Identification of sources of ammonium in groundwater using stable nitrogen and boron isotopes in Nam Du, Hanoi

Johan Lindenbaum

Dissertations in Geology at Lund University,
Master's thesis, no 300
(45 hp/ECTS credits)

Department of Geology
Lund University
2012

Identification of sources of ammonium in groundwater using stable nitrogen and boron isotopes in Nam Du, Hanoi

Master's thesis
Johan Lindenbaum
45 hp

Department of Geology
Lund University
2012

Contents

Cover Picture: Bana plantage from Nam Du

Identification of sources of ammonium in groundwater using stable nitrogen and boron isotopes in Nam Du, Hanoi

JOHAN LINDENBAUM

Lindenbaum, J., 2012: Identification of sources of ammonium in groundwater using stable nitrogen and boron isotopes in Nam Du, Hanoi. *Dissertations in Geology at Lund University*, No. 300, 38 pp. 45 hp (45 ECTS credits).

Abstract: In this study high concentrations of ammonium (NH_4^+) and arsenic (As) in groundwater are investigated in the Nam Du well-field, Hanoi, Vietnam. Arsenic is unwanted in drinking water since it has severe consequences for human health. High concentrations of ammonium in groundwater, while not directly harmful to human health, is often a sign of the groundwater being affected by anthropogenic activities, such as spreading of fertilizers and manure or leaking sewage water. Groundwater from two aquifers (one shallow Holocene and one deep semi-confined Pleistocene), the Red River, ponds in the area and wastewater canals were sampled and analyzed for stable isotopes of nitrogen (^{14}N and ^{15}N) and boron (^{10}B and ^{11}B), which were used to characterize potential pollution sources and investigate to what extent the groundwater are affected by pollution from anthropogenic sources. Samples were also taken for general chemistry, $^3H/^3He$ dating and bacteriological content. Arsenic concentrations were high and exceeded the WHO guideline value of 10 µg/L in all sampled groundwater and in several surface water bodies. Ammonium concentrations showed large variations but were generally very high. Based on the analyses of the stable isotopes and other parameters the following conclusions were made:

1. The main process responsible for the high ammonium concentrations are likely mineralization from sediments rich in organic matter

2. In some parts of the Nam Du area, pollution by leaking wastewater or animal manure is likely a source of ammonium

The quality problems associated with the groundwater in Nam Du are likely to prevail and as such an alternative source of drinking water should be considered.

Keywords: groundwater, contamination, ammonium, stable isotopes, $\delta^{15}N$, $\delta^{10}B$, arsenic, Hanoi, Vietnam

Johan Lindenbaum, Department of Geology, Lund University, Sölvegatan 12, SE-223 62 Lund, Sweden. E-mail: johan.lindenbaum@gmail.com

Identifiering av ammoniumkällor i grundvatten med hjälp av stabila kväve- och borisotoper i Nam Du, Hanoi

JOHAN LINDENBAUM

Lindenbaum, J., 2012: Identification of sources of ammonium in groundwater using stable nitrogen and boron isotopes in Nam Du, Hanoi. *Examensarbeten i geologi vid Lunds universitet*, Nr. 300, 38 sid. 45 hp.

Sammanfattning: I denna studie undersöks grundvattnet i en vattentäkt (Nam Du) i Hanoi, Vietnam. Grundvattnet innehåller höga halter av ammonium (NH_4^+) och arsenik (As). Arsenik är mycket giftigt och kan ha allvarlig inverkan på människors hälsa och är därför inte önskvärt i dricksvatten. Höga halter av ammonium i dricksvatten är inte skadligt i sig, men är ofta ett tecken på antropogen påverkan av grundvattnet, exempelvis spridning av gödningsmedel eller läckande avloppsledningar. Vattenprover togs från två akvifärer, en grund öppen holocen och en djup sluten pleistocen för att utvärdera föroreningssituationen. Ytvatten och avloppsvatten provtogs också för att kunna karaktärisera potentiella föroreningskällor. Proverna analyserades för stabila kväveisotoper (^{14}N och ^{15}N), stabila borisotoper (^{10}B och ^{11}B), allmänkemi, $^3H/^3He$-datering och bakterieinnehåll (*E. coli* och totalt antal koliforma bakterier). Arsenikhalten i alla provtagna grundvatten utom ett, var över den av WHO fastställda gränsen för dricksvatten på 10 µg/L. Även flera ytvatten påvisade höga halter av arsenik. Ammoniumkoncentrationen i de provtagna grundvattnen generellt mycket höga. Baserat på analysen av de stabila isotoperna och övriga parametrar drogs följande slutsatser:

1. De höga halterna av ammonium kommer troligtvis till största del från mineralisering vid nedbrytning av organiskt material i sedimenten.

2. Grundvattnet uppvisar på en del platser i Nam Du antropogen påverkan, på dessa platser är läckage av avloppsvatten eller stallgödsel en trolig ammoniumkälla .

Grundvattnet i båda akvifärerna är av låg kvalité och kommer troligtvis försämras ytterligare vid fortsatt pumpning. En alternativ dricksvattenkälla bör därför övervägas.

Nyckelord: grundvatten, förorening, ammonium, stabila isotoper, $\delta^{15}N$, $\delta^{10}B$, arsenik, Hanoi, Vietnam

Johan Lindenbaum, Institutionen för geologi, Lunds Universitet, Sölvegatan 12, 223 62 Lund, Sverige. E-post: johan.lindenbaum@gmail.com

Abbreviations

CETASD – Research Center for Environmental Technology and Sustainable Development

DNRA – Dissimilatory Nitrate Reduction to Ammonium

DO - Dissolved Oxygen

DOC – Dissolved Organic Carbon

DOM –Dissolved Organic Matter

DON - Dissolved Organic Nitrogen

EAWAG - Swiss Federal Institute for Environmental Science and Technology

GMWL - Global Meteoric Water Line

HUMG – Hanoi University of Mining and Geology

INST – Institute of Nuclear Science and Technology

LAS – Lower Aquifer System

LMWL - Local Meteoric Water Line

LOD – Limit Of Detection

MPN - Most Probable Number

SHE– Standard Hydrogen Electrode

STP – Standard Pressure = 1 atm

TDS – Total Dissolved Solids

TOC- Total Organic Carbon

UAS – Upper Aquifer System

1 Introduction

Water is the most important resource on Earth, for humans and other living organisms alike. Despite this, nearly half of the world's population does not have access to drinking water of acceptable standard. Groundwater is usually a good source of drinking water since water is naturally purified when it is slowly percolating through soil. The use of groundwater as a source for drinking water has expanded much in modern times and today makes up 25 to 30% of the total water extraction of the world (Younger, 2007).

Anthropogenic activities and over-exploitation of groundwater resources has led to degradation of the groundwater quality in many places. There are also several natural contamination sources of groundwater. A large problem in many parts of the world, especially South America and South East Asia is high concentrations of arsenic (As) in drinking water. Arsenic is unwanted in drinking water since it can have severe consequences for human health even in small doses. Arsenic is highly cancerogenic and known to cause skin, bladder and lung cancers as well as dermal lesions and peripheral vascular disease in people ingesting arsenic contaminated water (WHO, 2008). The provisional guideline value set by the WHO for drinking water of 10 μg/L is exceeded in many places in Asia. The most well known cases are perhaps Bangladesh and India but it is also a problem in parts of Cambodia, China, Mongolia and Vietnam.

1.1 Background

In Hanoi, the capital of the Socialist Republic of Vietnam, groundwater is the main source of drinking water. In and around Hanoi millions of people are depending on groundwater extracted from the Red River Delta for drinking water. The water distributed to the public is pumped from a semi-confined aquifer of Pleistocene age, which is overlain by a shallow open aquifer of Holocene sediments. Between the 1960s and the 1990s groundwater extraction increased from 141 000 m^3/d to 410 000 m^3/d and concerns were raised about possible degradation of the quality of the groundwater (Trafford et al., 1996). Water outtake today reaches 750 000 m^3/d, which has significantly changed the hydrogeological patterns in the Hanoi area (Winkel et al., 2011).

Subsequent studies regarding groundwater quality in Hanoi has shown that the quality of the groundwater is indeed becoming worse with high and increasing concentrations of arsenic and ammonium in the groundwater. In 1999 a study concerning heavy metals in the environment around Hanoi showed that the groundwater beneath Hanoi contained high concentrations of arsenic (As) (Berg et al., 2001). These results were later confirmed by among others Norrman et al. (2008) who reported concentrations of As in both the Pleistocene and Holocene aquifers far above the provisional guideline value of 10 μg/L set by the World Health Organization (WHO). The source of the arsenic is thought to be mobilization by reductive dissolution of iron-oxides due to reducing conditions in the aquifers (Norrman et al., 2008). The low redox-conditions are probably caused by decomposition of organic material, which is plentiful in parts of the Quaternary sediments underlying Hanoi. The high water outtake from the lower Pleistocene aquifer is likely to induce infiltration of As-rich water from the upper aquifer to the lower.

Several studies have also shown elevated concentrations of ammonium in the groundwater in the Hanoi area (Berg et al., 2001; Harms-Ringdal, 2007; Norrman and Andersson, 1998). Norrman and Andersson (1998) constructed a nitrogen budget for the area, which showed that large amounts of nitrogen are likely leached to the groundwater. Harms-Ringdal (2007) concluded that the elevated ammonium concentrations are probably due to infiltration from surface sources but the exact source of the ammonium remains unknown. The ammonium is also interesting in regard to the high arsenic levels since infiltrating water from surface sources could contain high quantities of organic material which could decrease oxygen levels and redox conditions even more, which might increase the mobilization of arsenic. Ammonium does not pose a risk for people's health in concentrations that can be expected in groundwater. However, there is health implications with high concentrations of nitrate in drinking water, which ammonium can be oxidized to if exposed to oxygen. High ammonium concentrations are also a common sign that surface water influenced by anthropogenic activities are infiltrating to the groundwater. It is of great importance to find the source causing the high ammonium concentration, since infiltration of surface water contaminated by for example wastewater or fertilisers could further degrade the quality of the groundwater as well as potentially increase the mobilization of arsenic.

1.2 Aim and scope of the study

The main aim of this study was to investigate the source(s) causing the high concentrations of ammonium in groundwater in the Nam Du well-field, Hanoi. A second objective was to look at the groundwater quality more generally and see if anthropogenic activities are affecting the groundwater quality. The third and final objective of this study was to investigate if there is any relationship between the high concentrations of ammonium and arsenic and its possible part in the process of mobilizing arsenic in the Red River delta sediments.

This study was carried out as a part of the project "*Identification of sources of ammonium and its implications for arsenic mobilization in the Nam Du well-field, Hanoi (AmonAs 2*)"

The AmonAs 2 is a collaborative research project between Lund University (Department of Geology), Hanoi University of Mining and Geology (HUMG), the Royal Institute of Technology (KTH), the Institute of Nuclear Science and Technology in Hanoi (INST), Research Center for Environmental Technology and Sustainable Development (CETASD, Hanoi University of Science) and the Swiss Federal Institute for Environmental Science and Technology (EAWAG).

2 Theory

2.1 Nitrogen

Nitrogen (N) is a very common element which is essential for almost all forms of life found on earth (Schlesinger, 1997). For plants, nitrogen is an important nutrient and often limits the primary production in ecosystems, both on land and sea. In living tissues nitrogen is important because it is part of enzymes needed for respiration and photosynthesis. Compounds containing N is commonly found both in liquid, solid and gaseous forms. Not counting nitrogen bound in rocks, the most common nitrogen compounds found in nature are, N_2 (nitrogen gas), N_2O (nitrous oxide), NH_4^+ (ammonium), nitrite (NO_2^-) and NO_3^- (nitrate). Nitrogen compounds are found at valence states ranging from -3 (NH_4^+) to +5 (NO_3^-). Many microbes use the potential energy of transformations of these compounds to sustain them with energy resulting in a complex geochemical cycle with many possible transformations.

2.1.1 The nitrogen biogeochemical cycle

Of all the nitrogen found on earth, 97.76% is bound in rocks, 2.01% is found in the atmosphere while the remaining 0.23% is located in the hydrosphere and biosphere (Kendall and McDonnell, 1998). The atmospheric nitrogen is however not available to most of the biosphere. There are two natural possible pathways for nitrogen to enter the biosphere., see Figure 1. N_2-gas in the atmosphere can be oxidised to the biologically more available form NO during thunderstorms, which is then dissolved in water and falls to the ground with precipitation (Atkins and Jones, 2010). Some plants are also able to directly fixate N_2 from the atmosphere (Schlesinger, 1997).

The pool of inorganic nitrogen (NH_4^+ and NO_3^-) in the soil is usually very small at any time because of rapid uptake by plants and microorganisms. Organic nitrogen may however exist in large quantities in the soil since N is not available to plants in this form. Organic N must first be decomposed to NH_4^+ by heterotroph microbes, a process known as mineralization. Mineralization is favoured in warm and moist environments. NH_4^+ is then oxidized by microbes to NO_3^- in the presence of oxygen, with NO_2^- and NO as intermediate forms. The whole process is known as nitrification. Nitrogen is leached from the soil as NO_3^- or in some cases NH_4^+ and reach the groundwater. NO_3^- is much more mobile in soils than NH_4^+ since the positively charged NH_4^+-ion, has a tendency to be adsorbed to negatively charged clay particles (Kresic, 2007).

Nitrogen re-enters the atmosphere from the soil or the sea through the multi-step process of denitrification in which NO_3^- is reduced to N_2 by microbes under anaerobe conditions, with NO_2^-, N_2O and NO as intermediate forms, see Figure 1. Nitrogen can also be returned to the atmosphere through the process of anaerobic ammonium oxidation, abbreviated annamox. Annamox is an important process in anaerobic freshwater lakes and the oceans were microbes oxidize NH_4^+ with the help of NO_2^- to form nitrogen gas and water according to (Dalsgaard et al., 2003);

$$NH_4^+ + NO_2^- \rightarrow N_2 + H_2O \quad (1)$$

If the redox-conditions are strongly reducing (i.e. anaerobic) combined with high amounts of carbon and limited amounts of nitrate, microbes may reduce nitrate to ammonium according to the following reaction;

$$NO_3^- + 4H_2 + 2H^+ \rightarrow NH_4^+ + 3H_2O \quad (2)$$

This reaction is known as dissimilatory nitrate reduction to ammonium or DNRA. An important difference between DNRA and the processes of denitrification and annamox is that nitrogen is retained in the system during DNRA while it is lost to the atmosphere during denitrification and annamox. The role of DNRA in the nitrogen cycle is however typically mi-

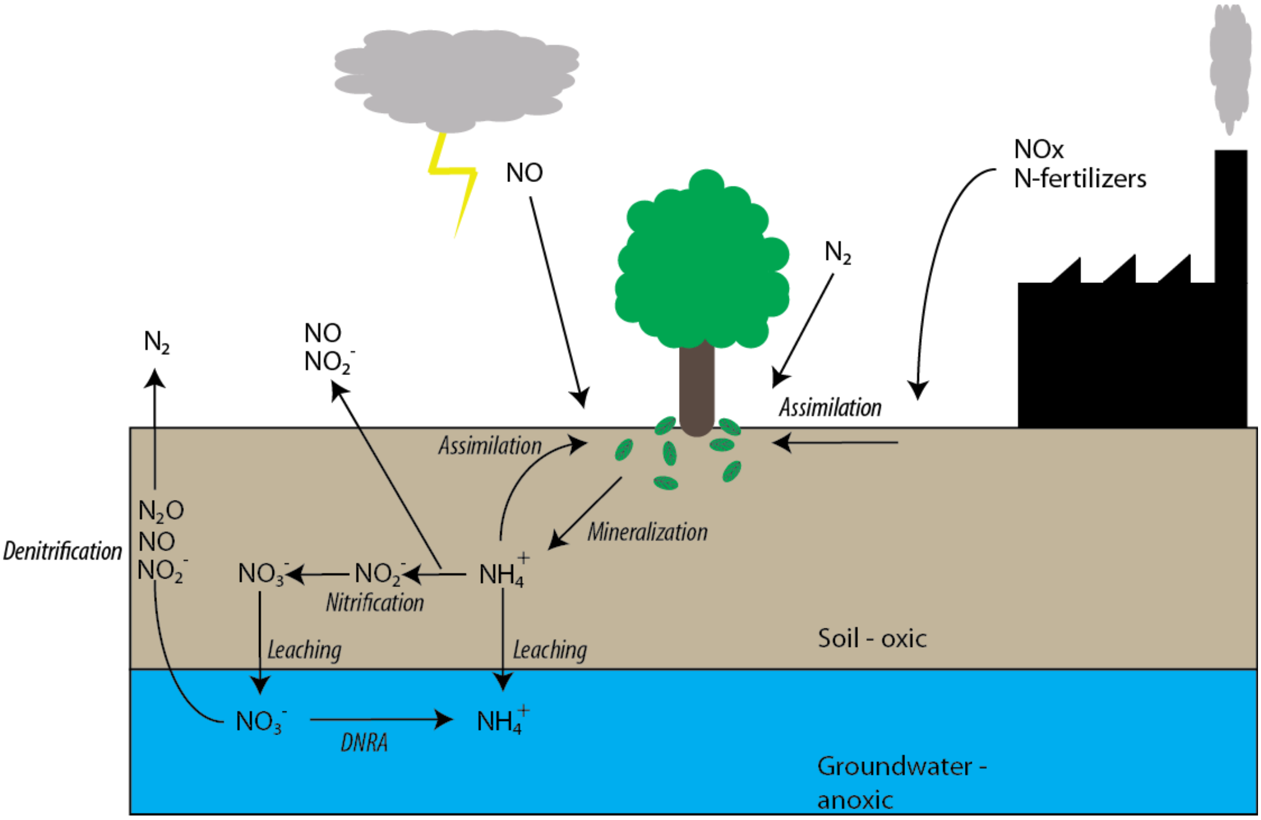

Figure 1. Simplified cartoon of pathways by which nitrogen enters the soil and groundwater by and possible reactions that occurs in the soil.

nor compared to that of denitrification (Tomaszek and Rokosz, 2007). Still recent studies have shown that it may be the dominant process of nitrate reduction in some environments (Rutting et al., 2011).

