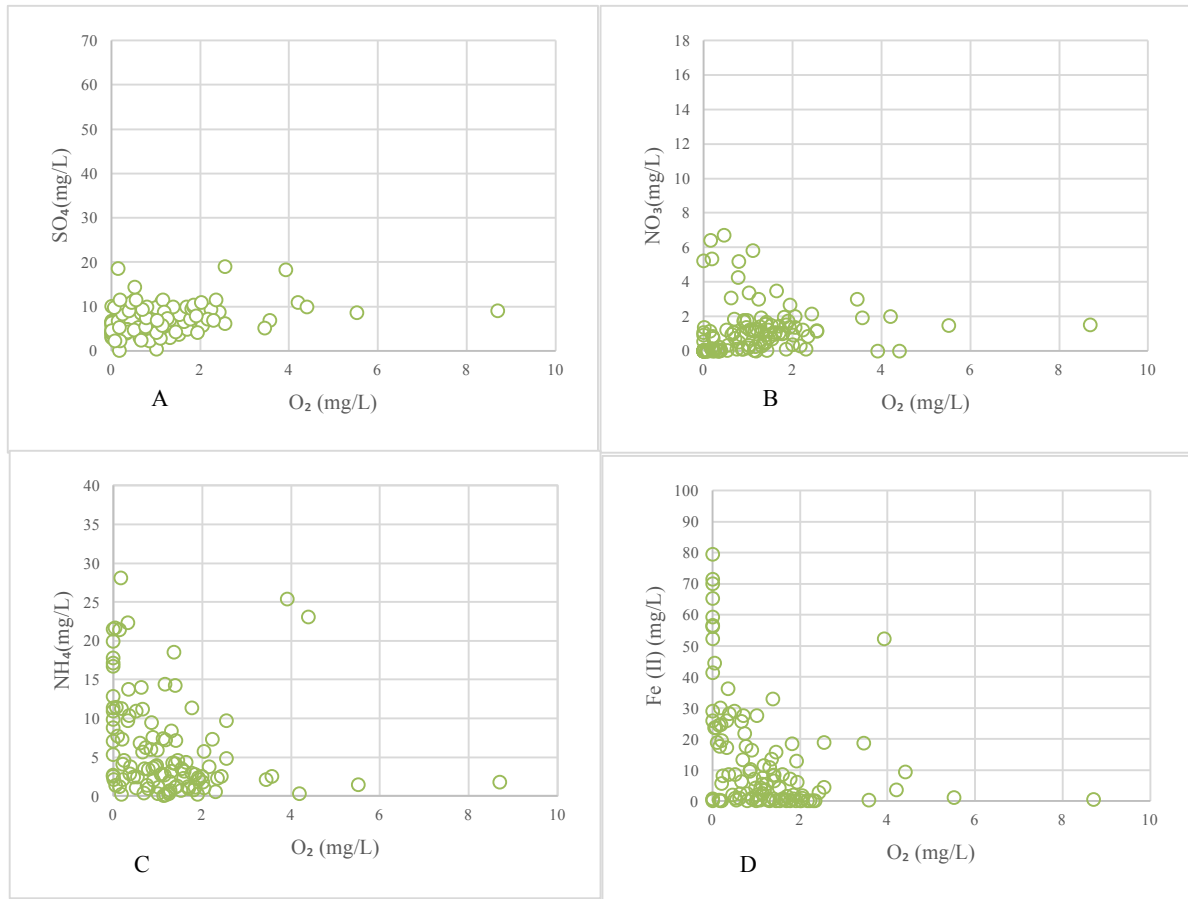

Figure 3-20: *Scatterplots showing correlations between SO_4^{2-}, NO_3^-, NH_4^+ and Fe^{2+} with O_2; represented by graphs A, B, C, and D respectively. The calculations were based on the sample mean values for each of the monitoring wells for every sampling during the 23 years of observations.*

4 Discussion

4.1 Leachate plume length

Due to variation in leachate composition, Lema et al. (1988) suggested that discussion of results should be carried out in terms of concentration ranges rather than mean values, which by themselves are not very meaningful. Each contaminant included in this study was treated separately in order to have a detailed understanding of processes it entangles into as it gets transported along the aquifer. Contaminants were observed to migrate up to a distance of over 324 m from the landfill. The total distance covered by pollutants is related to the aquifer material. Zanoni (1972) explained that unconsolidated materials of coarse sand and gravel, with high permeability would give less time for substantial degradation. This results in partially treated or poorly diluted leachate that migrate over long distances from the source. Despite of the aquifer matrix of Revdalen being sand and gravel, the length of the plume was shorter compared to many others reported by Christensen et al. (2001). Within a distance of 324 m from the landfill, the concentrations of pollutants decreased near background level. A rivulet located about 1000 m from the landfill have concentrations equal to that in R0. The low level of contaminants might have been due to the treatment provided by the aquifer, although changes in flow patterns beyond 324 m away from the landfill may be a possible explanation.

4.2 Transition from reducing to oxidising conditions

In general, the concentration of many leachate compounds decreased with time, a trend that has been observed in many related studies (Lema et al., 1988, Reinhart and Grosh, 1998, Kjeldsen and Christophersen, 2001, Bhalla et al., 2013). An exception to this trend was observed for SO_4^{2-}, NO_3^--N and O_2, whose concentrations increased with time. The decrease in concentration of inorganic ions is due to wash out and precipitation of soluble elements, such as heavy metals, while that in organics is mainly due to biological degradation of organic compounds (Reinhart and Grosh, 1998, Bhalla et al., 2013). In addition to time being a fundamental factor influencing the leachate-polluted groundwater quality, closing the landfill also greatly changed the groundwater quality. Prior to the landfill closure, concentrations of all parameters were higher than after the closure. This could be explained by the fact that infiltration into the aquifer through the landfill led to wash out of degradation products as well as soluble salts into the groundwater. Closing the landfill, on the other hand, limited infiltration

into the wastes and in turn into the aquifer, providing ample time for substantial degradation, mineralisation and other stabilisation processes. These processes produced small, but concentrated leachate that was then subjected to retardation by the aquifer. Statom et al. (2004) found a positive correlation between Cl^- levels and rainfall before closure, and evidenced an inverse relationship after closure. They attributed this to dissolution of soluble Cl^- salts by rain when the landfill was active and dilution effect after closure, due to less soluble Cl^-. Capping the landfill provided an ideal condition for establishment of reduced condition in the immediate vicinity of the landfill. For example, the decrease in SO_4^{2-}, NO_3^--N and O_2 concentration soon after the landfill closure could be due to reduction, a condition enhanced by capping. Maintenance of reduced condition is exclusively restricted to limited intrusion of O_2 into the landfill. The recent increase in level of O_2 may explain the increase in the concentration of particularly SO_4^{2-} and NO_3^--N, which have been observed to traverse the entire length of the aquifer. This illustrated a transition from reducing to oxidising environment, and indicated that lately, no substantial reduction of SO_4^{2-} and NO_3^- occur either within the landfill or after they are leached from the landfill. In the early years, the landfill could have produced highly reduced leachate that quickly depleted O_2, followed by reduction of NO_3^- and afterwards SO_4^{2-}. As the age of the tip increased, it started to produce less strength leachate with low reduction capacity, as evidenced by low pollutant load in recent years (Figure 3-2). The antagonistic variation in nitrogen species could be due to a shift in leaching pattern from NH_4^+-N to NO_3^--N, favoured by the presence of O_2. This was supported by the negative correlation between O_2 and NH_4^+ (r = -0.203; P-value = 0.031), which signified consumption of O_2 in conversion of NH_4^+ to NO_3^-. The O_2 in both the landfill and the aquifer has been replenished by precipitation as DO, although later intrusion as molecular O_2, due to compromised protective property of both the bedrock walls and the landfill cover could be possible. Östman et al. (2006) suggested that the degree of O_2 intrusion depends on the integrity of the cover. The roots of the spruce and black alder trees planted on the cover would create cracks to the landfill cover, while the ongoing quarrying of bedrocks just next to the aquifer could create fissure on the bedrock walls, thereby enhancing O_2 diffusion. However, it has been hypothesised that with time the rate of O_2 intrusion will exceed microbial depletion and so the landfill will become an aerobic ecosystem (Reinhart and Grosh, 1998, Mårtensson et al., 1999, Kjeldsen et al., 2002). This might also explain the recent rise in O_2.

4.3 Groundwater quality in wet and dry conditions

Groundwater quality examined in the present study has shown lower concentrations of pollutants in wet season and relatively higher concentrations in dry season, a pattern equally observed in other literatures (Tatsi and Zouboulis, 2002, Loehr and Haikola, 2003, Statom et al., 2004). However, prior to the landfill closure, a reversal situation was observed (see page 31). The higher pollutant load in dry conditions could be due to concentration effects, during which the groundwater level drops. Conversely, low pollutant load in wet periods could be due to dilution effect after recharge events. Contrary to other parameters, O_2 showed higher concentrations in wet season than in dry period. This can be explained by infiltration of oxygenated water from precipitation events into the aquifer. Lack of a coherent seasonal variation in some parameters such as NH_4^+-N, NO_3^--N (Figure 3-4) and TOC (Figure 3-5) could be due to transport effect, or due to seasonal dynamics in groundwater level that would influence natural attenuation processes. For example, Cozzarelli et al. (2011) reported vertical heterogeneity in the plume during wettest conditions, when the water table was highest. This would lead to haphazardly patchy distribution of pollutants due to variation in mixing rates of these compounds. Further, the strong positive correlation between NH_4^+-N and Cl^- (r = 0.656; P-value < 0.01) might support dissolution of ammonium chloride (NH_4Cl) by precipitation events, leading to a surge of this ions, and hence suppressing the dilution effect. Apparently, seasonal variation in Cl^- concentration (data not shown) follows that of NH_4^+-N closely. Association of nitrification with availability of O_2 discussed in the previous page could account for the behaviour of NO_3^--N in wet conditions, since the O_2 was supplied by precipitation.

Incidentally, the wet season coincided with lower groundwater temperatures, while slightly higher groundwater temperatures were measured in dry season. The rate of both chemical and biological reactions, as well as microbial growth may be influenced by temperature. Reinhart and Grosh (1998) wrote that deviations from the optimum growth temperature of microbes will decrease growth due to enzyme inactivation and cell wall rupture. On the other hand, solubility of many salts such as $Ca_3(PO_4)_2$ and NaCl increase with temperature (Reinhart and Grosh, 1998), while those of $CaCO_3$ and $CaSO_4$ show decrease in solubility with increase in temperature and vice versa (Stumm and Morgan, 1996). The temperature measured in this study (7.5 ± 1.9°C) would not cause the proposed influence on chemical and biological, as well as microbial growth, due to fairly a narrow range of temperature fluctuations.

4.4 Changes in groundwater quality, governed by natural attenuation processes (depth and distance factors)

4.4.1 pH and Oxygen

The pH values from the affected aquifer ranged from weakly acidic to weakly alkaline (5.2-8.4), which was higher than that from uncontaminated aquifer. This therefore means that the leachate emanating from the landfill was alkaline, supported by the high content of HCO_3^-. A decrease in pH with increasing distance from the landfill was observed, which could be attributed to the decrease in HCO_3^- with distance, probably due to buffering. Similar studies by Bjerg et al. (1995) and Kjeldsen (1993) in Grindsted and Vejen landfills (Denmark) measured pH of 6.5-7 and 6.7-6.9 respectively. They attributed the buffering capacity of the leachate to alkalinity. Further analyses have revealed slightly higher pH in R2 than in R1 for most of the years (Figure 3-18), which could be accounted for by the correspondingly high HCO_3^- content in the same location. The HCO_3^- might be leaching from one of the cells located close to R2, which is known to hold ashes and metals. The pH data in this study could not be used to precisely predict the stage of the landfill, because the results presented were from groundwater other than raw leachate. Nonetheless, studies e.g. Reinhart and Grosh (1998) never observed the expected trend in transition from acidogenic to methanogenic phase in Florida Landfill, even though they studied raw leachate. It is argued that either the degradation processes are so efficient that, it would give no chance for VOA to accumulate, often evidenced by low BOD and COD concentrations (Reinhart and Grosh, 1998), or the municipal landfill could have high alkalinity due to wastes that contain ashes and slag from the combustion of stone coal and coke in household furnaces (Słomczyńska and Słomczyński, 2004). The former claim could explain the high pH measured in the present study, but lack of data on VOA, BOD and COD limited its applicability. The latter suggestion, however, seemed relevant, because ashes and slag have been reportedly deposited.

In the absence of strongly anaerobic leachate, the aquifer environment is aerobic. This is supported by data from R0, which represents unpolluted aquifer. Rapid depletion of O_2 by strongly reduced plume in the leachate-affected aquifer might explain the observed increase in O_2 with distance from the landfill. Further away from the landfill, the strength of the leachate decreases due to processes that retard the pollutants, which would give time for the aquifer to become re-oxidised. A similar pattern of increase in levels of O_2 with distance has been

observed in Grindsted landfill by Bjerg et al. (1995), though the increase oriented upwards, probably due to the phreatic aquifer in Grindsted that would permit intrusion from top as opposed to a confined aquifer in Revdalen, which represents a closed system. Thus the increase in levels of O_2 at R4 is entirely due to the recovery phase of the aquifer rather than of replenishment experienced in unconfined aquifers.

4.4.2 Potassium, Sodium, Calcium, Magnesium, and Ammonium

Concentration of K^+, Na^+, Ca^{2+} and Mg^{2+} showed an obvious decrease with distance from the landfill. The attenuation of K^+ due to cation-exchange processes is significant, comparable to that of NH_4^+ (Bjerg et al., 2003, van Breukelen and Griffioen, 2004). Sodium takes little part in cation-exchange processes (Bjerg et al., 2003) and thus dilution seemed a major attenuation strategy in the present study. Attenuation through sorption, precipitation and dilution could account for the clearance of Ca^{2+} and Mg^{2+}. A number of researchers have observed low concentrations of Ca^{2+} and Mg^{2+} in methanenogenic phase and linked it to lower DOC and high pH (Christensen et al., 2001, Kjeldsen et al., 2002, Bjerg et al., 2003, Öman and Junestedt, 2008). DOC would form complexes with the cations, while high pH leads to enhanced sorption and precipitation. As previously discussed, the pH in Revdalen Aquifer remained reasonable high, which could indeed favour the proposed attenuation processes regulated by pH changes.