Humans have affected the global nitrogen cycle in a profound way. Since Haber and Bosch, in the early 20th century, discovered how to synthesis ammonia using nitrogen and hydrogen gas enormous amounts of nitrogen has been added to nature in the form of synthetic fertilizers (Smil, 2001). In 2001, an estimated 130 million tonnes of ammonia were added to nature as fertilizer, mostly in the form of urea (CH_4N_2O). High temperature combustion from industry and vehicles also produces large amounts of nitrous oxides, NO_x, that reaches the atmosphere and is later deposited on land and in oceans with precipitation. As much as 60 % of N that is fixated to the land surface from the atmosphere each year is estimated to originate from anthropogenic sources (Schlesinger, 1997). Wastewater is another potential source of elevated levels of N in soil or groundwater. Wastewater typically enters the soil by infiltration from wastewater ponds, leaking sewage systems or septic tanks.

2.1.2 Ammonium and nitrate in groundwater

Nitrogen is found in groundwater as dissolved organic nitrogen (DON), NO_3^-, NO_2^- or NH_4^+. The most common N compound found in groundwater is NO_3^-, but in strongly reducing environments NH_4^+ can be the dominant form. NH_4^+ is found in groundwater naturally as a result of anaerobic decomposition of organic material (Böhlke et al., 2006). It is also commonly found in groundwater due to anthropogenic activities, primarily due to leaching from fertilizes, organic waste disposal or leaking sewage systems. NO_3^- is usually not found in concentrations over 2 mg/L in unpolluted groundwater, though this may be higher in arid environments (Kresic, 2007). Higher concentrations of NO_3^- in the groundwater are usually an effect of these anthropogenic activities.

The World Health Organization has set the recommended guide line values for NO_3^- in drinking water to 50 mg/L. The primary health concern regarding NH_4^+ and NO_2^- is so called methaemoglobinaemia (WHO, 2008). Methaemoglobinaemia is a condition where NO_3^- or NO_2^- reacts with haemoglobin in the red blood cells to produce methaemoglobin. Methaemoglobin binds oxygen hard and does not release it, which can cause oxygen deficiency if methaemoglobin concentrations are too high. This state is also known as cyanosis or blue-baby syndrome, since infants are especially sensitive.

The WHO has not issued any guidelines for NH_4^+ in drinking water since NH_4^+ has no known toxic effects in concentrations that can be expected to be found in drinking water. High concentrations of NH_4^+ in drinking water are however not desirable, since it can be converted to nitrate in the water distribution net, compromise disinfection quality, cause failure of filters for removal of manganese as well as taste and odour problems (WHO, 2008). If high levels of NH_4^+ are found in groundwater it is likely that the ground water is being contaminated by anthropogenic sources and may as such contain pathogens, pesticides or other unwanted substances.

2.2 Nitrogen isotopes as environmental tracers

There are two stable isotopes of nitrogen, ^{14}N and ^{15}N. Since nitrogen in compounds can have a wide range of oxidation numbers and take part in many different reactions, there are many natural isotopic compositions of nitrogen. The average concentration of ^{15}N in the atmosphere is constant with a $^{15}N/^{14}N$ ratio of 1/272 (Kendall and Aravena, 2000). Stable nitrogen isotopes ratios ($\delta^{15}N$) are expressed in per mille relative to N_2 in atmospheric air:

$$\delta^{15}N(‰) = \left[\frac{\left(\frac{^{15}N}{^{14}N}\right)_{sample}}{\left(\frac{^{15}N}{^{14}N}\right)_{air}} - 1\right] \times 1000 \; (3)$$

Fractionation of isotopes can occur during many chemical, biological and physical reactions. Fractionation means that the relative isotope composition in the reactant and the product will change as one isotope is favoured over the other during a reaction. During kinetic (unidirectional, irreversible) reactions, generally the lighter isotope (that with fewer neutrons) reacts more readily creating products that are isotopically lighter than the reactant (Kendall and McDonnell, 1998). For example when ammonium is converted to nitrate by microbes during nitrification, ^{14}N will be favoured over ^{15}N resulting in the isotopically lighter nitrate being formed compared to the ammonium left behind.

Many biological processes have multiple steps (like nitrification) where each step has a possibility to cause isotopic fractionation. The overall fractionation during a process is dependent on the number of steps in the process, soil pH, and species of organism and size of the reservoirs of compounds involved in the reaction. Different reactions will cause different fractionations of N, meaning that $\delta^{15}N$-values can possibly be used to identify the origin of the nitrogen in a sample. Stable nitrogen isotopes has been used by many to identify sources of nitrate or ammonium in groundwater, for example; Jiang et al. (2009), Li et al. (2010), Liu et al. (2006), Moore et al. (2006) and Widory et al., (2004; 2005). Following here is a description of which $\delta^{15}N$-values that can be expected from samples containing nitrogen of different origin and how different processes affect N-isotope fractionation, see also Figure 2.

2.2.1 Fertilisers

Synthetic fertilisers produced by fixation of atmospheric N_2 such as urea, ammonium nitrate and potassium nitrate usually show $\delta^{15}N$-values quite similar to that of atmospheric N_2, between -4‰ to +4‰ (Kendall and Aravena, 2000). Organic fertilisers (e.g. plant composts and animal waste) have a wider range of compositions of $\delta^{15}N$ of +2‰ to +30‰. Animal manure commonly has high $\delta^{15}N$-values in the range of +10‰ to +20‰ (Widory et al., 2005). Wastewater N can usually be differentiated from fertilisers using $\delta^{15}N$ alone, but it can be hard to separate fertiliser nitrate from soil nitrate enriched in $\delta^{15}N$ due to denitrification.

2.2.2 Wastewater and septic systems

Septic systems and wastewater can be important point sources for releasing contaminated water containing high levels of NH_4^+ or NO_3^- to the groundwater. Nitrogen in human and animal waste is hydrolyzed to ammonia (NH_3) and then ammonium. NH_3 is easily lost to the atmosphere as gas depleted in ^{15}N. This leaves remaining NH_4^+ highly enriched in ^{15}N. The NH_4^+ is usually oxidized by microbes in the presence of oxygen to NO_3^- with high $\delta^{15}N$-values. Widory et al. (2004; 2005) reported $\delta^{15}N$-values in NO_3^- between 4.3 ‰ and 17.4 ‰ for sewage water while Liu et al. (2006) reported $\delta^{15}N$-values in NH_4^+ between 4.7 ‰ and 5.6 ‰ in sewage water. Water contaminated by human or animal waste yields similar $\delta^{15}N$-signals and can as such not be differentiated from each other using ^{15}N alone.

2.2.3 Soil nitrogen

Organic soil nitrogen can be a significant source of both NO_3^- and NH_4^+ in the groundwater (Kendall and Aravena, 2000). Soil NO_3^- is commonly enriched in ^{15}N due to denitrification. Soil nitrogen usually has $\delta^{15}N$-values in between fertilisers and human/animal

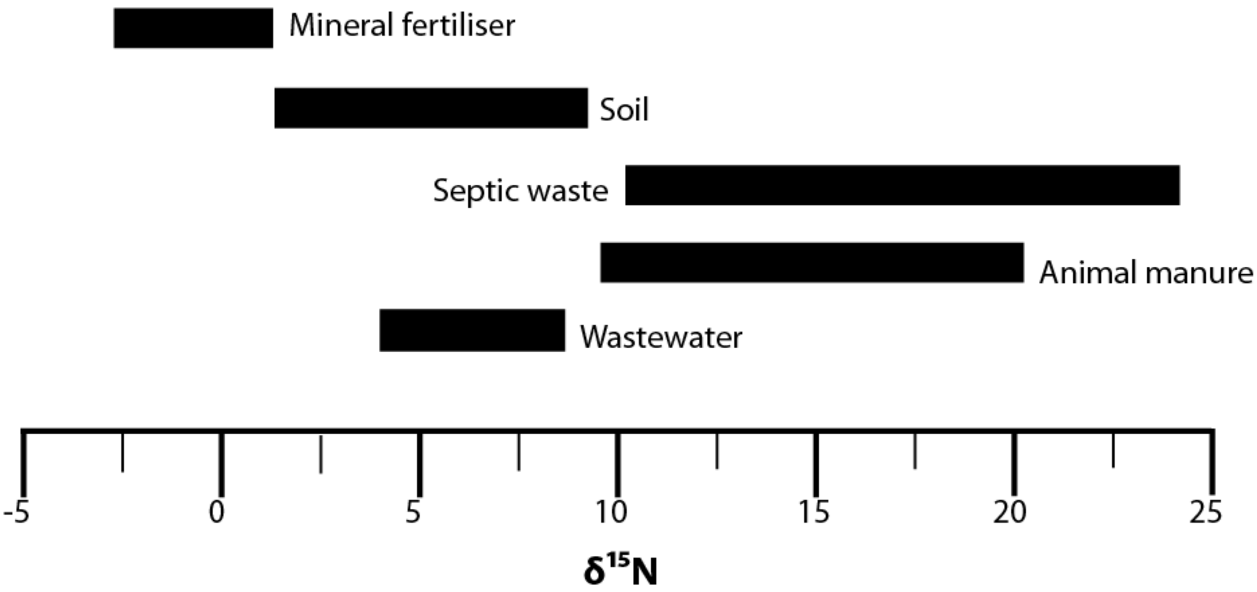

Figure 2. Reported ranges of δ^{15}N-values expressed in ‰ for different anthropogenic sources of N. Data compiled from; Widory et al. (2004), Liu et al. (2006), Kendall and Aravena (2000) and (Heaton, 1986).

waste and overlaps both their ranges of δ^{15}N-values. Soil nitrogen is often successfully separated from wastewater because of the sometimes very high ^{15}N-values in wastewaters. NO_3^- originating from soil nitrogen is however not usually distinguishable from fertiliser NO_3^- based on ^{15}N analyses alone.

2.2.4 Assimilation

Assimilation is the uptake of N-containing compounds (NH_4^+, NO_2^- or NO_3^-) by living organisms. Assimilation discriminates between isotopes and favours the isotopically lighter ^{14}N over ^{15}N. The apparent fractionation caused by assimilation of microorganisms ranges between -1.6 and +1.0 ‰ (Kendall and Aravena, 2000). Assimilation by plants does not significantly change the isotopic composition of residual soil nitrogen.

2.2.5 Nitrification

Nitrification is a multistep process where organic material is first degraded to produce NH_4^+ which is then oxidized to NO_2^- and then NO_3^- as described in chapter 2.1.1. If a system is N-limited, nitrification rates will be low and hence minimize fractionation of N. However if there is a large amounts of NH_4^+ available, for example from fertilisation, nitrification will be stimulated and the oxidation of NH_4^+ is likely to cause a large fractionation of N. Studies have shown that the resulting NO_3^- may be depleted in ^{15}N with up to 35 ‰ compared to the source of the NH_4^+ (Kendall and Aravena, 2000). As the NH_4^+ is used up, nitrification rates decreases until oxidation of NH_4^+ is no longer the rate-determining step. The δ^{15}N-values of total soil nitrate will then start to increase towards the pre-fertilisation levels. Mineralisation of organic N to NH_4^+ does not cause a significant amount of fractionation (Kendall and Aravena, 2000).

2.2.6 Denitrification

Denitrification is a multi-step biochemical process where NO_3^- is transformed to nitrogen gas (N_2) by microorganisms under low-oxygen conditions. During denitrification residual NO_3^- is enriched in ^{15}N exponentially as NO_3^- concentrations decreases while resulting N_2 is depleted in ^{15}N (Kendall and Aravena, 2000). This effect can be substantial, denitrification of a nitrate fertiliser with an original δ^{15}N-value of +0‰ can yield residual NO_3^- with δ^{15}N-values of +15 to +30 ‰. This can be a problem in the search for the N source, since this is the range of δ^{15}N-values that can be expected from manure or septic waste.

2.2.7 Dissimilatory nitrate reduction to ammonium (DNRA)

Under anaerobic conditions ammonium can be reduced to nitrate by microbes. DNRA favors the lighter ^{14}N isotope and as such the resulting NH_4^+ will be depleted in ^{15}N compared to the remaining NO_3^- (Lehmann et al., 2003).

2.3 Boron isotopes as environmental tracers

Boron, B, in not found in nature as a pure element but instead in compounds such as the borate minerals and boric acid. Boron compounds are usually found in small concentrations (<0.05 mg/L) in natural groundwater in the form of boric acid, $B(OH)_3$, and as the $B(OH)^{4-}$ anion but studies have shown that groundwater can show considerable variations in B levels (Vengosh et al., 1999). Groundwater affected by anthropogenic activities may show greatly elevated concentrations of boron. The most common anthropogenic use of boron is production of sodium perborate ($NaBO_3{\cdot}nH_2O$), which is commonly used as a bleaching agent in detergents, soaps and toothpaste, and results in its common occurrence in anthropogenic wastewater (Barth, 1998). Boron is also sometimes added to mineral fertilizers for use in areas with low amounts of boron in irrigation water and high amounts of precipitation (Vengosh et al., 1999). Boron has two stable isotopes, ^{10}B and ^{11}B which have the natural abundances of about 20 % and 80 % each respectively. The ratio $^{11}B/^{10}B$ is usually expressed as $\delta^{11}B$ in per mille relative to the standard sample of boric acid according to;

$$\delta^{11}\mathrm{B}(‰) = \left[\frac{\left(\frac{^{11}\mathrm{B}}{^{10}\mathrm{B}}\right)_{\mathrm{sample}}}{\left(\frac{^{11}\mathrm{B}}{^{10}\mathrm{B}}\right)_{\mathrm{NBS951}}} - 1\right] \times 1000 \; (4)$$

where NBS951 is the standard for boric acid. Boron isotopes has previously been used as an environmental tracer by among others Basset et al. (1995), Komor (1998), Vengosh et al. (1999) and Widory et al. (2004; 2005) to identify possible contamination sources of groundwater and surface waters. Boron is generally considered to be a conservative tracer. As such an advantage of using $\delta^{11}B$ in conjunction with $\delta^{15}N$ is that the $\delta^{11}B$-values are not influenced by for example nitrification, volatilization, and oxidation/reduction reactions (Bassett, 1995). Fractionation of boron can however occur by adsorption to clay particles where the lighter ^{10}B isotope is favoured, leaving water enriched in ^{11}B. This effect is however small in most environments since uncharged boric acid, $B(OH)_3$, is the dominant form of boron where pH<9.24 and the sorption affinity of clay for $B(OH)_3$ is fairly weak (Hem, 1985; Palmer et al., 1987).