Ammonium-N concentration measured in the plume was in the range of 0-35 mgN/L. This was lower compared to that measured in Grindsted (30-116 mg/L) by Bjerg et al. (1995), and lower than a median of 151 mg/L measured in Norman Oklahoma (USA) by Cozzarelli et al. (2011). The natural attenuation of NH_4^+ has been very substantial, shown by slow migration of NH_4^+-N from R1 through R2, to R4 where the value has always been close to background level (Figure 3-12). Such similar pattern of slow migration was also observed by Bjerg et al. (2003) and Cozzarelli et al. (2011). They attributed this to attenuation by sorption and/or biodegradation/oxidation. According to Christensen et al. (2001) and Cozzarelli et al. (2011), NH_4^+ and K^+ have high affinities for cation exchange sites in sediments, and are as such the most attenuated cations in leachate plumes. In spite of the aquifer matrix in Revdalen being sand and gravel, cation exchange as an explanation could not be dismissed. Freeze and Cherry (1979) explained that a deposit composed of clean sand or gravel can have a significant colloid content, to which the ion-exchange processes are almost exclusively limited to. Oxidation of NH_4^+ could be yet another reason behind NH_4^+ elimination, because there has been an increase

in O_2 content from R2 to R4, which coincided with increase in NO_3^--N concentration in the same spot. This was substantiated by weak negative correlations between NH_4^+ and; NO_3^- (r = -0.310; P-value < 0.01), and O_2 (r = -0.203; P-value = 0.031). Christensen et al. (2001) reported disappearance of NH_4^+ coinciding with elevated NO_3^- in Grindsted Landfill, and linked it to NH_4^+ oxidation. Association of aerobic NH_4^+ oxidation with anaerobic NH_4^+ oxidation by anammox reaction has been suggested by Cozzarelli et al. (2011) and Christensen et al. (2001). This could be a potential mechanism for NH_4^+ attenuation, because anammox process is considered as the major pathway for loss of fixed nitrogen (van Niftrik and Jetten, 2012, Kartal et al., 2013). There has been a slight increase in levels of NH_4^+-N in R4 from 2010. The fact that the value in R4 continued to fluctuate above those in R1 and R2 eliminated transport effect as a reason. The increase could rather be due to reversed conversion of NO_3^- to NH_4^+ by microorganism, in which nitrate act as an electron acceptor for these group of anaerobes. This reaction is referred to as dissimilatory nitrate reduction to ammonium (DNRA) (van Niftrik and Jetten, 2012). Another reason for the increase could be release of NH_4^+ from the aquifer sediment. Cozzarelli et al. (2011) wrote that clay-bearing sediment constitutes an important reservoir of NH_4^+ that can support sustained release of this contaminant. Despite the fact that the aquifer sediment is primarily sand and gravel, possibilities of clay occurring could not be dismissed and may present explanation to the observation. Contrary to what was observed in this study, Kjeldsen et al. (2002) suggested that NH_4^+ concentrations will remain high even in leachate from older landfills that is otherwise low in organic content. The relatively low NH_4^+ concentration could probably be due to less content of putrescible wastes, thus producing minimal NH_4^+.

4.4.3 Iron and Manganese species

The highest Fe^{2+} concentration (90.83 mg/L) quantified in this study was much higher than that measured by Cozzarelli et al. (2011) (23 mg/L). The authors noted that this could have been a result of iron (III) oxide reduction by leachate plume. In contrast, the Fe^{2+} in the present study was believed to originate from the landfill, since the highest measurement was obtained in samples close to the landfill. This was supported by presence of other reduced species such as NH_4^+ and Mn^{2+}, both showing positive correlation with Fe^{2+} (r = 0.766; P-value < 0.01, and r = 0.381; P-value < 0.01, respectively). This association demonstrated relatedness in source and clearance of these ions in the ambient groundwater. The natural attenuation for Fe^{2+} was

far much better than for any other contaminant studied. Iron (II) clearance between R1 and R2, and after R2, but before R4, was significant. This was illustrated by the fact that, Fe^{2+} concentration in R4 was always close to the background level. Bjerg et al. (1995) made such similar observations of strong Fe^{2+} retardation. They suggested that it was due to precipitation, ion exchange with the aquifer material and dilution. In addition to dilution, the decrease between R1 and R2 could probably be due to precipitation as FeS and $FeCO_3$. In a classical chemical reaction, formation of FeS is favoured more than $FeCO_3$, due to its lower solubility product ($10^{-18.1}$) than for $FeCO_3$ ($10^{-10.7}$) (Fetter, 1993). But practically, formation of $FeCO_3$ might explain the strong attenuation of Fe^{2+} more than FeS in accordance to the law of mass action, owing to the high HCO_3^- content of the leachate plume in the present study. Furthermore, lack of S^{2-} data made it challenging to quantitatively link its participation in Fe^{2+} precipitation. On the other hand, strong clearance of Fe^{2+} midway between R2 and R4 besides dilution, might have been due to ferrous oxidation of both free Fe^{2+} and upstream reaction products such as $FeCO_3$, according to equation E4-1 for $FeCO_3$.

$$FeCO_{3(s)} + 2H_2O_{(l)} \quad \longrightarrow \quad FeOOH_{(s)} + HCO_{3(aq)}^- + 2H_{(aq)}^+ + e^- \qquad \text{(E4-1)}$$

The oxidation reaction leading to formation of $Fe_2O_{3(s)}$ and $FeOOH_{(s)}$ was highly anticipated, because of availability of O_2 in the same location as visualised in data for June 1999 (Figure 3-7), which coincided with Fe^{2+} clearance at about the same spot (Figure 3-15). Further evidence in support of this concept of oxidation reaction was provided by a weak negative correlation between Fe^{2+} and O_2 (r = -0.342; *P*-value < 0.01). Iron (II) plume was observed to infiltrate the aquifer from the deepest part, which contradicts that observed by Cozzarelli et al. (2011), who reported decrease in concentration of Fe^{2+} with depth. The density effect could be an explanation, where the leachate would sink to the bottom near the landfill. The geological formation of Revdalen Aquifer with such peculiar hydraulic gradient might further aided downward migration of the leachate. Based on the groundwater flow velocity of 1.3 m per day (Klempe, 2015), it would take ~249 days for pollutants to reach R4. Therefore, the reported increase in Fe^{2+} at R2 for 2009, 2010 and 2012 could not be due to transport effect. The increase could, however, be due to Fe^{3+} reduction, or leaching from a nearby landfill cell that contained mainly metals. Reduction could be supported by slight decrease in O_2 in the same location during the same periods.

The highest Mn^{2+} concentration (35 mg/L) was detected close to the landfill. Bjerg et al. (1995) also measured the maximum concentration (40 mg/L) close to the landfill. They suspected the high Mn^{2+} concentrations to be due to microbial reduction of Mn oxides by oxidation of organic matter or by chemical oxidation of Fe^{2+} or S^{2-}. Manganese concentration decreased between R1 and R2, while measurements at R4 were slightly above that of R2 for most of the observations. Soluble Mn^{2+} undergoes similar attenuation processes undergone by Fe^{2+}, such as precipitation as S^{2-} or CO_3^{2-}, ion exchange, oxidation and dilution (Bjerg et al., 2003). These processes could account for the decrease in Mn^{2+} from R1 to R2, while the slight increase in R4 could be explained by reduction of sediment-associated Mn oxides, which Bjerg et al. (2003) explained could increase Mn^{2+} concentrations further out in the plume. However, reduction of Mn oxide by Fe^{2+} suggested by Bjerg et al. (1995), and corroborated by van Breukelen and Griffioen (2004) after they measured elevated Mn/Fe ratio at the fringe could be a possible reaction accounting for the increased Mn^{2+} concentration. This could be likely since low Fe^{2+} content has been measured in the same location.

4.4.4 Heavy metals

The concentrations of the heavy metal species in this study were higher than that quantified in Vejen Landfill by Christensen et al. (2001). Nevertheless, the concentrations of most of the heavy metals did not have a deleterious effect on the groundwater quality, as the measured values were below the Norwegian drinking water standards, except for Cd^{2+} and Pb^{2+}. A number of similar studies reported low concentrations of heavy metals (Reinhart and Grosh, 1998, Kjeldsen and Christophersen, 2001, Han et al., 2014), although the actual concentrations may vary due to variations in waste composition, which is decisive on leachate composition. Mobility of heavy metals may be enhanced by the complexing capacity of organic matter leaching from the landfill (Jensen et al., 1999). The high content of Zn^{2+} measured in this study was in line with observation by Christensen et al. (2001) that Zn^{2+} usually occur in orders of magnitude greater than other heavy metals. Major contributors of Zn^{2+} are scrap metal and rubber (Kjeldsen et al., 2002), waste batteries and fluorescent light bulbs (Han et al., 2014). Sources of Cd^{2+} are plastics (Kjeldsen et al., 2002) and electronic wastes. Pb^{2+} contamination may be from batteries, photographs, old lead-based paints and lead pipes disposed at the landfill (Han et al., 2014).

The low level of heavy metals reported in landfill studies have led to a general deduction that heavy metals do not constitute a substantial pollution problem in landfill leachate (Reinhart and Grosh, 1998, Christensen et al., 2001, Kjeldsen et al., 2002, Slack et al., 2005, Han et al., 2014). It is argued that low heavy metal content is mainly attributed to strong attenuations of heavy metals. These processes include direct reduction to element (for Hg^{2+}) (Reinhart and Grosh, 1998), sorption, precipitation and dilution (Christensen et al., 2001, Bjerg et al., 2003, Han et al., 2014). The result is poor migration of heavy metals into the leachate plume (Slack et al., 2005). Heavy metals Cd^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+} and Pb^{2+} are in most cases thought to precipitate as S^{2-} or CO_3^{2-}, although phosphates and hydroxides present additional retardation mechanisms (Christensen et al., 2001). However, precipitation by hydroxides is favoured by neutral or above neutral leachate conditions (Reinhart and Grosh, 1998). Sulphide, which is formed from SO_4^{2-} reduction during waste decomposition in landfills accounts for most of heavy metal precipitation (Kjeldsen et al., 2002). According to Christensen et al., (2001), Cr^{3+} and Ni^{2+} are exceptions to precipitation because they form soluble S^{2-} and CO_3^{2-} respectively. Lack of data about the contents of S^{2-}, phosphates and hydroxides further limited understanding of the processes involved. But the high content of HCO_3^- in Revdalen provided a strong suggestion for its participation in heavy metal attenuation. The proposed mechanisms of heavy metal attenuation remained speculation since there were no data on the waste composition at the site. Despite of low heavy metal contents reported in the literatures, concentrations of heavy metals might be high elsewhere, due to variations in waste composition, which is decisive on the chemical nature of landfill leachate. The low levels of heavy metals reported in the present study could be due to low contents of hazardous wastes deposited in the landfill.

4.4.5 Reactive anions: Hydrogen carbonate, Sulphate and Nitrate

Hydrogen carbonate constituted the major pollution problem identified in the present study. Christensen et al. (2001) suggested that HCO_3^-, and CO_2 pressure, are usually high in leachate. The high alkalinity in landfill leachate could be due to decomposition of organic carbon, SO_4^{2-} reduction, denitrification and dissolution processes. Christensen et al. (2001) explained that HCO_3^- and CO_3^{2-} in the plume would contribute to formation of complexes with Ca^{2+}, Mg^{2+}, Na^+, Fe^{2+} and Mn^{2+}, and to precipitation of Ca^{2+}, Mg^{2+}, Na^+, Fe^{2+} Mn^{2+} including heavy metals. Complexation and precipitation could account for the decrease in HCO_3^- observed between R1 and R2, while the decrease in R4, which coincided with low pH, could be explained

by oxygenation of ferrous iron to ferric oxide, nitrification and oxidation of S^{2-}. Concomitant with disappearance of Fe^{2+}, and appearance of NO_3^--N and SO_4^{2-}. These reactions are known to consume bases (Stumm and Morgan, 1996). The negative correlation between HCO_3^- and; O_2 (r = -0.459; *P*-value < 0.01), and NO_3^- (r = -0.401; *P*-value < 0.01) would provide support for oxidation reactions that liberate H^+, which then consumed the HCO_3^-.

The SO_4^{2-} concentration range (0.2-65.33 mg/L) in Revdalen was lower than 1-1000 mg/L reported in Cozzarelli et al. (2011), and also lower than 0 - >100 mg/L measured in Grindsted by Bjerg et al. (1995). According to Christensen et al. (2001), potential SO_4^{2-} source in landfill leachate are demolition waste or ashes. This was after they observed very high concentrations of SO_4^{2-} in Grindsted Landfill in areas known to contain plaster boards (gypsum, $CaSO_4$). Another source of SO_4^{2-} proposed by Cozzarelli et al. (2011) is sulphur assimilated by plants and released during vegetative decay. The wastes in Revdalen Landfill were a mixture of all types of municipal wastes, and thus the two sources suggested could account for the presence of SO_4^{2-}. Sulphate concentration in Revdalen increased with distance from the landfill, a distribution similarly observed by Bjerg et al. (1995) in Grindsted Landfill, which they suggested to have been due to oxidation. The same explanation appears to suffice in the case of Revdalen Landfill, because the increase in SO_4^{2-} coincided with increased O_2 concentrations. More evidence in support of oxidation was the weak positive correlation between SO_4^{2-} and O_2 (r = 0.274; *P*-value = 0.004). The low or complete absence of SO_4^{2-} in R1 could be due microbial SO_4^{2-} reduction, a reaction catalysed by members of obligate anaerobic genus *Desulfovibrio,* which extract the energy and hydrogen necessary for life from organic carbon (Rail, 1989). This process seemed likely to proceed downstream of R1, producing S^{2-} and CO_2. The CO_2 might be responsible for the rise in pH at R2, while the S^{2-} precipitated metals. However, Bjerg et al. (1995) stressed that S^{2-}/SO_4^{2-} concentration as criterion for SO_4^{2-} reduction may be complicated by uneven leaching pattern. Lack of a coherent increase in SO_4^{2-} content with distance (Figure 3-8) could be a result of the uneven leaching from the landfill. Cozzarelli et al. (2011) reported temporal and spatial variation in the extent of SO_4^{2-} reduction. They believed it was due to changing hydrologic conditions, and variations in carbon quality that is known to be responsible for SO_4^{2-} reduction.