Barth (1998) and Widory et al. (2004, 2005) reported significant differences in both $\delta^{11}B$-values and B-concentrations between wastewater and natural groundwater. Manure and mineral fertilizers as well as wastewater have also been found to give different distinct isotope signals for boron (Widory et al., 2004; Widory et al., 2005). As can be seen in Figure 3, synthetic borate products seem to have much lower $\delta^{11}B$-values compared to organic substances. The low $\delta^{11}B$-values of wastewater might be due to high concentration of synthetic borates (i.e. sodium perborate) in

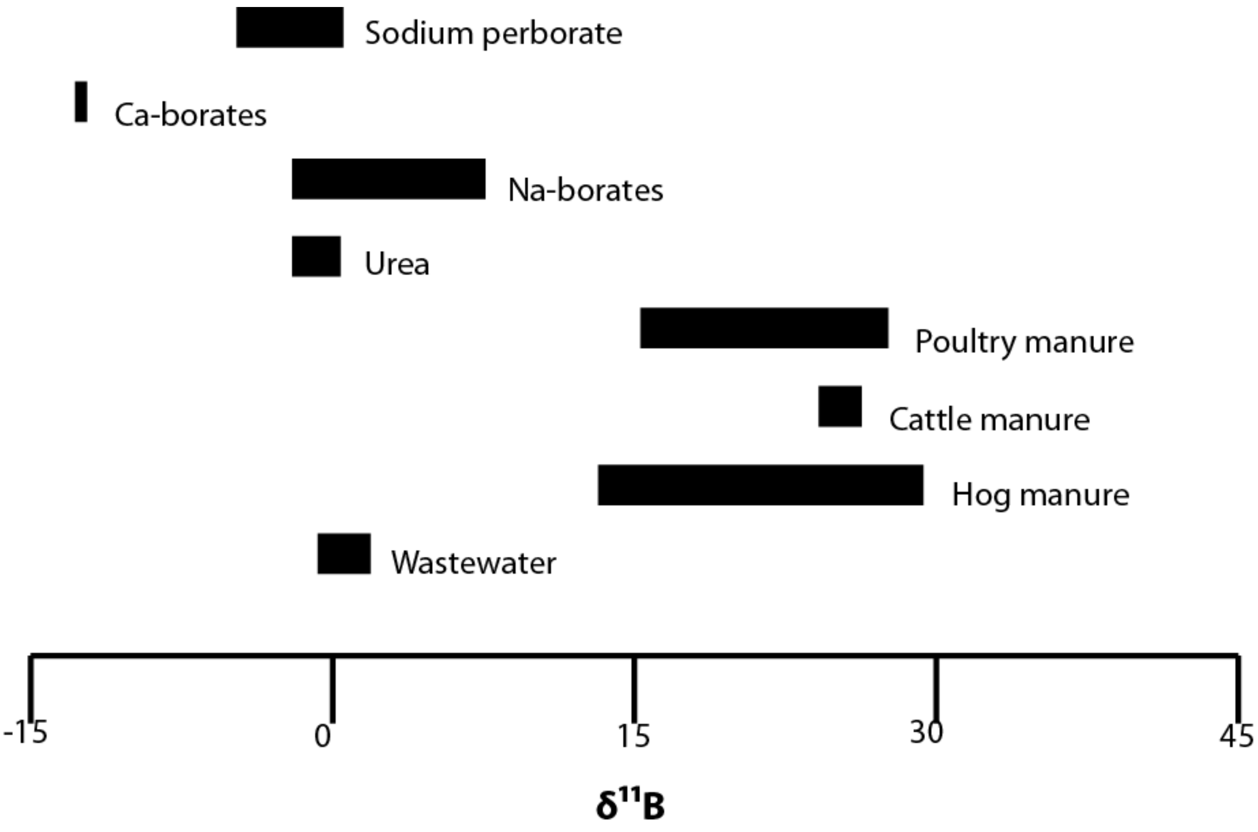

Figure 3. Reported ranges of $\delta^{11}B$ –values expressed in ‰ for different anthropogenic sources of boron. Data compiled from; Barth (1998), Bassett (1995), Komor (1997), Vengosh et al. (1999) and Widory et al. (2004).

wastewater. The $\delta^{11}B$-signature of the sodium perborate is similar to the borate minerals used in the production of the sodium perborate (Vengosh et al., 1999). Ca-borates are not used in bleaching agents but only as fertilizers.

2.4 Oxygen and hydrogen isotopes as environmental tracers

There are two stable isotopes of oxygen, ^{16}O (99.7% of all oxygen atoms) and ^{18}O (0.2%), and hydrogen, ^{1}H and ^{2}H (^{2}H is also known as deuterium and makes up 0.016 % of all hydrogen atoms) (Kresic, 2007). These isotopes combine to make up water molecules of different molecular mass (between 18 and 22). Ratios between the isotopes ($^{18}O/^{16}O$ and $^{2}H/^{1}H$) are expressed in δ-units relative to a reference standard (Vienna standard mean ocean water) in the same way as nitrogen and boron isotopes as described earlier. Fractionations of oxygen and hydrogen isotopes in water occur during freezing, melting, evaporation, condensation as well as chemical and biological reactions. As such $\delta^{18}O$ and $\delta^{2}H$ values in precipitation vary greatly around the world and seasonally in the same region. Average annual δ-values in precipitation is however rather constant at a single location. $\delta^{18}O$ and $\delta^{2}H$ values in groundwater will vary depending on the source of recharge and as such it is often used as an hydrological tracer to identify potential differences in the source of recharge. There is a strong correlation between $\delta^{18}O$ and $\delta^{2}H$ values which has been used to create a global meteoric water line (GMWL) with the equation (Kresic, 2007):

$$\delta_s^2\mathrm{H} = 8.17 \cdot \delta_s^{18}\mathrm{O} + 10.35 \; (5)$$

At a smaller scale local meteoric water lines (LMWL) can be constructed by measuring $\delta^{18}O$ and $\delta^{2}H$ in precipitation. This can then be used as a reference when evaluating the isotopic composition of groundwater.

2.5 Tritium/^{3}He dating of ground water

Tritium, ^{3}H, is an unstable isotope of hydrogen with a half-life of 12.43 years. Tritium is found naturally in low amounts in the upper atmosphere where it is created when nitrogen is bombarded by cosmic radiation (Kresic, 2007). Tritium levels are usually measured in tritium units (TU) where 1 TU equals 1 tritium atom per 10^{18} hydrogen atoms. Natural concentration of tritium in precipitation is about 5-20 TU. The testing of nuclear weapons during the 1950s and early 1960s lead to a massive increase of tritium in the atmosphere and precipitation during that time. The amount of tritium in precipitation during the bomb peak varies around the world, but for example it was around 2000 TU in parts of the USA in 1962. Concentrations have since then declined rapidly due to the short half-life of tritium. Tritium can be used to assess the age of a groundwater that has received recharge from precipitation in modern time. However since groundwater is usually not derived from a single source but rather subject to mixing, the tritium concentration in a groundwater sample can only provide a rough estimate of the age of the groundwater.

A more exact dating can be provided by also measuring the ^{3}He concentrations of a sample. ^{3}He is the daughter product of decaying tritium (Kresic, 2007). ^{3}He is a noble gas and as such virtually inert in groundwater and is not usually derived from anthropogenic sources. Subsurface sources of ^{3}He are usually minor and the following equation can be used to calculate the amount of tritiogenic ^{3}He (^{3}He resulting from radioactive decay of ^{3}H) in a sample (Kresic, 2007):

$$^{3}He_{trit} = 4.021 \cdot 10^{14} \cdot \left(^{4}He_{tot}(R_{tot} - R_{atm}) + {}^{4}He_{eq}R_{atm}(1 - \beta) \right) (6)$$

Where $^{3}He_{trit}$ is the amount of tritiogenic ^{3}He in TU, $^{4}He_{tot}$ is the measured ^{4}He concentration (cm^3 STP/g H_2O), R_{tot} is the $^{3}He/^{4}He$ ratio of the sample, R_{atm} is the atmospheric $^{3}He/^{4}He$ ratio (1.384 x 10^{-6}),$^{4}He_{eq}$ is ^{4}He concentration in air-equilibrated water (cm^3 STP/ g H_2O) and β is the difference in solubility between ^{3}He and ^{4}He (0.983).

If the amount of tritiogenic ^{3}He in a sample is known the age can be calculated by:

$$\tau = \frac{T_{1/2}}{ln2} ln\left(1 + \frac{^{3}He_{trit}}{^{3}H}\right) (7)$$

Where τ is the ^{3}H-^{3}He age in years,$^{3}He_{trit}$ is the amount of ^{3}He resulting from tritium decay, ^{3}H is the measured tritium concentration in TU and $T_{1/2}$ is the half-life of tritium. The above equations make the assumption that the sampled groundwater is unmixed . They also do not take into account the possible effects of dispersion and diffusion of the gases. As such modelling techniques might need to be applied to provide a more accurate estimation of the age of a groundwater.

3 Study area

3.1 Hanoi

Hanoi is the capital of the Socialist Republic of Vietnam and is situated by the Red River in the middle of the Red River delta, northern Vietnam. In 2005, urban Hanoi had approximately 3.1 million inhabitants (Van Horen, 2005). In and around Hanoi there is a lot of surface waters apart from the Red River, ranging from small ponds and streams to larger lakes. The water resources are used for irrigation, aquaculture, transportation, sewage disposal and recreation. Outside of urban Hanoi the land is dominated by cultivated fields and rice paddies, which equals about 53 % of the total land use of the Hanoi province (Thapa and Murayama, 2008). The most common crops are rice and corn but large fields of bananas can also be found. Large amounts of fertilisers are used in the agriculture. Chemical fertilisers dominate but manure (chicken) and wastewater are also commonly used (Khai et al., 2007).

3.2 Climate and hydrology

Northern Vietnam has a humid subtropical with generally high temperatures and lots of rain. The weather in Vietnam is dominated by the monsoon and as such there are two distinct seasons, a dry and cold one between November-April and a wet and warm between May-October. During the winter temperatures can fall to 6°C but reaches up to 45 °C during summer (Van Horen, 2005). Total annual average precipitation is 1678 mm, where 80-90% of the rainfall occurs during the rainy period. The Red River drains a catchment with an area of approximately 160 000 km^3. Discharge and water levels in the Red River varies considerably over the year and reaches annual maximum discharge of about 23 000 m^3/s in July-August and minimum during the dry season (January-May) of 700 m^3/s in Hanoi (Tanabe et al., 2003). The Red River carries heavy loads of sediment and the abundance of suspended silt particles colours the river red and has given it its name. Smaller streams, ponds and lakes are a common occurrence in the Hanoi province; about 16 % of the total area of the province are water bodies of some kind (Thapa and Murayama, 2008).

3.3 Geological setting and hydrogeology

Hanoi is located on a large sedimentary basin known as the Bac Bo plain. The city is underlain by unconsolidated Quaternary sediments of marine, deltaic and alluvial origin, which rests upon Tertiary deposits of Neogene age (Trafford et al., 1996). Climatic changes and past sea level transgressions and regressions have created a complex stratigraphy with rapid lithological changes both vertically and laterally. The sediments consist of lenticular channel deposits such as sand, gravel and cobbles interbedded with layers of finer material such as clay and silt. The total thickness of the sediments reaches over 400 m, whilst individual layers of sand and gravel sometimes exceed 30 m. In the south-western part of Hanoi, large peat deposits are found in the Quaternary sediments.

Beneath Hanoi are six different geological formations that make up two aquifer systems which are separated by a discontinuous semi-permeable layer of clay, see Figure 4. At some places only one of the aquifer systems is present due to large variations in

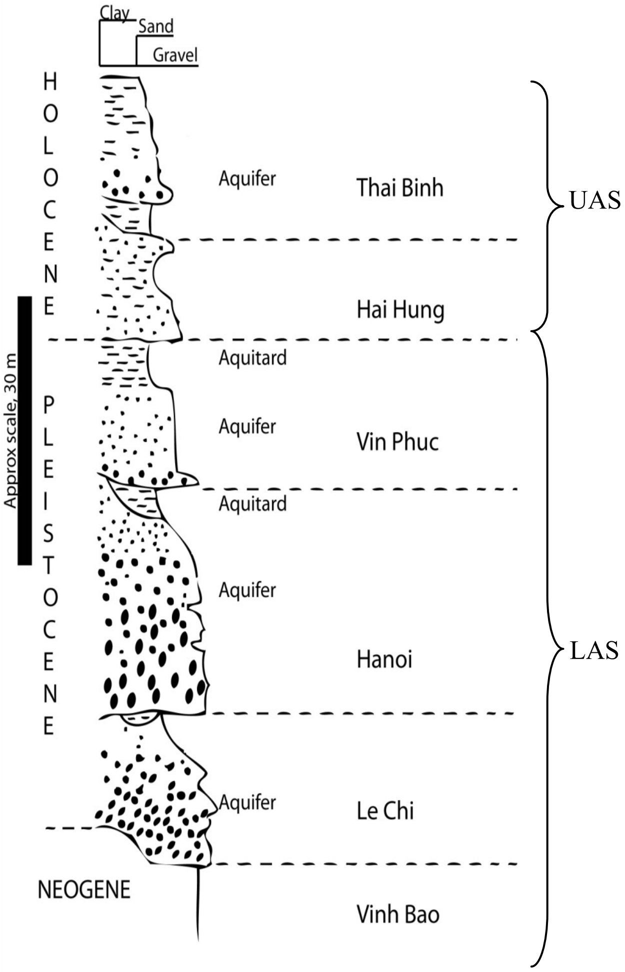

Figure 4. Generalized stratigraphy for the Hanoi area. The sediments make up two aquifer systems, the Upper Aquifer System (UAS) and the Lower Aquifer System (LAS). Modified from Harms-Ringdal (2007).

thicknesses caused by the meandering of the Red River channel.

The upper aquifer system (UAS) is made up of Quaternary sediments consisting of sand, silts and clays with a typical thickness of 20-40 m, but are at some places up to 70 m thick (Trafford et al, 1996). Two geological formations are found within the UAS, the Thai Binh formation and the Hai Hung formation. The Thai Binh formation makes up an unconfined shallow aquifer of Holocene age, consisting of alluvial deposits from the Red River with grainsizes ranging from silty clay to medium grained sand and cobbles (Van et al., 1996). Lacustrine and marine sediments consisting of silty clay, silty sand and peat makes up the underlying Hai Hung formation. Groundwater extraction from these layers is limited to a number of shallow private wells in more rural to semi-urban areas outside of central Hanoi.

Separating the upper aquifer system from the lower aquifer system (LAS) is the upper member of the Vin Phuc formation, a semi-confining layer of alluvial clay deposits (Trafford et al., 1996; Van et al., 1996). This aquitard is however discontinuous which makes the amount of leakage between the two aquifer systems highly variable, for example in the Yen Phu area north-east of Hanoi the aquitard is completely missing, resulting in total connectivity between the two aquifer systems.

Three formations of Pleistocene age create the lower aquifer system. The uppermost part of the LAS consists of the lower member of the Vin Phuc formation. This layer is characterised by gravels, pebbles and sand mixed with silt and clay (Van et al., 1996). Underlying Vin Phuc is the thick Hanoi formation. The Hanoi formation is made up of three members. The uppermost consists mostly of fine sediments like clayey silt with lenses of silty clay mixed with humus. The other members are mostly made up of coarser sediments ranging from coarse sand to gravel and cobbles. The lowermost formation of the LAS is named Le Chi. The upper part of Le Chi consists of poorly sorted clay, sand and silts of flood plain facies. The middle part is made up of old river beds consisting of well sorted silty fine sand. Coarser sediments of a river facies, like sand, cobble and pebbles dominate the lower part of the formation. These layers are generally highly permeable and yield large amounts of water. Reported values for transmissivities and storage coefficients are 700-2300 m^2/d and 0.002-0.1 respectively (Trafford et al., 1996). As such this is a major supply of water for the city of Hanoi. Underlying the Quaternary sediments is the Vinh Bao formation which consists of unconsolidated conglomerate, sandstone and claystone of Pliocene age.