The NO_3^- concentration range (0-15.75 mgN/L) measured in the present study was much lower compared to that reported in Han et al. (2014) (0.1-487 mg/L). The authors attributed the high NO_3^- content to use of fertilisers, as opposed to point source from landfill in the present study. The distribution in nitrate concentration in the order R1 < R2 < R4 similarly resembled the scenario observed by Bjerg et al. (1995) and Han et al. (2014). The increase in NO_3^- concentration as a function of distance could be due to oxidation of NH_4^+. The shift in pattern of distribution to R1 < R4 < R2 could be due to denitrification processes in R4. Bjerg et al. (1995) explained that DOC from the landfill, solid organic matter associated with the aquifer material, or CH_4 might be the potential carbon source for denitrification. The authors further stressed that denitrification would be limited once CH_4 is exhausted, and that the concentration of NO_3^- formed from oxidation of NH_4^+ might increase. This mechanism appeared to be responsible for the observed increase in NO_3^- concentrations between R1 and R2. The proposed denitrification at R4 could have been supported by data on the NO_2^- content. Unfortunately, its analysis was discontinued after initial measurements showed very low levels. Stumm and Morgan (1996) proposed that denitrification process occur via an indirect mechanism, where NO_3^- is reduced to NO_2^-, followed by reaction of NO_2^- with NH_4^+ to produce nitrogen and H_2O. This reaction could remove the residual NH_4^+ from upstream processes. Bhalla et al. (2013) proposed that decrease in NO_3^- concentration could be due to microbial utilisation of NO_3^- and denitrifying as ammonia gas. Microbial analysis for denitrifiers and intermediate such as NO_2^- would be ideal to precisely understand the processes behind NO_3^- attenuation in the plume.

4.4.6 Other anions: Chloride, and Phosphate

Chloride level in the study (2.09-122.67 mg/L) was comparable to that measured by Reinhard et al. (1984) (>100 mg/L). The measurements at R1 in early years were slightly above 100 mg/L, while lower values were registered for R4 throughout the monitoring programme except only once in November 2013. The decrease in Cl^- concentration with distance demonstrated the significance of natural attenuation provided by the aquifer. For nonreactive components such as Cl^-, dilution provides the only attenuation mechanism (Christensen et al., 2001, Bjerg et al., 2003). Dilution is governed by macroscopic dispersion and molecular diffusion, but can also be affected by local vertical gradients, leachate density, and to some extent, viscosity (Bjerg et al., 2003). Vertical distribution from MLS in R1 showed increase in concentration with depth, which agreed with a study by Christensen et al. (2001), but contradicted that identified by Reinhard et al. (1984). By measuring densities and Cl^- concentrations,

Christensen et al. (2001) found the highest density and Cl⁻ concentration in the deepest part of the aquifer, and attributed it to vertical gradient. The vertical distribution of plume in Revdalen has been dealt with under Fe^{2+} in subsection 4.4.3. Pearson's correlation between Cl⁻ and Na^+, Cl⁻ and Ca^{2+}, Cl⁻ and NH_4^+ were 0.816, 0.797 and 0.656 respectively. This implied that the source of Cl⁻ was primarily dissolution of NaCl, $CaCl_2$, and NH_4Cl. Statom et al. (2004) found Na:Cl ratio of 1.08 and concluded that the species could have been derived from dissolution of salt.

Very low concentrations of Tot-P were registered. Other studies such by Bhalla et al. (2013) measured very high content of Tot-P. Phosphorus is one of the key elements required in metabolic pathways such as Kreb's Cycle, and a major component of Deoxyribonucleic acid (DNA) (Bhalla et al., 2013). The low level could be due to rapid depletion of this important nutrient for microbial growth. Tatsi and Zouboulis (2002) noted that low phosphorous content act as an important limiting factor in aerobic biological treatment of leachate, demonstrating its nutritional usefulness. Luck of phosphorous containing wastes could yet present another explanation for the low level of Tot-P. Although Fetter (1993) explained that dissolved phosphorous readily gets sorbed onto soil and as such has very low mobility in groundwater.

4.4.7 Xenobiotic Organic Carbon and Total Organic Carbon

It has been emphasised that detection of these compounds in leachate is more significant than mean values, because the concentration of these parameters may be low, but present serious health risks (Reinhart and Grosh, 1998). All the PCB variants included in the present study were reported as BDL, an observation similarly reported in Danish landfills (Kjeldsen and Christophersen, 2001) and in Swedish landfills (Öman and Junestedt, 2008). The former authors however, reported relatively higher concentrations in American landfills. They attributed the very low levels to lack of co-disposal practiced on the Danish sites, while the high levels in American landfills to co-disposal of hazardous waste on some of the sites. They further argued that, the low levels might have been due to volatilisation of these pollutants in the landfill gas, or degradation by microbial or abiotic processes. Bjerg et al. (2003) and Slack et al. (2005) attributed the low levels of chlorinated organic compounds detected in leachate to reductive dechlorination reactions that occur during anaerobic conditions. Meanwhile, 13 of the 16 PAHs searched for were detected, although at low concentrations. Kjeldsen and Christophersen (2001) reported similar low levels of PAHs in Danish landfills. Potential

attenuations of PAHs by dilution, sorption, and chemical/microbial degradation have been suggested (Ruegge et al., 1995, Christensen et al., 2001). Lack of data on the aquifer sediment in addition to a single sampling point limited the understanding of attenuation processes for PAHs in Revdalen Landfill. Bjerg et al. (2003) suggested consolidation of field observations, laboratory experiments, field tests and reactive solute transport modelling, if natural attenuation processes for XOCs in a landfill leachate is to be expeditiously addressed.

The low TOC quantified in Revdalen revealed mild input of DOC into the groundwater from the landfill. The TOC content in the plume decreased tremendously downgradient of the landfill, a pattern that was consistent with those observed elsewhere (Reinhard et al., 1984, Christensen et al., 2001, Eggen et al., 2010). Even though the deductions in the literatures were based on the levels of COD, BOD, VOC and DOC, all contribute to TOC. For example, Öman and Junestedt (2008) found a linear relationship between COD, TOC and BOD. The observed decrease in TOC with distance from the landfill could be attributed to effective attenuating factors (Reinhard et al., 1984). These attenuating factors according to Christensen et al. (2001) besides dilution, could be sorption and degradation. Lack of data on BOD, COD, NVOC, VOA, humic acids and the aquifer sediment restricted the interpretation of the result to general attenuation processes other than specific factors. The TOC concentration in R4 was below the background level. This only signified the efficiency of natural attenuation introduced by the leachate, probably due to proliferation of microbial biofilm, because of available nutrients. This would enhance the degradation beyond the natural level.