The upper aquifer system receives its recharge from percolating rain water and surface water as well as the Red River which is in direct hydraulic contact with both the upper aquifer system and the lower aquifer system. During the rainy period the Red River is a major source of recharge for both aquifers. However during the dry season the water level in the Red River drops significantly and groundwater flow is reversed so the Red River is recharged by ground water from the aquifers. It has been proven that the groundwater level in both the Holocene and Pleistocene aquifers close to the river correlate closely with the water level in the Red River, indicating strong hydraulic contact. (Norrman et al., 2008; Van et al., 1996). The lower aquifer system also receives recharge in the form of leakage from the upper aquifer system.

Before groundwater extraction started in large scale during the 1960's, the piezometric level of the groundwater in the lower aquifer system was at about the same as the water table in the upper aquifer system, which means the system was static with little or no seepage between the two aquifer systems (Trafford et al., 1996). The large-scale extraction of groundwater has lowered the piezometric water level considerably in the LAS, which has induced steep vertical hydraulic gradients from the upper aquifer system to the lower. The high leakage is also seen as a lowering of the water table in the upper aquifer system. Trafford et al. (1996) calculated that the two aquifer systems had a combined storage capacity of 945 million m^3, while the total extraction between 1912 and 1996 was about 3.5 billion m^3 of groundwater. This calculation clearly shows that most of the groundwater pumped today should be of fairly recent origin. Today water outtake from the lower aquifer system reaches 750 000 m^3/d (Winkel et al., 2011).

3.4 The Nam Du well-field

The Nam Du well-field is located south of central Hanoi close to the Red River, see Figure 5. The Nam Du well-field is dominated by cultivated fields where the main crops grown are corn and bananas. In the area are also many canals and ponds used for irrigation and aquaculture. Large amounts of fertilizers and pesticides are used in the agriculture in the area. Nam Du is surrounded by the suburbs of Hanoi to the west and the Red River to the east. The well field consist of 18 production wells pumping water from the Pleistocene aquifer at a rate of 60 000 m^3/day (Pham, 2012, pers. comm.). In the area are also several monitoring wells used for a national monitoring program of groundwater levels and quality. A sewage plant lies in close vicinity to the Nam Du well field. Wastewater from Hanoi is drained in open canals to the sewage plant, not far from the Nam Du-area, where the water is collected in large basins. The only treatment domestic waste water receives is time for sedimentation and some biological purification. Industrial wastewater is treated by the respective industries before being led to a wastewater plant. From the wastewater plant the wastewater is led out in canals and discharged into the Red River.

4 Methods

4.1 The field study

The field study was carried out during April and May in 2011. Water samples were collected from 20 wells/boreholes spread throughout the area, 10 in the Pleistocene aquifer and 10 in the Holocene aquifer, see Figures 5C and 6. The wells that are labelled P(number) A/B are observation wells part of a national monitoring program. PX and PY are private wells while the ND wells are used for ground water extraction in large scale. The DHA/DHB boreholes were made for scientific purposes. The sampled locations in this study have been used in several previous studies regarding ammonium and arsenic mobilisation (Baric and Sigvardsson, 2007; Harms-Ringdal, 2007; Norrman et al., 2008). Samples were also collected from wastewater canals, ponds, the Red River and shallow groundwater from the Red River riverbank, see Figure 5. In total 29 objects were sampled. See Appendix 1 for a summary of all samples that were collected, what they were analysed for and which laboratory did the analyses of the different parameters.

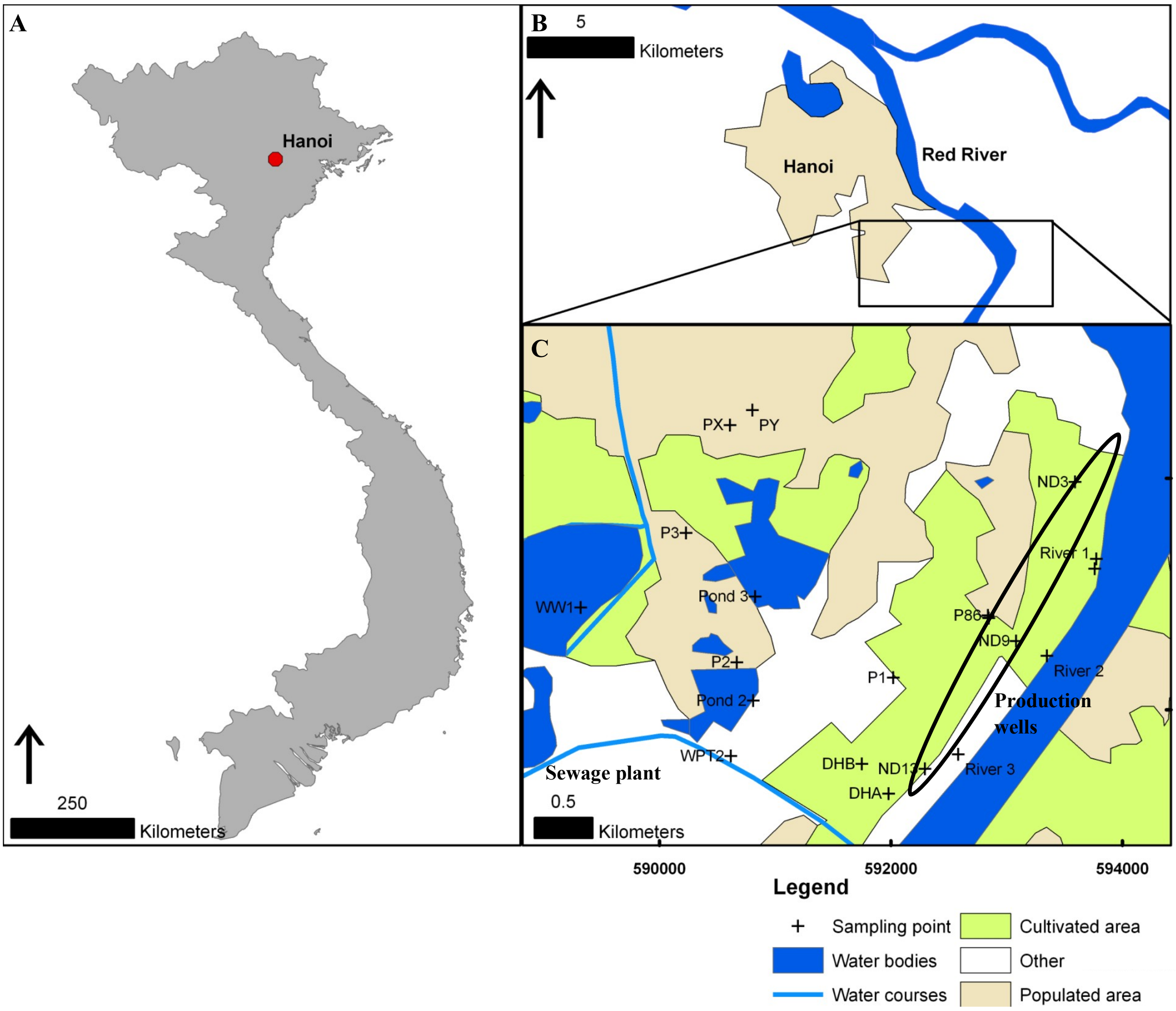

Figure 5. Location of the study area and sampling points. The production wells is located in the marked area. Geodetic model: WGS 84. Projection: UTM 48 N. Data from ESRI and Natural Earth Data. Land cover digitized from Google Earth (2009) .

Figure 6. To the left, one of P-boreholes and to the right one of the ND-wells.

4.2 Sampling and analyses

4.2.1 Sampling of water

Groundwater was extracted from existing wells using a Grundfos MP1 submersible pump driven by a gasoline fuelled generator or a battery driven SuperNova submersible pump. The pumps were directly connected to a flow-through cell with an Aquaread AP-800 Aquameter probe, see Figure 7. Water was led through the flow cell into contact with the probe, which was equipped with electrodes for measurement of pH, dissolved oxygen (DO), total dissolved solids (TDS), redox potential (against standard hydrogen electrode, SHE), temperature and conductivity. Water was pumped up and led through the flow cell until the values for dissolved oxygen had stabilized. The values for the measured parameters were noted after which sampling of groundwater commenced. Groundwater levels were also measured in the P and DHA/DHB boreholes.

Wastewater (collected from canals and ponds) and surface waters (collected from the Red River and ponds) were sampled in much the same way as the groundwater samples except that the samples were collected directly from the water bodies. A bottle attached to a long stick was used to collect the samples at a depth around 50 cm, although some ponds and canals were too shallow to allow for sampling at the 50 cm depth.

Samples were collected in acid washed polypropylene bottles (unless otherwise noted). Before sampling the bottles were rinsed three times with water from the source. Samples were taken so that no air (or as little as possible) was caught in the bottles. The lids of the bottles were screwed on tightly and then taped to prevent air from entering the samples. Samples for analyses of TOC, DOC, $\delta^{15}N$, $\delta^{11}B$ and bacteriological content (*E. coli* and total coliform) were kept cool at all times using chilly boxes filled with ice.

For analysis of major elements, metals, DOC and $\delta^{18}O$/ $\delta^{2}H$, 30 mL of water were filtered through a 0.45µm cellulose nitrate filter using a 60 mL plastic syringe connected to the filter using a short bit of silicon tubing and then acidified to pH <2 using 1mL of concentrated HNO_3 (65%). To separate arsenite, As (III), from arsenate, As(V), the sample was filtered through an As-speciation cartridge as described by Meng and Wang (1998) . Samples for determination of anions, alkalinity, NH_4^+ and TOC were collected unfiltered and non-acidified in 250 mL plastic bottles. Samples for TOC analyses performed by CETASD in Hanoi were collected in 24 mL glass bottles, and were acidified to pH <2 in the field using concentrated HCl.

Samples for analyses of $\delta^{15}N$ were taken in 500 mL acid washed PET bottles and stored in chilly boxes filled with ice before they were delivered to INST. The

Figure 7. The Aquaread AP-800 Aquameter probe with a flow-through cell.

$\delta^{15}N$ samples were neither filtered nor acidified. For analyses of $\delta^{11}B$, 125 mL of water was collected (not filtered or acidified) according to the normal procedure described above. One sample of rainwater was also taken from the roof of INST, for analyses of $\delta^{11}B$. The water samples for $\delta^{11}B$ analysis were kept cool at all times except during transport from Hanoi to Lund and later from Lund to Luleå. Samples for $\delta^{18}O$/ $\delta^{2}H$ consisted of 30 mL of unfiltered water.

Samples for analyses of bacteriological content were collected in clean 500 mL PET-bottles. These samples were immediately put on ice and delivered to the laboratory the same day as the samples were collected to prevent bacterial growth.

Samples for dissolved noble gases and tritium were taken from three of the boreholes (P1A, P1B and P2A), two from the Pleistocene aquifer and one from the Holocene. Water samples for tritium analyses were collected using a submersible pump in the same way as the other water samples and collected in 500 mL plastic bottles. Sampling of dissolved noble gases was done using a passive gas sampler supplied by the Noble Gas Lab in Utah. The sampler consists of a small metal cylinder with a permeable membrane (Gardner and Solomon, 2009). The samplers were connected to a long piece of plastic tubing and lowered into the boreholes to a depth corresponding to about the centre of the screen of the borehole. The samplers were left there for about 72 hours before they were collected. During collection a bicycle pump was connected to the plastic tube and a pressure was applied to the sampler to close it while the sampler was still submerged in the well. The samplers were then retrieved and immediately shut tight using special clamps.

4.2.3 Analyses of general groundwater chemistry and $\delta^{18}O$/ $\delta^{2}H$

General chemical analyses were performed by EAWAG, Switzerland. Element concentrations were measured with ICP-MS. Phosphate and ammonium ions were determined by photometry while nitrate, sulphate and chloride were determined by ion chromatography. TOC and DOC were analyzed with a TOC 5000A analyzer

Isotope ratios $^{18}O/^{16}O$ and $^{2}H/^{1}H$ of the surface water and groundwater samples were determined by cavity ring-sown spectroscopy (Picarro L1102-i, Santa Clara, CA) against calibrations performed with water isotope standards of the International Atomic Energy Agency. The overall analytical errors are 0.2‰ and 1.2‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively.

4.2.4 Analyses of $\delta^{15}N$ and $\delta^{11}B$

$\delta^{15}N$ were measured at INST. Samples were filtered through a 0.45 μm Millipore filter and then passed through a column packed with 2 g AAG 50W X8 cation exchange resin to retain $NH4^{+}$. The enriched ammonium was eluted from the column with 10% HCl. The excess HCl was neutralized with NaOH (0.05M) to pH 6.8. The ammonium-chloride was crystallized using a dry freezer and approximately 385 μg NH4Cl was placed in a tin capsule for analysis of $\delta^{15}N$ in a mass-spectrometer.

ALS environmental in Luleå, Sweden analysed the $\delta^{11}B$ samples using inductively coupled plasma sector field mass spectrometry (ICP-MFS). For a description of the methodology, see http://www.isotope-analysis.com/

.

4.2.5 Bacteriological content

The samples for bacteriological content was analysed by the Centre for Preventive Medicine in Hanoi. Bacteria from the water samples were grown on substrates and then the number of bacteria were counted, or approximated in case of large number of bacteria. Results were reported as most probable number of bacteria (MPN) / 100 mL of water.

4.2.6 Tritium dating of groundwater and noble gas measurements

$^{3}H/^{3}He$ and dissolved noble gases were performed by Dissolved and Noble Gas Lab in Utah. Concentrations were measured using magnetic-sector mass spectrometry. For a detailed description of the methodology see Bayer et al. (1989) and http://www.earth.utah.edu/noblegaslab/.

4.3 Mixing models

A pollution process were a polluted end-member is diluted by an unpolluted end-member can be described with a simple binary mixing model. The concentration of a substance, X, in a sample can be described with the following equation:

$$[X] = [X_b] \cdot f + [X_p](1 - f) \quad (8)$$

Where X_p is the polluting end-member, X_b is the baseline (unpolluted) end-member and f ($0 \leq f \leq 1$) is the proportion of the unpolluted end-member in the mixing (Buschmann and Berg, 2009; Widory et al., 2005). When using staple isotopes as environmental tracers the following equation system can be acquired: (Widory et al., 2005):

$$\left[\begin{array}{c} [X] = [X_b]\cdot f + [X_p]\cdot(1-f) \\ [X]\cdot\delta X = [X_b]\cdot f\cdot\delta X_b + [X_p]\cdot(1-f)\cdot\delta X_p \end{array}\right. \quad (9)$$

The equations above allow for estimations of the amount of mixing if concentrations and isotope ratios are known. In this study the above mixing model was used to construct mixing lines to see if the high ammonium concentrations could be explained by binary mixing from a pollution source rich in ammonium.

5 Results and interpretation

Below are the results concerning ammonium and possible sources, while arsenic in detail will be treated in a different Master's Thesis by Olsén (in pub.). During this project, large amounts of data have been gathered and samples have been analyzed by several different laboratories, see Appendix 1 for a list of all samples. Measured parameters that are discussed in detail in this chapter are found in Table 1 while all data are found in Appendix 2.

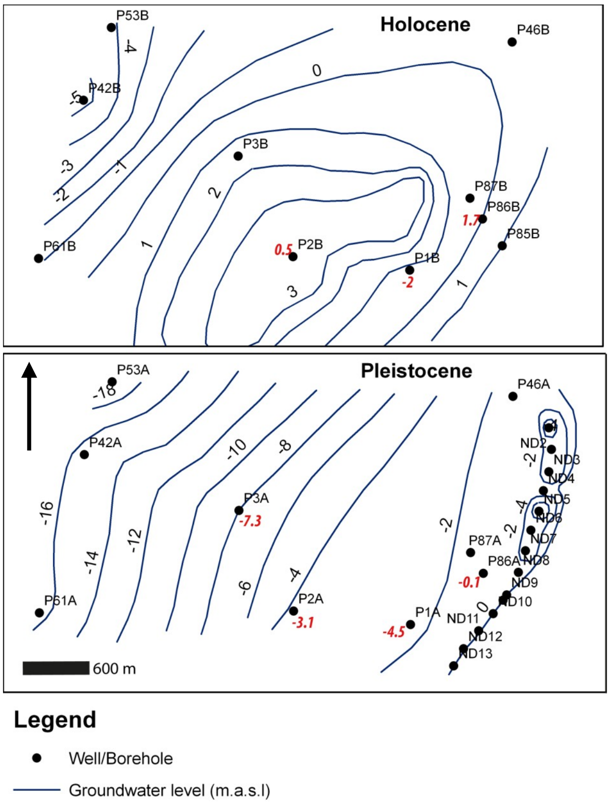

Figure 8. Groundwater levels and piezometric head levels in the Holocene and Pleistocene aquifer respectively. Groundwater levels are from late April in 2004, data from Norrman et al. (2008). The red numbers indicate the groundwater levels that were measured in this study.

5.1 Groundwater flow and general chemistry

Though groundwater levels were measured in the P, DHA and DHB boreholes, a satisfactory map of the groundwater flow could not be constructed due to too few data points. Figure 8 shows maps, revised from Norrman et al. (2008), of groundwater levels (or piezometric head in case of the Pleistocene aquifer) constructed using groundwater monitoring data from 2004. The groundwater levels measured in this study are added to this map and differ slightly from those measured in 2004. This can be attributed to the poor elevation data for this study and/or different pumping rates and slightly different time of year for the measurements. Considering that, the pattern for groundwater flow today is probably similar to 2004.

Groundwater flow in the Holocene aquifer is divided by a groundwater divide around P2B and flows inland towards the west and towards the Red River and ND-wells to the east. In the Pleistocene aquifer system, groundwater flows inland towards the production wells (ND-wells) from the Red River. A clear drawdown around the production wells can be observed. Around P2A there is a groundwater divide and water flows inland to the west and towards the Red River and production wells to the east. There is also a clear difference in groundwater level and piezometric head level between the two aquifers signifying that induced leakage from the Holocene aquifer to the Pleistocene aquifer is occurring. A modflow calculat-

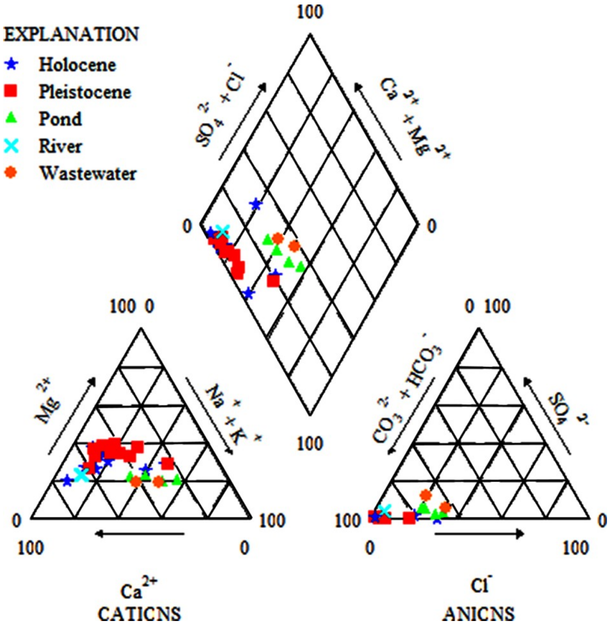

Figure 9. Piper diagram showing main chemical composition of the water samples taken from the Nam Du area.

ion with input field values collected in 2009, shows that leakage from the Holocene aquifer constitutes between 13 and 23 % (depending on season) of the total recharge to the Pleistocene aquifer (Pham, 2012, pers. comm.).

The distribution of major an- and cations are shown in a piper diagram, Figure 9. For exact concentrations, see Appendix 2. The sampled groundwater and the Red River are generally dominated by HCO_3^- and Ca^{2+} with low amounts of Cl^- and SO_4^{2-}. The sampled ponds and wastewater are more influenced by Cl^- and SO_4^{2-}, of which Cl^- are a typical constituent of sewage water (Kresic, 2007; Liu et al., 2006; Widory et al., 2004). Wastewaters and ponds also shows a higher tendency toward Na^+ and K^+ compared to the groundwater in the two aquifers and the Red River. The hydrogeochemical composition of the groundwater is usually similar to the Red River, indicating that the Red River is a major source of recharge. Some samples plot closer to the ponds, indicating that standing water bodies contribute to a significant amount of recharge.

Measured $\delta^{18}O$ and δ^2H plotted against each other reveals two distinct groups of water in the Pleistocene aquifer system, see Figure 10. The lines in Figure 10 represents the LMWL (local precipitation) with a slope of 9.9 and the GMWL with a slope of 8.17 (Berg et al., 2008). The GMWL is a good approximation for the isotopic composition of the Red River . One group of wells from the Pleistocene aquifer plots on the GMWL and close to the values measured in the Red River indicating that river water is probably the main source of recharge. The wells with the isotopic composition closest to that of the Red River are the ND-wells which are used for large scale groundwater abstraction. The other group of wells plot in between that of the river values and that of the Holocene aquifer system and the ponds. It indicates that these wells receive large amounts of recharge by leakage from the Holocene aquifer system. Many samples plot beneath the LMWL indicating that the source of recharge has been subject to evaporation. The groundwater in the Holocene aquifer system plots on a straight line between the river isotope signal and surface water (ponds) indicating that one group might be receiving most recharge from a source similar to that of the ponds, while those with lighter isotopic composition may be receiving more recharge from the Red River. It should however be noted that the hydrogeochemical and isotopic composition of the surface waters (ponds and the Red River) measured in this study might not be representative since they could vary seasonally.

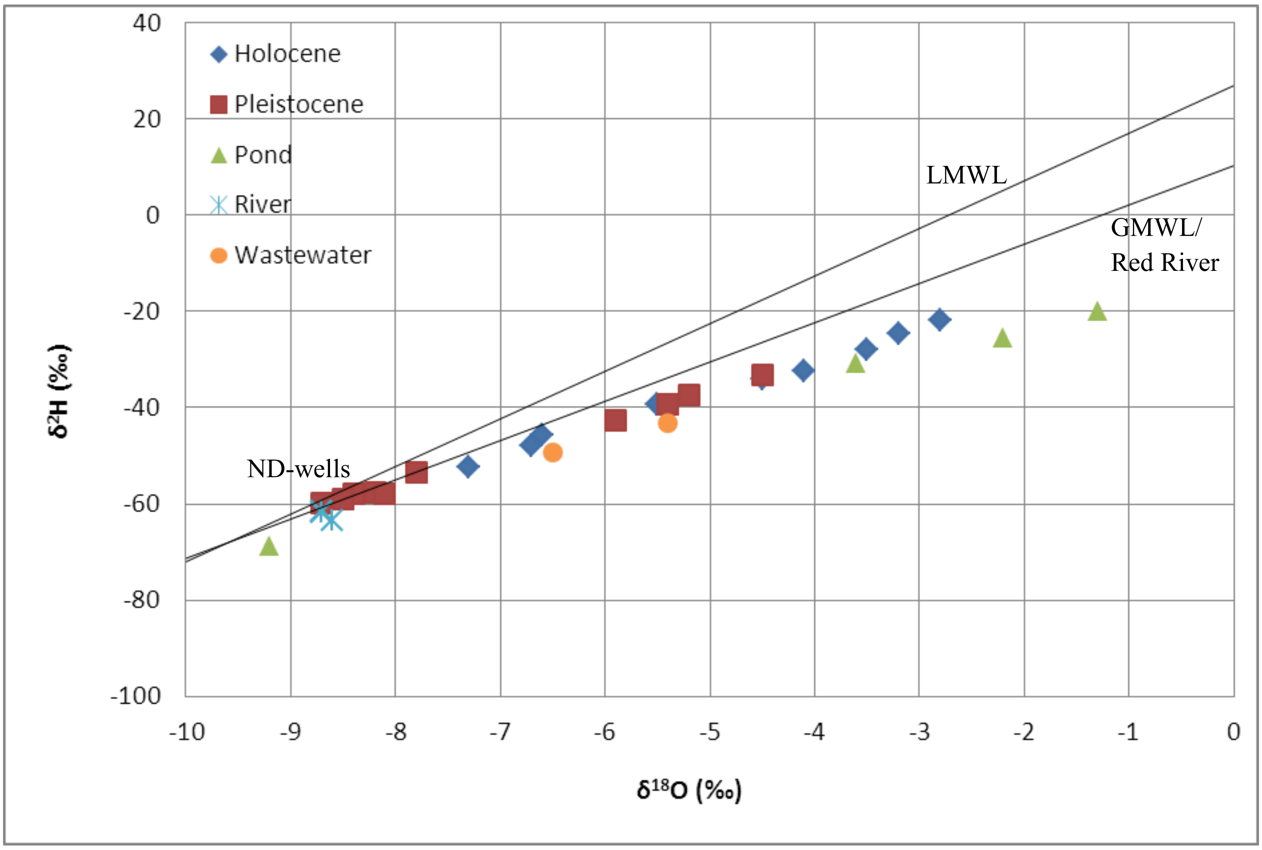

Figure 10. δ^2H vs. $\delta^{18}O$ in groundwater, ponds, wastewater and the Red River in April and May 2011. The LMWL is derived from $\delta^2H=9{,}9\delta^{18}O+27$ (Berg et al. 2008)

Table 1. Selected measured parameters. Values highlighted with red and bold text exceeds the WHO guidelines recommended values for drinking water. Empty cells mean that either a sample has not been taken, no analyses could be performed (due to economical or technical limitations) or that the sample has been lost due accidents like bottles breaking during transport. The light grey color and the *-annotation means that the concentration is below the limit of detection. Values for pH, Eh and DO were measured in the field using an Aquaread flow cell AP-800. For values of all measured parameters see Appendix 2.

ID	Sample type	pH	Eh mV	DO (%)	As(tot) µg/L	As(III) µg/L	Ni µg/L	Mn mg/L	NO_3^- mg/L	TOC mg/L	B µg/L	$\delta^{11}B$ ± ‰	NH_4^+ mg/L	$\delta^{15}N$ ± ‰	Colifrom MPN/100 mL	E-coli MPN/100 mL
DHA14	Holocene	7.29	-205,0	1.2	**594**	**523**	0.72	0.28	<0.25*	3.7	12		14.5	8.59	0	0
DHA18	Holocene	7.18	-179,0	1.4	**504**	**488**	1.50	0.21	<0.25*	3.7	16	-10.2	18.0	7.46	9	**4**
DHA22	Holocene	7.09	-182,0	1.8	**420**	**397**	<0.1*	0.22	<0.25*	2.1	16		7.5	6.84		
DHA30	Holocene	6.83	-135,6	1.9	**200**	**186**	<0.1*	0.22	<0.25*	5.0	27	11.5	29.0	4.15	4	0
DHB22	Holocene	7.08	-173,3	1.7	**375**	**356**	<0.1*	0.36	<0.25*	2.8	16		5.7	6.85	7	0
P1B	Holocene	6.96	-176,3	1.0	**374**	**330**	15.00	0.34	<0.25*	12.6	47	11.5	35.2		23	**9**
P2B	Holocene	6.92	-152,7	0.6	**95**	**17**	6.20	0.11	<0.25*	19.9	40	18.4	69.8	13.09	43	**7**
P3B	Holocene	6.33	-92,4	1.2	**40**	**38**	0.90	0.36	<0.25*	10.9	15	-2.7	8.3	0.42	150	**9**
PY	Holocene	6.68	-131,3	2.6	**11**	**11**	0.14	0.17	<0.25*	1.9	7.7		1.2	3.87	0	0
Riverbank	Holocene	7.64	-43,2	1.2	9.3	7.1	<0.1*	**0.51**	<0.25*	1.2	<1.3*		0.1		4	0
DHA52	Pleistocene	6.96	-154,4	0.7	**114**	**102**	1.60	0.17	<0.25*	8.5	12	7.9	27.0	2.14	43	**7**
DHB52	Pleistocene	6.96	-145,6	0.9	**80**	**78**	1.90	0.11	<0.25*	3.2	12		10.8	4.13	9	**4**
ND13	Pleistocene	6.99	-134,2	6.5	**91**	**88**	0.20	0.22	<0.25*	2.0	6.2		4.1		0	0
ND3	Pleistocene	6.93	-139,6	1.6	**72**	**72**	<0.1*	**0.41**	<0.25*	1.8	5.2		2.4	1.39	0	0
ND9	Pleistocene	6.78	-109,4	1.3	**85**	**84**	0.32	0.39	<0.25*	1.9	5.1		5.3	5.84	0	0
P1A	Pleistocene	7.06	-173,4	0.1	**412**	**388**	<0.1*	0.37	<0.25*	4.7	18	20.9	18.3	4.17	9	**4**
P2A	Pleistocene	6.85	-148,3	0.4	**152**	**145**	2.20	0.07	<0.25*	4.0	15	5.0	13.5	4.42	23	**4**
P3A	Pleistocene	6.65	-132,3	1.0	**139**	**132**	3.20	0.08	<0.25*	10.5	10	-0.6	22.5	6,5	0	0
P86A	Pleistocene	7.02	-179,8	0.4	**299**		<0.1*	0.19	<0.25*	3.9	17	19.2	6.0	5.51		
PX	Pleistocene	6.51	-61,1		**22**	**21**	<0.1*	**0.63**	<0.25*	1.9	5.4		4.1		0	0
Pond DHA	Pond				4.5	1.7	3.00	0.01	1.9	9.1	31	8.9	0.7		>2400	**1100**
Pond2	Pond				9.3	1.6	2.60	0.01	2.2	13.4	53	10.0	0.9		>2400	**>2400**
Pond3	Pond				**172**	5.4	2.30	0.02	2.1	17.8	74	6.5	1.5		>2400	**460**
Pond86	Pond				**80**	4,3	2.10	**0.51**	9.8	6.3	36	5.4	0.6	13.85	>2400	**1100**
River1	River				3.6	0.7	0.33	<0.01*	<0.25*	2.5	3.9	-1.3	0.4		>2400	**460**
River2	River				3.4	<0.5*	0.38	<0.01*	<0.25*	1.6	2.4		0.3		>2400	**>2400**
River3	River				3.3	<0.5*	<0.1*	<0.01*	0.3	1.2	2.4		0.1		>2400	**460**
WPT2	Wastewater				**19**	**16**	3.30	0.20	6.9	12.3	46	4.6	5.2	13.05	>2400	**460**
WW1	Wastewater				**10**	1.6	3.70	0.14	6.1	15.4	42	-0.9	1.1	12.4	>2400	**460**

Almost all groundwater samples have very high concentrations of iron, Fe, with an average of 11.56 mg/L in the Holocene aquifer system and 10.83 mg/L in the Pleistocene aquifer system. Several groundwater samples also show high concentrations of manganese (Mn), between 0.11-0.36 mg/l in the Holocene aquifer system and 0.07-0.63 mg/L in the Pleistocene aquifer system. Four samples, (3 in the Pleistocene aquifer, 1 in the Holocene aquifer) exceeded the guideline value for drinking water set by WHO of 0.40 mg/L. Additionally five samples (3 in the Holocene aquifer, 2 in the Pleistocene aquifer) showed concentrations very close to the guideline value, between 0.34 – 0.39 mg/L. The high concentrations of the redox sensitive Mn and Fe species can as such be attributed to the reducing conditions (Appelo and Postma, 2005).

Arsenic concentrations in all sampled groundwater are very high, between 9-594 µg/L in the Holocene aquifer and 22-412 µg/L in the Pleistocene aquifer. Arsenic concentrations in all groundwater samples except one are well above the provisional guide line value of 10 µg/L set by the WHO. The highest concentrations are found in the shallow DHA wells where concentrations range between 200 µg/L (DHA30) and 594 µg/L (DHA14). Arsenic in groundwater is mainly present in the oxidation state of +3 (arsenite) which corresponds well to the reducing conditions (Berg et al., 2008; Kresic, 2007; Norrman et al., 2008). Several of the sampled surface and waste waters also contains high concentrations of As, see Table 1. High concentrations of As in water is usually a sign of anthropogenic activities but in this case it is likely "recycled" groundwater that is causing the high As concentrations in waste- and surface waters. The Vietnamese national standard for arsenic in drinking water is 10 µg/L (Pham, 2012, pers. comm.), as such water originating from the civic water network (for example treated groundwater pumped from Nam Du) and is released as wastewater into open canals may contain arsenic concentrations of up to 10 µg/L, while groundwater pumped from private wells with no purification may have concentrations of several hundred µg As/L . If this water is then discharged into canals and ponds it could cause the measured high As concentrations.