4.5 Redox conditions in Revdalen Aquifer

Oxidation-reduction reactions provide the framework for establishment of redox zones in groundwater environment. These zones are principally governed by chemical reactions, where participating elements change their valence states, through gain or loss of electron(s) (Fetter, 1993). The preference for redox indicator species in oxidation reactions will be in the decreasing order $O_2 > NO_3^- > Mn$ (III, IV) $> Fe^{3+} > SO_4^{2-}$ (Stumm and Morgan, 1996, Bjerg et al., 2003, McMahon and Chapelle, 2008), a course referred to by McMahon and Chapelle (2008), as the ecological succession of terminal electron-accepting processes. Close to the landfill, dissolved electron acceptors such as O_2, NO_3^- and SO_4^{2-} are depleted or lowered in concentration (Christensen et al., 2001, Bjerg et al., 2003). In Revdalen, complete absence of O_2, NO_3^- and SO_4^{2-} have been observed in R1, suggesting that R1 was located in the

methanogenic and SO_4^{2-} reducing environment. Ruegge et al. (1995) proposed that this zone is to be found within the first 30 m of the plume. The authors postulated iron reducing condition from 30 to 75 m, a situation that has not been precisely observed in Revdalen, although the recent increase in Fe^{2+} concentration in R2 would appear to be due to iron (III) reduction. The observed decrease in O_2 concentration during the same period would support iron (III) reduction, but leaching of Fe^{2+} from a nearby cell have also been suggested. Manganese reducing zone could be between R2 and R4, evidenced by increased Mn^{2+} concentration measured in R4. This was consistent with a suggestion by Stumm and Morgan (1996) that this process occurs at higher redox potentials than iron (III) reduction. It was in the same location where substantial precipitation of iron took place, shown by very low Fe^{2+} concentrations in R4. Reduction of Mn oxide by Fe^{2+} suggested by Bjerg et al. (1995) and corroborated by van Breukelen and Griffioen (2004) could explain the increased Mn^{2+} concentration. The differential variation in concentrations of Fe^{2+} and Mn^{2+} in presence of O_2 could further be accounted for by oxygenation of Fe^{2+}, which according to Stumm and Morgan (1996) even if is catalysed by surface and/or microorganisms, usually occurs faster than oxygenation of Mn^{2+} to Mn (III, IV) oxides. The oxygenation of Fe^{2+} to ferric oxide is coupled with release of H^+ according to the stoichiometric equation E4-2, a reaction that could also explain the decrease in pH at R4.

$$4Fe_{(aq)}^{2+} \ + \ O_{2(g)} \ + \ 4H_2O_{(l)} \ \rightleftharpoons \ 2Fe_2O_{3(s)} \ + \ 8H_{(aq)}^+ \qquad \text{(E4-2)}$$
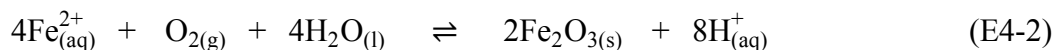
Furthermore, the low pH at R4 could be due to oxidation of sulphides such as HS and FeS_2, formed during SO_4^{2-} reduction occurring upstream of R4, that were transported to aerobic zones. These reactions yield H^+ and SO_4^{2-}, according to equations E4-3 and E4-4. The H^+ could lower pH, while the SO_4^{2-} might account for increase in SO_4^{2-} concentrations at R4.

$$HS_{(aq)}^- \ + \ 2O_{2(g)} \ \longrightarrow \ SO_{4(aq)}^{2-} \ + \ H_{(aq)}^+ \qquad \text{(E4-3)}$$

$$FeS_{2(s)} \ + \ \tfrac{15}{4}O_{2(g)} \ + \ 3\tfrac{1}{2}H_2O_{(l)} \ \longrightarrow \ Fe(OH)_{3(s)} \ + \ 4H_{(aq)}^+ + 2SO_{4(aq)}^{2-} \qquad \text{(E4-4)}$$
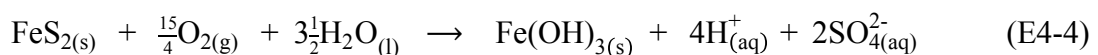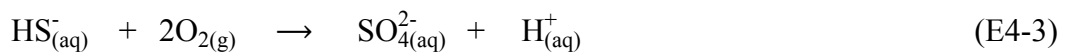
Nitrate reducing environment would supposedly exist just after Mn reducing, but as Stumm and Morgan (1996) explained, reduction of MnO_2 if present, should occur at about the same redox potential as that of NO_3^-. It follows that the observed decrease in NO_3^--N concentration at about the same spot (between R2 and R4) could be explained by NO_3^- reduction, which

according to Ruegge et al. (1995) should be followed by aerobic conditions, about 250 m from the landfill. This was also consistent with the observed increase in O_2 concentration in R4 higher than in R2. Heron and Christensen (1995) reported such similar insignificant concentrations of dissolved Fe^{2+} (< 1 mg/L) in the NO_3^- reducing zone, which was in aerobic parts of the plume. Therefore, based on redox sensitive species concentrations from the present study, compared with those in Heron and Christensen (1995) and criteria for assigning redox zones (Lyngkilde and Christensen, 1992, Bjerg et al., 1995), the redox zones for Revdalen Aquifer would be as follows; SO_4^{2-} reducing zone at R1, iron reducing upstream of R2, manganese reducing and NO_3^- reducing zones between R2 and R4, and lastly aerobic condition from R4 onwards (Figure 4-1). This is in line with redox zones proposed by many other researchers (Bjerg et al., 1995, Ruegge et al., 1995, Stumm and Morgan, 1996, Bjerg et al., 2011). Freeze and Cherry (1979) stated that, microorganisms catalyse nearly all important redox reactions that occur in groundwater, including thermodynamically spontaneous reactions so that they procced at a significant rate. The proposed zones could thus be substantiated by studying the distribution of microorganisms in these proposed zones, a similar study conducted elsewhere (Ludvigsen et al., 1999) confirmed the redox zones in the stated literatures.
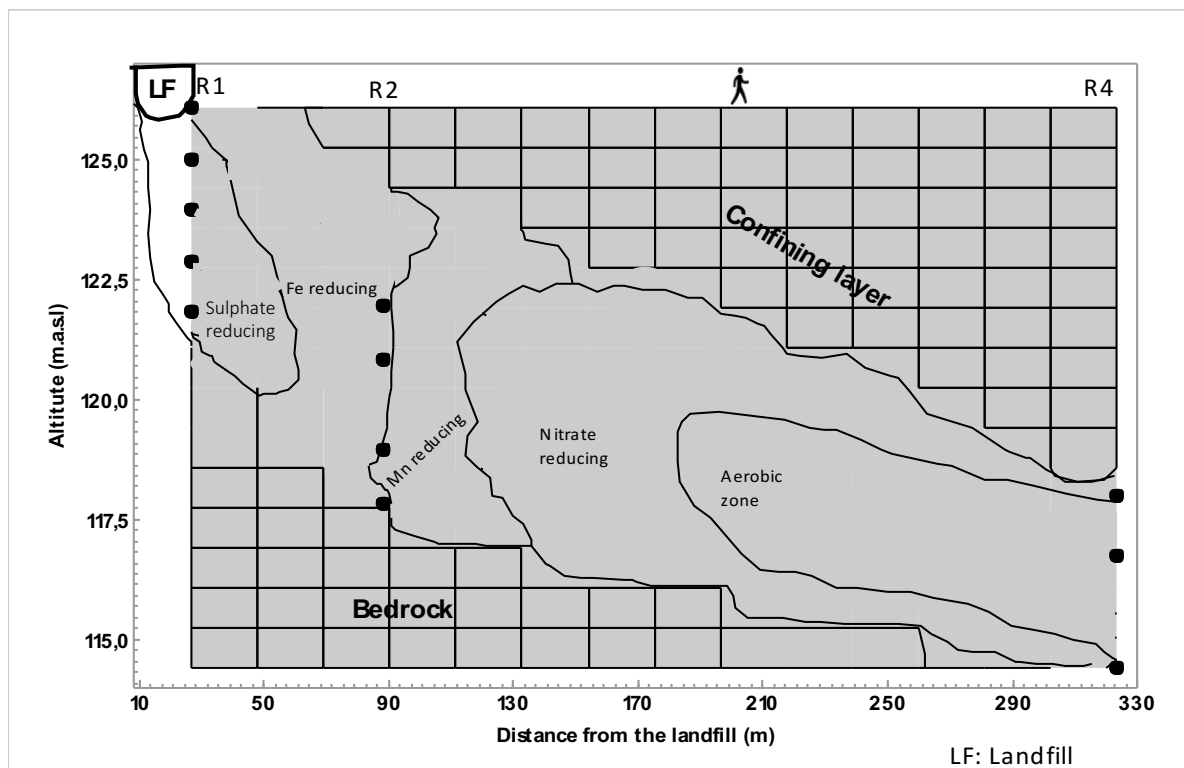
Figure 4-1: *Proposed distribution of redox zones for Revdalen Aquifer. The black dots denote the sampling levels in R1, R2 and R4, located downgradient of the landfill.*