5.2 Ammonium

The highest levels of NH_4^+ are found in the samples taken from the Holocene aquifer system where concentrations vary widely, between 0.1 (Riverbank, which probably contains a high amount of Red River water) to 69.8 mg/L (P2B). The average concentration of NH_4^+ in the Holocene aquifer system is 18.9 mg/L. In the Pleistocene aquifer system concentrations vary between 2.4 and 27.0 mg/L with an average concentration of 11.4 mg/L. NO_3^- concentrations are below the limit of detection (<0.25 mg/L) in all sampled groundwater, which seems reasonable considering that the anoxic and reducing conditions in the groundwater would prevent nitrification of NH_4^+. The reducing conditions would cause any infiltrating NO_3^- to be lost as N_2(g) due to denitrification or be reduced to NH_4^+ by the process of DNRA. The importance of DNRA is

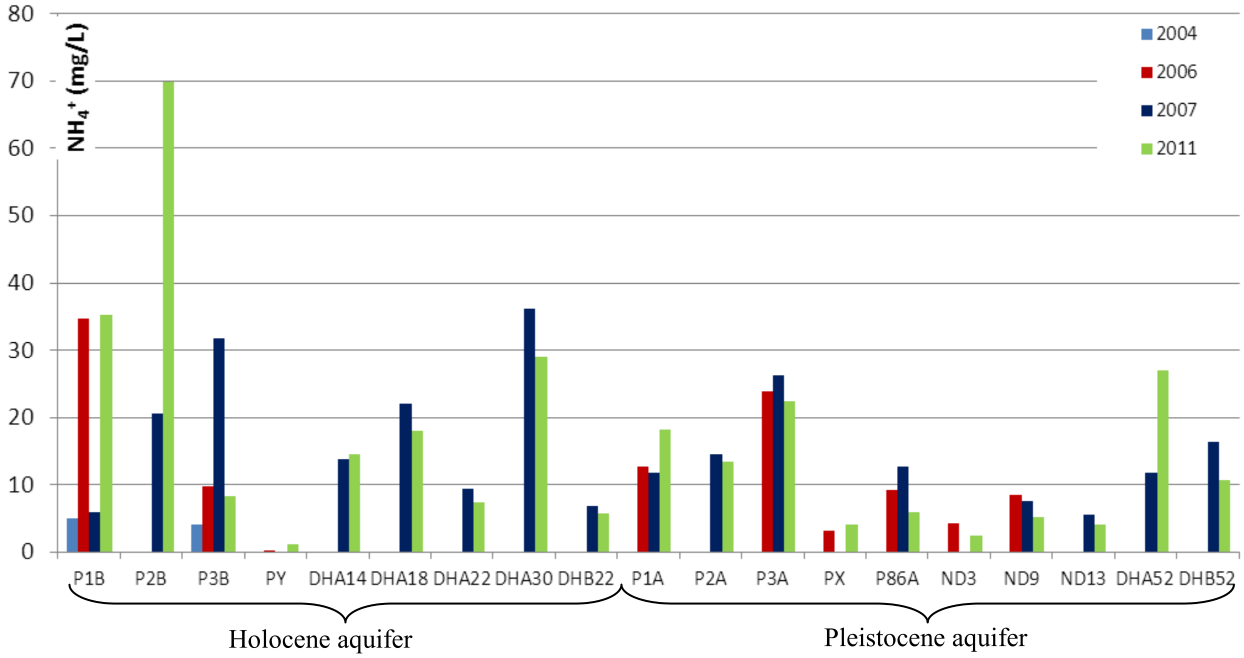

Figure 11. NH_4^+ concentrations in groundwater measured in this study (2011) compared to concentrations reported by Harms-Ringdal (2007) for years 2004 and 2006 and Baric and Sigvardsson (2007) for 2007.

usually subordinate to that of denitrification (Appelo and Postma, 2005; Smith et al., 1991), but in some climates, especially warm and humid, DNRA may be an important process (Rutting et al., 2011). Surface water samples had much lower concentrations of NH_4^+ than the groundwater, an average of 3.2 mg/L in the wastewater and 0.9 and 0.3 mg/L in the ponds and Red River respectively. NO_3^- concentrations were detectable in most surface waters, in medium levels in ponds and wastewater (average of 4.0 and 6.5 mg/L) and in low levels in the Red River (average of 0.1 mg/L). All samples were also tested for nitrite (NO_2^-), but concentrations were below the limit of detection in all samples. Overall the concentration of total N in the groundwater samples is usually in the same range as the sampled wastewater. In several groundwater samples, the total N concentration however far exceeds that of any surface water sample. The measured concentrations of ammonium are mostly in good agreement with previous studies (Baric and Sigvardsson, 2007; Harms-Ringdal, 2007). When comparing the results of this study with results from previous studies in the same area, the measured concentrations of a NH_4^+ seems to be quite stable in most wells, see Figure 11. In a couple of wells from the Holocene aquifer (P1B, P2B) the measured concentrations of NH_4^+ has varied significantly. Drastic changes (increases) in NH_4^+ concentrations probably indicate that the NH_4^+ is derived from an anthropogenic source but could also be attributed to contamination of samples or measurement errors.

When studying all water groups (groundwater, surface waters, wastewaters, and ponds) no relationship can be found between TOC and total N, see Figure 12. The comparison to total N instead of NH_4^+ are to correct for possible effects DNRA since surface waters had very low concentrations of NH_4^+ but quite high concentrations of NO_3^-. However studying just the groundwater there is a quite strong correlation (R^2=0.77, n=20) between NH_4^+ and TOC concentrations. This correlation was also found to be significant P<0.00. This means that the ammonium likely originates from a source rich in TOC.

NH_4^+ concentrations corresponds well to concentrations of nickel, Ni, when removing an outlier, P1B (R^2=0.70, n=19), see Figure 13. Including the outlier gives a much weaker correlation, R^2=0.38. Ni concentrations in the groundwater vary between below the LOD (<0.1 µg/L) and 6.2 µg/L. Most groundwater samples have concentrations below 2 µg/L. One borehole (P1B) has a much higher concentration reaching 15.0 µg/L. High concentrations of Ni are usually an indicator of anthropogenic influence, for example Ni-Ca battery disposal, metal industries and sewage sludge deposition (Uren, 1992). Ni is also a micronutrient for plants and commonly adsorbed to dissolved organic matter, DOM (Fageria et al., 2002). Since concentrations of Ni in the groundwater are in the trace amounts that could be expected naturally, degradation of organic matter in the sediments is a likely source of Ni. The very high level of Ni in the P1B sample compared to the others is possibly a sign of that P1B is influenced by anthropogenic activities. No correlation could be seen between As concentrations and NH_4^+

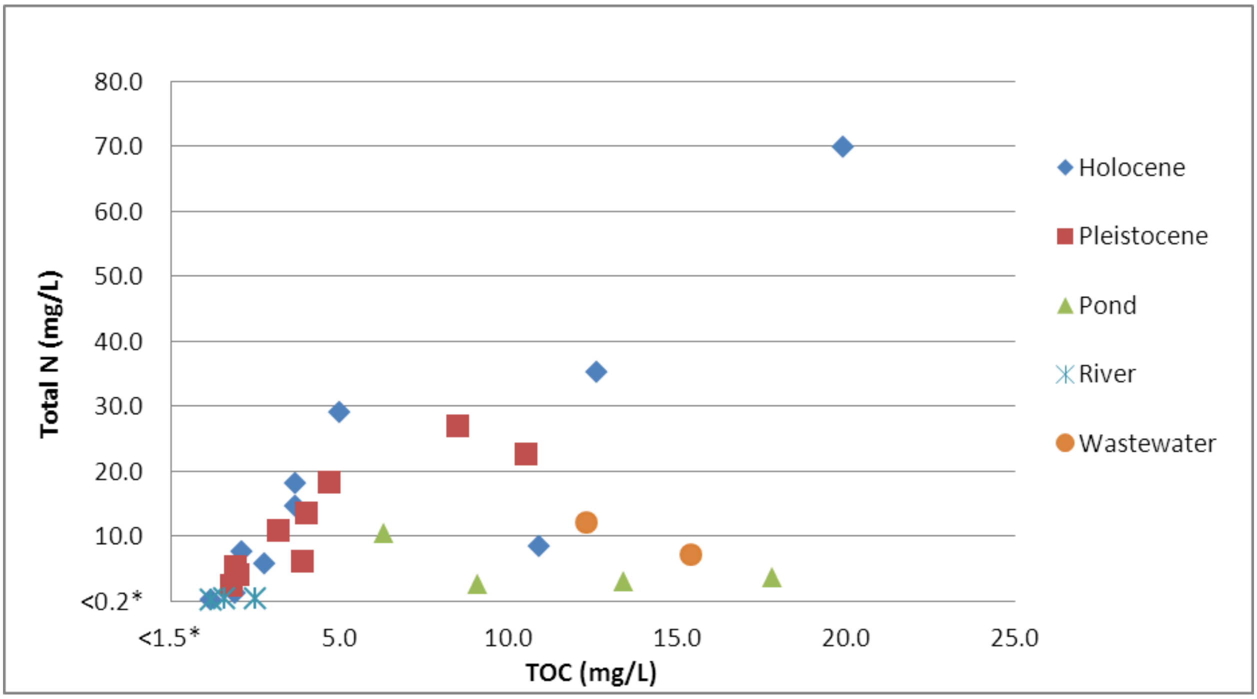

Figure 12. The graph is showing total N concentrations vs. TOC. A significant correlation between the two was found in the sampled groundwater, R^2=0.77.

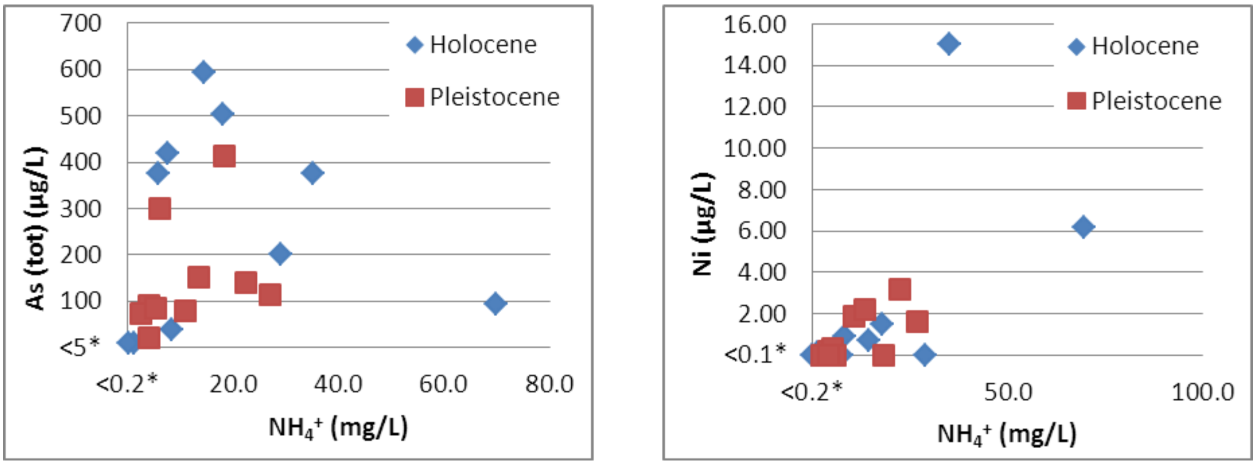

Figure 13. Correlation plots between NH_4^+ and As and Ni. R^2 values are 0.38 and 0.70 respectively.

concentrations in groundwater (R^2=0.013, n=20).

The measured $\delta^{15}N$ values in groundwater vary between 0.42 - 13.09 ‰ (average 6.41‰) and 1.39-6.50 ‰ (average 4.26) in the Holocene and Pleistocene aquifer respectively. The NH_4^+ in Pond86 and wastewaters are highly enriched in ^{15}N, between 12.4 and 13.85 ‰, in the range normally found in animal manure or wastewater. These values are much lower than those reported by Harms-Ringdal (2007), which showed $\delta^{15}N$ values between 26 - 31 ‰ in most groundwater samples. Harms-Ringdal also reported isotopic signals for ponds, between 23 and 28 ‰. Most of the samples from both the Holocene and the Pleistocene aquifer system show $\delta^{15}N$ values corresponding to what can be found in soil organic matter, see Figure 14. Most of the samples are also in the isotopic range that could be expected in sewage water. If the NH_4^+ in groundwater are originating from a source enriched in ^{15}N (e.g. animal manure) there should be a trend of increasing $\delta^{15}N$ values with increasing concentrations of ammonium. No such trend can be seen here (R^2=0.37). Few samples are in the isotopic range of mineral fertilisers which makes it unlikely that mineral fertilisers are a major source of NH_4^+. One sample from the Holocene aquifer system (P2B) has a very high concentration of NH_4^+, 69.8 mg/L, and is heavily

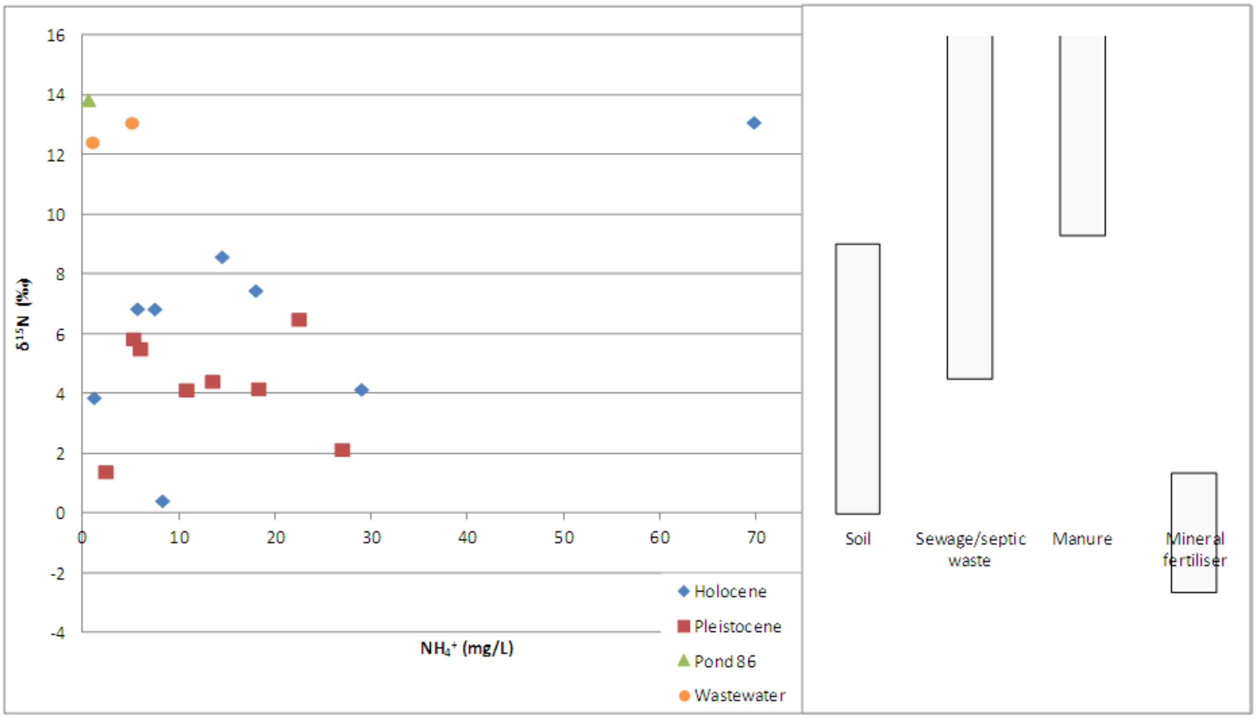

Figure 14. The graph is showing $\delta^{15}N$ values vs. NH_4^+ concentrations. Most groundwater samples plots in the $\delta^{15}N$ range of both soil N and sewage. $\delta^{15}N$ values for soil, sewage, manure and fertilizers are compiled from Heaton (1986), Kendall and Aravena (2000) Liu et al. (2006) and Widory et al. (2004).

enriched in ^{15}N (13.09 ‰) indicating pollution from a source highly enriched in ^{15}N, most likely by leaking sewage water or manure. Since this type of anthropogenic influence is only seen in this well it is possible that the well is poorly constructed and therefore receives a high amount of leaking wastewater or manure. Interestingly this borehole has an isotopic signal very similar to that of the sampled wastewaters, but with much higher concentrations of NH_4^+ possibly indicating that the sampled wastewater is heavily diluted by for example precipitation.

Figure 15 below shows a mixing line constructed using a binary mixing model (equation 9), using the groundwater sample with the lowest NH_4^+ concentration (PY) as the unpolluted end-member and P2B as the polluting end-member. δ^{15}N -values are plotted against total N concentration to make sure possible effects of DNRA is taken into account. Most groundwater samples plots far below and to the right of the mixing line which shows that a simple binary mixing model with one polluting end member does not explain the high NH_4^+ concentrations in Nam Du. Studying the way the data plots, it seems like there should be at least one more end member, characterized by high NH_4^+ concentrations and low δ^{15}N –values. Interestingly the sampled wastewaters plot very close to the mixing line, which could indicate that the wastewater is indeed heavily diluted and that P2B is polluted by wastewater.

Two profiles were also created from well-logs to see if there was a connection between NH_4^+ concentrations and/or δ^{15}N values depending on the thickness of the aquitard and distance to the Red River, see Figure 16. While no clear trend can be seen in the profiles, some things of interest can be seen. In locations P3, DHA and DHB the highest ammonium is found in the deeper borehole(s). If the ammonium is derived from a surface source the higher concentration would be expected to be found in the shallower borehole. From the different groundwater levels in the aquifers it is evident that induced leakage from the Holocene to the Pleistocene occurs.

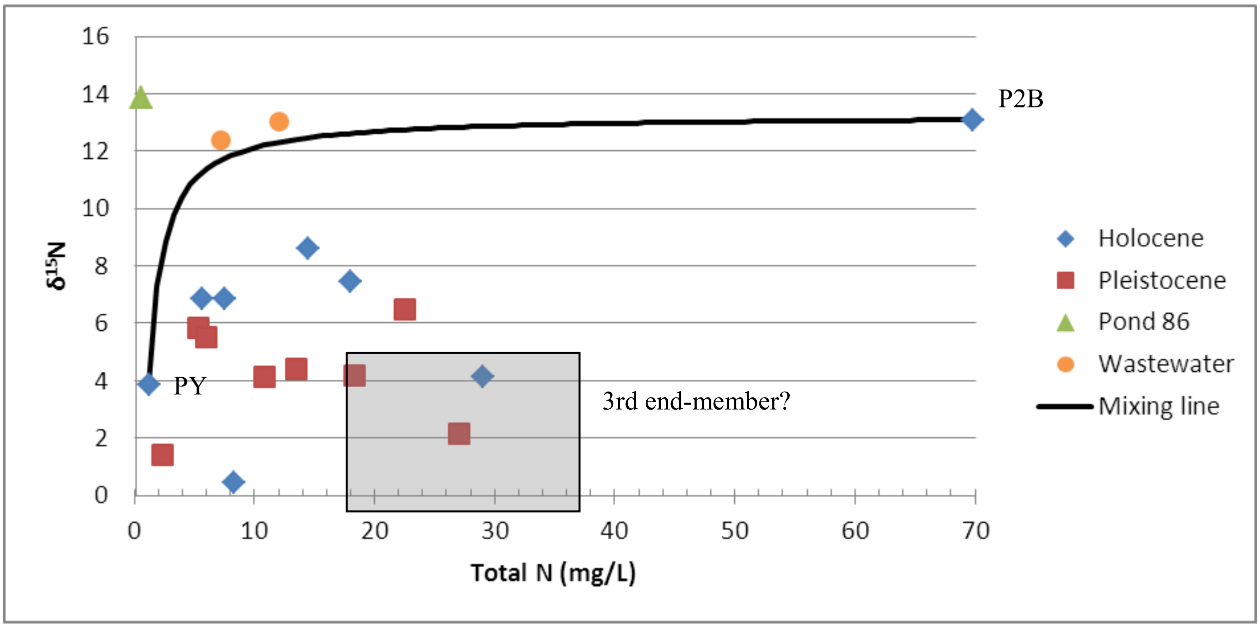

Figure 15. Graph showing a binary mixing model using the least polluted and the most polluted boreholes as end members. The grey box represents possible δ^{15}N and N ranges of a third end member.

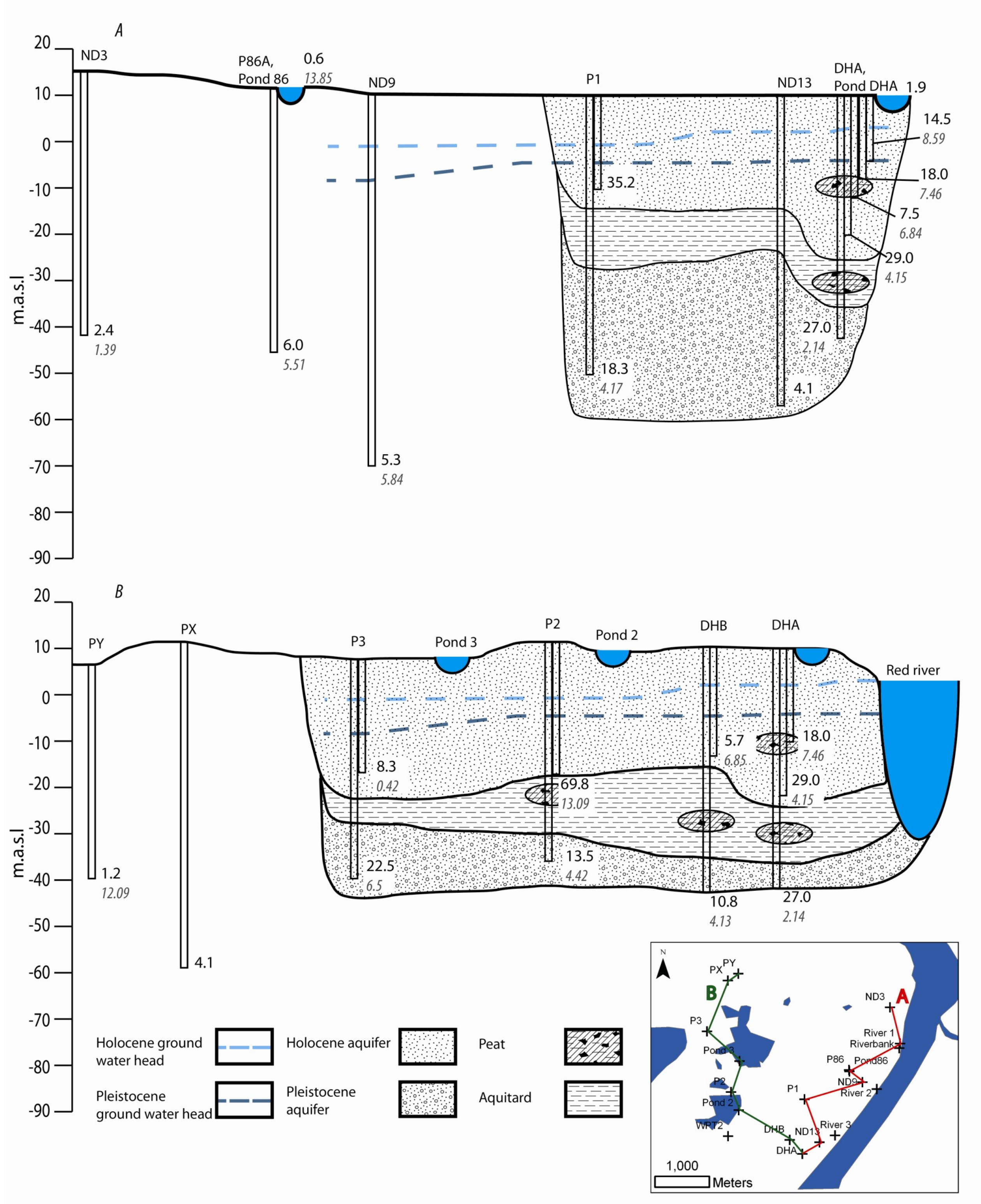

Figure 16. NH_4^+ concentrations (bold black numbers) and $\delta^{15}N$ values (italic grey numbers) for those samples that were analysed, in wells/boreholes along two transects, one parallel to Red River (A) and one from boreholes close to the Red River to boreholes further inland (B). Horizontal distances, ponds and the Red River are not to scale. For boreholes where logs could not be acquired, stratigraphy has been left out.

5.3 Boron

Boron concentrations are overall quite low in most samples. Boron is found in varying concentrations between 5.1 and 17.0 µg/L (average of 10.2 µg/L) in groundwater samples from the Pleistocene aquifer. The concentrations measured in the Holocene aquifers varies between below the limit of detection (<1.3 µg/L) and 45.0 µg/L (average concentration of 18.8 µg/L) and seems to be higher compared to samples from the Pleistocene aquifers, though this difference can not be confirmed statistically. The highest concentrations of B were found in the wastewaters and ponds. Even though B concentrations in the sampled wastewaters are quite low, it is still higher than in almost all sampled groundwater, indicating that "high" B concentrations in groundwater could be a sign of infiltrating surface water such as ponds or wastewater. A correlation plot between the depth of the borehole and B-concentrations possibly shows no clear correlation between B-concentration and borehole depth (R^2=0.35, n=20), see Figure 17 to the right. By studying the shape of the plot is seems like there might be a trend of decreasing B concentrations with increasing depth of the well, more samples are needed to confirm this. The highest concentration in groundwater is found in the shallowest borehole and the lowest concentration is found in the deepest borehole.

The measured δ^{11}B values vary greatly, ranging from -0.6 to 20.9 ‰ in the Pleistocene aquifer and -10.2 to 18.4 ‰ in the Holocene aquifer. Pond and wastewater samples exhibit a narrower range of values between 5.4 to 10.0 ‰ and -0.9 to 4.6 ‰, respectively.

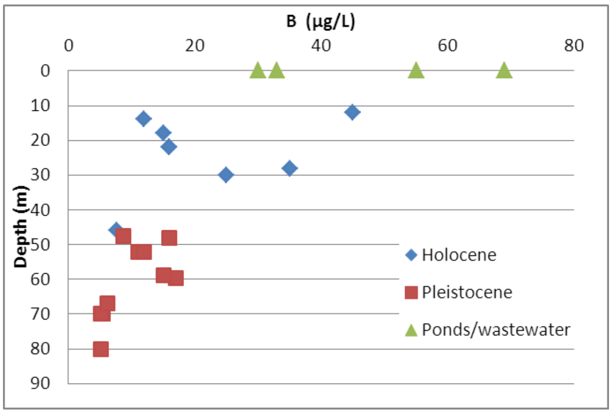

Figure 17. Correlation plot between depth of the borehole and B-concentrations. R^2=0.35.

The isotopic signal of wastewater corresponds relatively well to those reported by other authors, though boron concentrations are much lower than previously reported (Bassett et al., 1995; Vengosh et al., 1999; Widory et al., 2004; 2005). The Pleistocene aquifer does not show any clear signs of anthropogenic influence when looking at B since concentrations are low and δ^{11}B –values are in the range of the sampled rain and river water, see Figure 18 below. B concentrations and δ^{11}B –values are also shown along two profiles, see Figure 19. Two samples from the Pleistocene aquifer has δ^{11}B values slightly above that of rain, which could be a sign of anthropogenic influence (manure), but since the B concentrations are very low this is probably due to natural variations or processes such as fractionation by adsorption to clay particles (Palmer et al. 1987). One of the Holocene samples (P2B) has a fairly high B concentration of 40 µg/L and a δ^{11}B val-

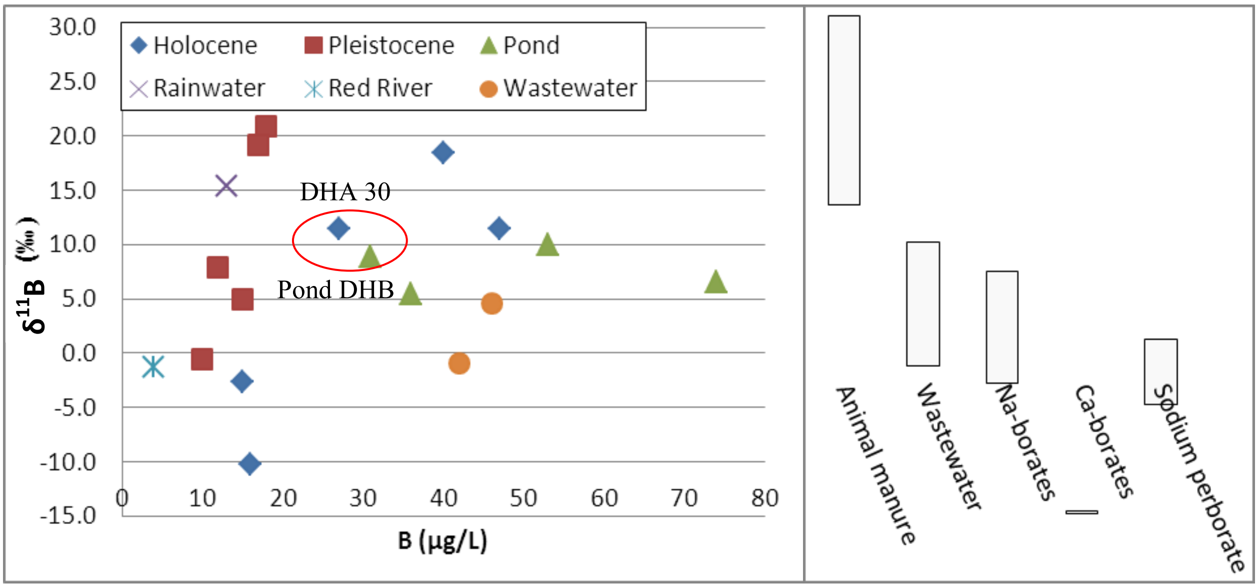

Figure 18. δ^{11B} values vs. B concentrations. δ^{11B} values for different anthropogenic sources compiled from Barth (1998), Bassett et al. (1995), Komor, (1997) Vengosh et al. (1999) and Widory et al. (2004).