5 Conclusion

Operation of Revdalen Landfill has compromised the groundwater quality beneath the waste, evidenced by the presence of a wide range of inorganic compounds that have been detected in the leachate plume. Some of these pollutants exceeded the Norwegian drinking water standards, while some were below the standards, although above the background level. HCO_3^- was the major pollution problem originating from the landfill. Of the two classes of anthropogenic organic substances PAH_{16} and PCB_7 studied, 13 of the PAH_{16} were detected, albeit at low concentrations, while all the PCB variants were BDL. Seasonal variations in groundwater quality has indicated slightly higher concentrations of pollutants in dry season than in wet season. The results further demonstrated that, closing the landfill was followed by decrease in concentrations of contaminants in groundwater, a situation referred to as "enhanced natural attenuation". Generally, all the parameters were found to be on the verge of attaining the natural background level as the age of the landfill approached 21 years. The redox condition that has played a pivotal role in retarding the contaminants have been identified in the aquifer in the order of increasing distance from the landfill; sulphate reducing, iron reducing, manganese reducing, nitrate reducing and finally aerobic condition. The order of strength of natural attenuation for the pollutants was strongest for cations ($Fe^{2+} > NH_4^+ > K^+$ etc.), moderate for anions ($Cl^- > HCO_3^- > NO_3^- > SO_4^{2-}$), and least for heavy metals.

The work conducted at Revdalen Landfill is technically known as "Monitored Natural Attenuation", which has helped in obtaining an in-depth knowledge about the chemical composition of the polluted groundwater, and evaluating natural attenuation provided by the aquifer as a remediation strategy. Based on the results, the feasibility of the aquifer acting as a treatment plant to the pollutants is very substantial, thus eliminating any serious environmental risk associated with the leachate emanating from the landfill. Thus future reclamation of both the land and the groundwater resource is achievable. Therefore, other kinds of intervention as a remedial strategy are deemed unnecessary for now. The monitoring programme can, however, continue until the level of all the contaminants attain the natural background level. Future studies and in particular, reactive transport model for Revdalen Landfill leachate plume will be ideal to complement the present study. This will provide a comprehensive biogeochemical processes in Revdalen aquifer.

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List of Tables and Figures

Tables

Figures

Annexes

Annex A: Pearson's correlation (r) and P-value for the water chemistry

Pearson's Correlation	Temp	pH	Cond	O_2	SO_4	Cl	Mg	Na	K	Ca	Mn	Fe	NO_3	NH_4	HCO_3	TOC
pH	-0,154															
	0,199															
Cond	-0,128	0,461														
	0,296	0,000														
O_2	-0,037	-0,153	-0,178													
	0,762	0,122	0,070													
SO_4	-0,134	0,101	0,237	0,274												
	0,277	0,211	0,003	0,004												
Cl	-0,120	0,377	0,761	-0,077	0,145											
	0,314	0,000	0,000	0,408	0,056											
Mg	-0,024	0,359	0,648	-0,104	0,223	0,605										
	0,878	0,000	0,000	0,363	0,020	0,000										
Na	-0,151	0,396	0,791	-0,176	0,092	0,816	0,622									
	0,210	0,000	0,000	0,058	0,225	0,000	0,000									
K	-0,050	0,503	0,735	-0,184	0,250	0,622	0,810	0,722								
	0,751	0,000	0,000	0,107	0,009	0,000	0,000	0,000								
Ca	-0,114	0,464	0,802	-0,244	0,249	0,797	0,807	0,871	0,824							
	0,467	0,000	0,000	0,031	0,009	0,000	0,000	0,000	0,000							
Mn	-0,007	0,150	0,186	-0,165	-0,021	0,233	0,314	0,424	0,292	0,429						
	0,967	0,130	0,061	0,148	0,833	0,011	0,001	0,000	0,001	0,000						
Fe	-0,022	0,435	0,723	-0,342	-0,016	0,635	0,588	0,767	0,638	0,807	0,381					
	0,856	0,000	0,000	0,000	0,831	0,000	0,000	0,000	0,000	0,000	0,000					
NO_3	0,034	-0,003	-0,272	0,082	-0,007	-0,266	-0,424	-0,295	-0,378	-0,365	-0,305	-0,310				
	0,779	0,968	0,000	0,386	0,923	0,000	0,000	0,000	0,000	0,000	0,001	0,000				
NH_4	0,002	0,410	0,793	-0,203	0,068	0,656	0,719	0,754	0,833	0,788	0,322	0,766	-0,310			
	0,987	0,000	0,000	0,031	0,381	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000			
HCO_3	-0,013	0,479	0,805	-0,459	0,184	0,583	0,640	0,811	0,760	0,796	0,363	0,687	-0,401	0,812		
	0,935	0,000	0,000	0,000	0,061	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000		
TOC	0,021	0,377	0,626	-0,226	0,058	0,626	0,650	0,771	0,759	0,742	0,317	0,673	-0,311	0,812	0,733	
	0,865	0,000	0,000	0,016	0,453	0,000	0,000	0,000	0,000	0,000	0,001	0,000	0,000	0,000	0,000	

Cell Contents: Pearson correlation
                 P-Value

NB: - The calculations were based on the sample mean values for each of the monitoring wells for every sampling during the 23 years of observations.
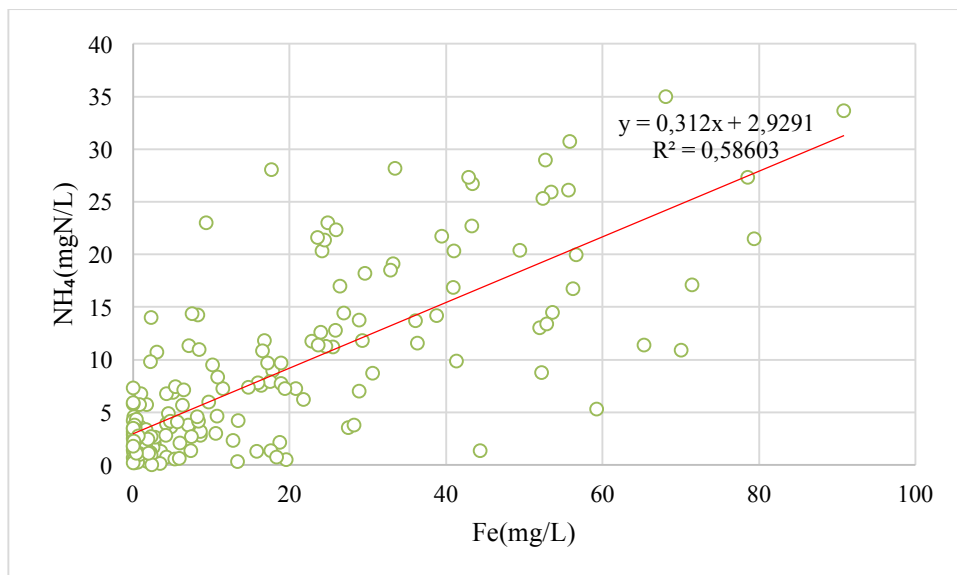   - Also see Table 3-1 for sample size N

Annex B: scatterplots and regressions for some parameters

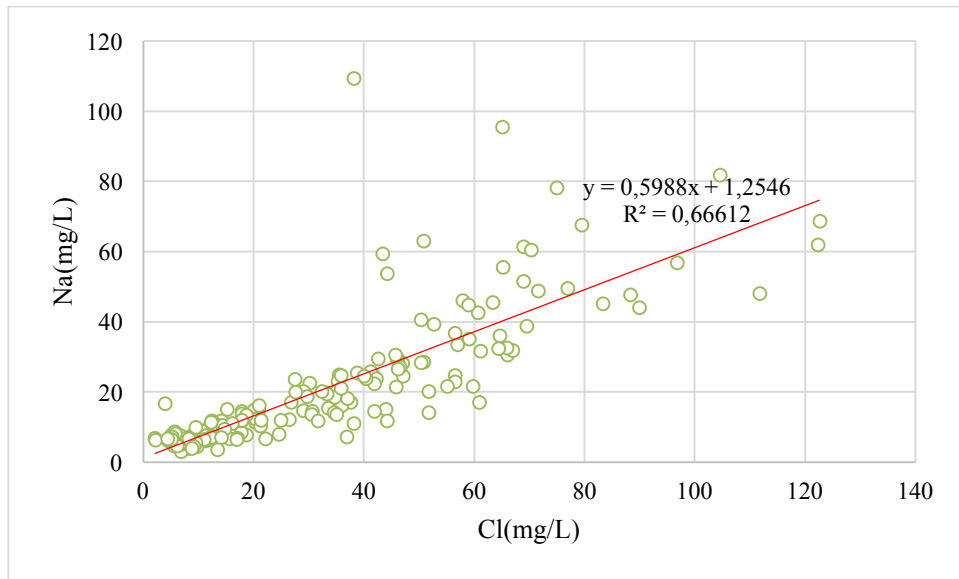## 1B: Scatterplot showing correlation between iron and Manganese
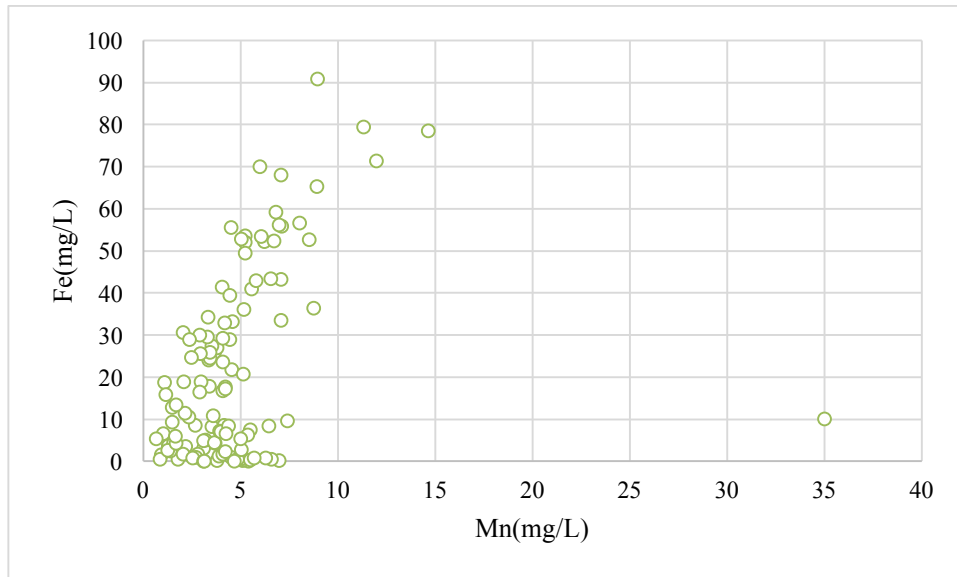
A weak positive correlation

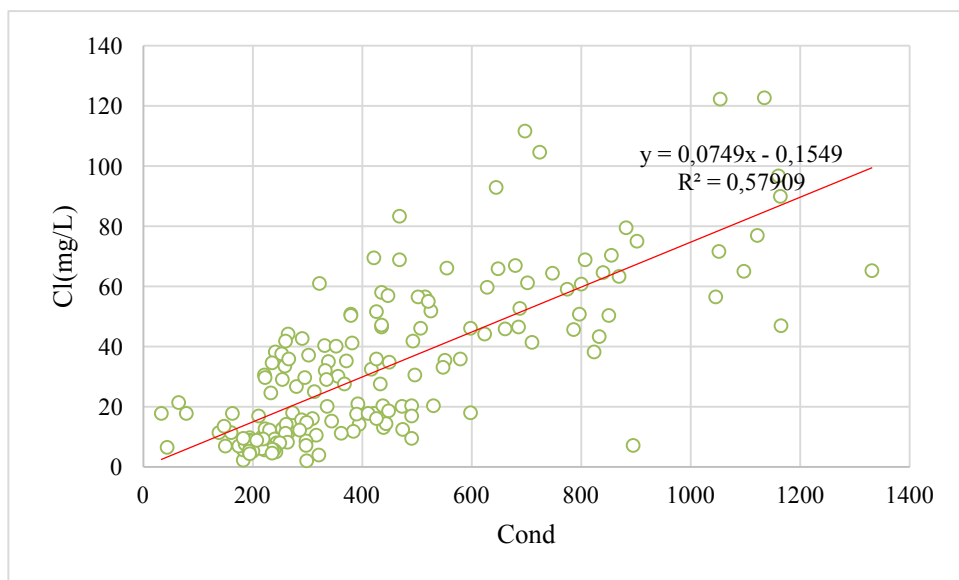## 2B: A correlation with regression equation for ammonium-N against iron

$y = 0,312x + 2,9291$
$R^2 = 0,58603$

A strong positive correlation

3B: A correlation with regression equation for sodium against chloride

$y = 0,5988x + 1,2546$
$R^2 = 0,66612$

A strong positive correlation

4B: A correlation with regression equation for chloride against conductivity

$y = 0,0749x - 0,1549$
$R^2 = 0,57909$

A strong positive correlation