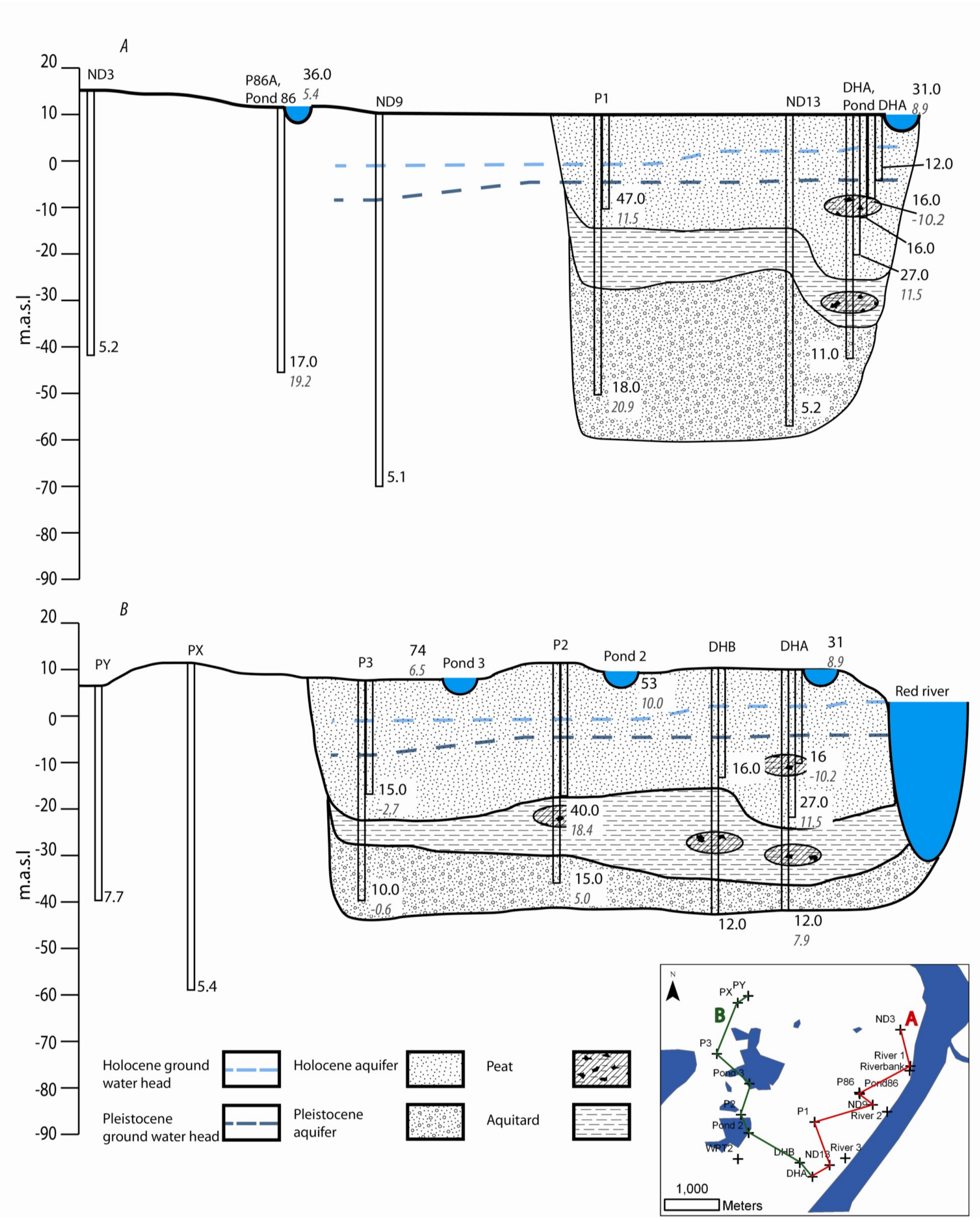

Figure 19. B concentrations (bold black numbers) and $\delta^{11}B$ values (italic grey numbers) for those samples that were analysed, in wells/boreholes along two transects, one parallel to Red River (A) and one from boreholes close to the Red River to boreholes further inland (B). Horizontal distances, ponds and the Red River are not to scale. For boreholes where logs could not be acquired, stratigraphy has been left out.

ue of 18.2 ‰ possibly indicating influence of animal manure which would be consistent with the high $\delta^{15}N$-value and NH_4^+ concentration also found in this borehole. B concentrations and $\delta^{11}B$ values of two samples from the Holocene aquifer are similar to the values measured in some of the ponds which might indicate that groundwater from these boreholes are effected by infiltrating surface water. This is especially true in the case with the sample DHA30 which has a B concentration and $\delta^{11}B$-value similar to that of Pond DHA which lies in the immediate vicinity of the DHA boreholes. However water from DHA18 has a low B concentration and is highly depleted in ^{11}B. If Pond DHA is the source of B in DHA30, water from DHA18 would be expected to have a similar concentration of B and $\delta^{11}B$ -value, since it is more likely to be in hydraulic contact with the pond than the deeper borehole. In fact water from DHA30 has the highest concentration of all DHA -boreholes, see the profile in Figure 18. An explanation for this could be that the pollution event occurred some time ago and traces can no longer be seen in the shallower boreholes. However, as can be seen in Figure 18, in boreholes P1, P2 and P3, there is higher B concentrations in the shallower borehole which is what would be expected if the B is derived from an anthropogenic source.

There seems to be a trend of increasing NH_4^+ concentrations with increasing B concentrations in the sampled groundwater (R^2=0.58). This indicates that at least some amount of the NH_4^+ in the groundwater could be derived from a source rich in B. However as seen in Figure 20, the sampled wastewaters and pond are characterized by high B concentrations and low NH_4^+ concentrations, indicating that the sampled wastewaters and ponds are not a likely source. B is an essential micronutrient for some plants and is frequently incorporated to organic matter as borates which are released when organic matter is degraded (Yona, 1996). If mineralization from organic matter is major source of NH_4^+ it is possible that B is also mineralized at the same time which would explain the possible trend between NH_4^+ and B.

5.4 Bacteriological content

Coliform and E-coli bacteria are found in large amounts (>2400 MPN/100mL) in all surface waters indicating pollution from wastewater, human and/or animal excrement (WHO, 2008). Coliform bacteria are found in seven wells in the Holocene aquifer and in four wells in the Pleistocene aquifer. E-coli are also encountered in four of the wells in both the Holocene and Pleistocene aquifers. The average number of total coliform bacteria, 27/100 mL of water, seems to be higher in water from the Holocene than in the Pleistocene aquifer with an average of 9 MPN/100 mL of water, although this difference cannot be verified statistically due to the low number of samples. Corre-

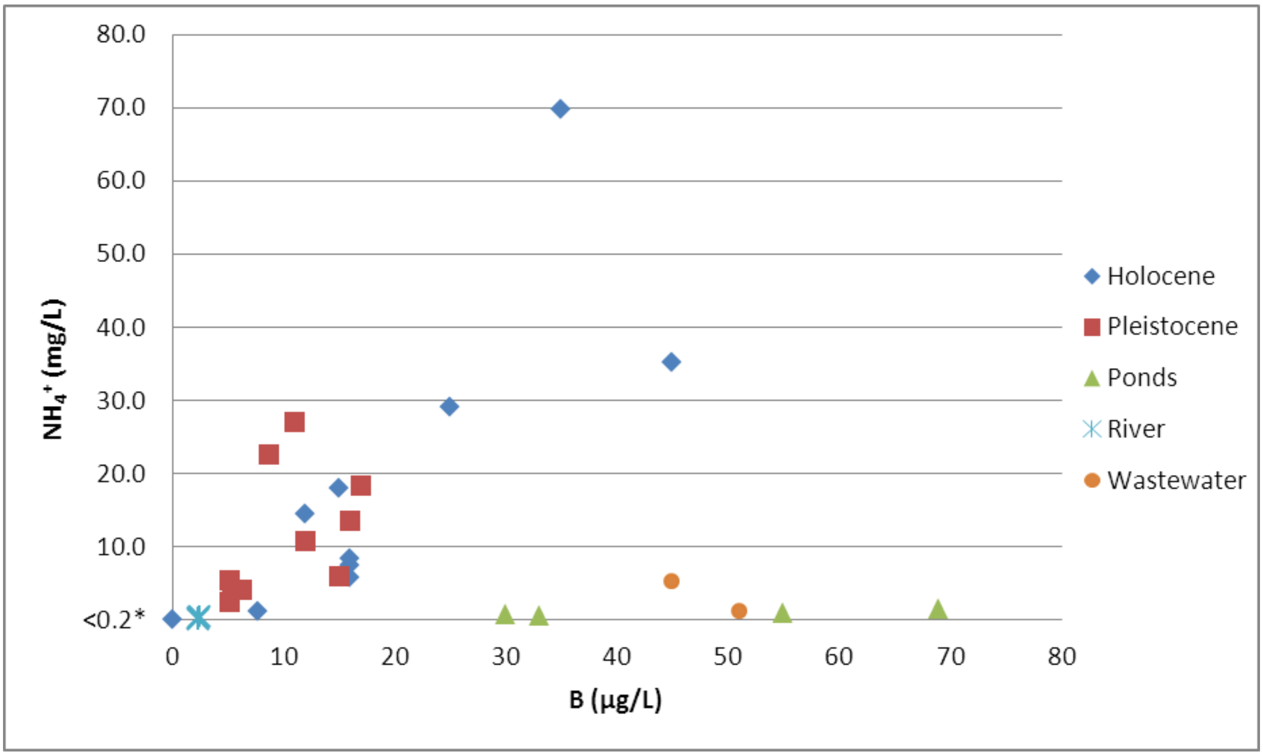

Figure 20. Correlation plot between NH_4^+ and B in groundwater. R^2=0.58.

sponding values for *E. coli* are 3 MPN/100 mL and 2 MPN/100 mL for the Holocene and Pleistocene aquifers respectively. According to the WHO-guidelines, water where the presence of *E. coli* has been confirmed is not suitable for drinking. The WHO has not issued any guide line value for the number of total coliform bacteria, but according to for example the Swedish drinking water guidelines, water containing 10 coliform bacteria per 100 mL of water is unsuitable for drinking (SLVFS 2001:30). The presence of bacteria in just some wells could indicate that leakage of wastewater is localized to a few point surface sources or that some wells are poorly constructed. Care should be taken when interpreting the results of the bacteriological content since samples are easily contaminated. This is especially true for the Pleistocene wells/boreholes since microorganisms like bacteria are usually encountered in shallow aquifers with high permeability (Kresic, 2007). The presence of coliform bacteria or *E. coli* in some wells in the Pleistocene aquifer could also be explained by poor well construction, allowing dirty surface water to leak into the well/borehole on the side of the well casting if it is not sealed tightly. However, coliform bacteria are present in wells showing other signs of anthropogenic influence like P2B and P1B which has isotopic signals of NH_4^+ and B similar to that of animal manure as well as high concentration of NH_4^+ and B. This indicates that coliform bacteria or *E. coli* can be expected to be found in wells affected by anthropogenic activities and are as such a clear sign that surface water is infiltrating down to the groundwater, at least to the Holocene aquifer.

5.5 Tritium and noble gas dating

The samples taken for $^3H/^3He$-dating were stripped of He and other noble gases. Stripping (degassing) of noble gases in groundwater can occur if some other processes are generating gas below the water table, like $N_2(g)$ from denitrification or methane, $CH_4(g)$, from methanogenesis (Visser et al., 2007). This can cause the total dissolved gas pressure to exceed the hydrostatic pressure which causes some of the gases to be lost to the atmosphere. Considering the reducing conditions and low (non-detectable) nitrate concentrations in both aquifers it seems reasonable that production of $N_2(g)$ and/or $CH_4(g)$ is the cause for degassing the samples. The degassed samples did not fit any of the age models used by Dissolved and Noble Gas Lab in Utah and as such the age of the groundwater could not be determined.

It is however possible to make a qualitative estimation of the age using only the measured tritium levels. Measured tritium levels are between 1.62 TU (P1A) and 1.99 TU (P2A) in the Pleistocene aquifers. In P1B the tritium levels were measured to 0.81 TU. This indicates a mix of pre-bomb water (before 1952) and modern water in all boreholes (Kresic, 2007).

6 Discussion

6.1 Hydrogeology

There are several sources of recharge to the aquifers in the Nam Du well-field. The Holocene aquifer receives recharge from the Red River as well as infiltration from precipitation and surface water (ponds, streams, canals). The Pleistocene aquifer receives recharge from its hydraulic contact with the Red River and from leakage from the Holocene aquifer. From $\delta^{18}O/\delta^2H$ data it is evident that the production wells (ND-wells) close to the Red River receives the highest amount of recharge from the Red River while the PA-boreholes further inland shows a isotopic signal more similar to that of water from the Holocene aquifer and ponds.

The large difference in groundwater levels in the Holocene aquifer and the piezometric head in the Pleistocene aquifer also indicate that leakage from the Holocene aquifer occurr.

The age of the groundwater could not be determined properly due to degassing, but the ^3H data indicates that at least some amount of water is of modern origin. Berg et al. (2001) dated the groundwater in the Pleistocene aquifer to between 5-15 years old using ^3H, so it is reasonable to assume that the groundwater being extracted from the Pleistocene aquifer is fairly young. The abstraction has doubled from 30.000 m^3/d in 1996 to 60.000 m^3/d today (Nhan, 2012, pers. comm.), which has increased the turnover rate of groundwater and leakage from the Holocene to the Pleistocene aquifer significantly. This is a cause for concern since the water quality in the Holocene aquifer is lower than in the Pleistocene aquifer.

6.2 Sources of ammonium

Mineralization of NH_4^+ from organic-rich sediments and infiltration of anthropogenic pollution sources such as wastewater/animal manure or leaching of inorganic fertilizers, are the plausible explanations for the high concentrations of NH_4^+ found in many of the investigated wells. Inorganic fertilizers can be ruled out as a major source of NH_4^+ due to the relatively high $\delta^{15}N$ values found in most samples. The isotopic signature of the sampled NH_4^+ can however not be used to differentiate between soil organic nitrogen and wastewater or animal manure. Most samples in both the Pleistocene aquifer and the Holocene aquifer plots in the range of both possible sources (see Figure 14). The correlation found between TOC and NH_4^+ indicates that the ammonium likely originates from a source rich in organic material, see Figure 12. This also fits with both the organic-rich sediments and wastewater or animal manure as possible sources. However the vastly different concentrations of NH_4^+ found in the groundwater compared to the wastewaters and ponds indicates that NH_4^+ and organic carbon in groundwater is not derived from the same sources as the NH_4^+ and/ or TOC in the sampled surface waters. The wastewaters are also characterized by high B concentrations (compared to groundwater) and low NH_4^+ while the opposite is usually the case for groundwater in both aquifers.

Based upon this I would argue that the main source of ammonium is degradation of peat in the sediments. Large amounts of buried peat and organic material in the sediments has been reported by other researchers (Berg et al., 2008; Trafford et al., 1996). The anoxic conditions in the aquifer would cause reduction of Mn-oxides, Fe-oxides and SO_4^- , using organic carbon as the reduction agent (Appelo and Postma, 2005). This causes degradation of the organic matter, which leads to mineralization of the NH_4^+ as peat is degraded. The high concentrations of dissolved Mn, Fe, and low concentrations of SO_4^- support this theory. Harms-Ringdal (2007) reported $\delta^{15}N$ values of 2.4 and 4.1 ‰ in soil organic nitrogen for two samples. Most of the groundwater samples in this study show similar $\delta^{15}N$ values, further supporting the hypothesis of peat degradation as a source of NH_4^+. However Harms-Ringdal (2007) also reported much higher $\delta^{15}N$ values for NH_4^+ in groundwater, and attributed the high NH_4^+ concentrations to anthropogenic sources.

Even though mineralization of NH_4^+ from organic rich sediments seems to be contributing to the high NH_4^+ levels, it is not likely to be the sole cause of the high concentrations in the Nam Du well-field. In many of the sampled wells, NH_4^+ concentrations are much higher than what would be expected in unpolluted groundwater. The sample with the by far highest NH_4^+ concentration, P2B (observation well in the Holocene aquifer), shows clear signs of anthropogenic influence. The $\delta^{15}N$ value in this borehole is much higher than in the others with values corresponding well to that of wastewater. P2B also shows higher than average concentrations of B and $\delta^{11}B$ values corresponding to that of manure as well as presence of both coliform and *E. coli* bacteria. Leakage of animal manure seems like a possible source affecting P2B since the borehole was located right next to a small cropland but leakage of wastewater is also likely. Several other wells, especially in the Holocene aquifer, show $\delta^{15}N$-values in the upper range of what can be expected from soil organic nitrogen, indicating that they are possibly affected by leaking wastewater or manure, especially since these wells show high NH_4^+ concentrations too. If two (or more) sources rich in NH_4^+ with different $\delta^{15}N$-values (for example peat and wastewater) are influencing the groundwater it would result in high NH_4^+ concentrations and intermediate $\delta^{15}N$-values. This is likely the case here since a binary mixing model does not describe the situation in Nam Du, see Figure 15.

The presence of coliform bacteria and *E. coli* in several wells is also a clear sign that wastewater or manure is, at least locally, leaking to the groundwater. Whether this is a result of contaminated water percolating through the soil or entering wells directly due to poor well construction is not clear. In the case of the deeper boreholes the second scenario is probably more likely.

One could argue that the correlation between Ni and NH_4^+ is a sign that NH_4^+ is originating from an anthropogenic source. But since Ni concentrations are usually low it is more likely that the correlation between Ni and NH_4^+ is due to mineralization of both species from degrading organic matter as described in chapter 5.2.

There is also a weak trend of increasing B concentrations with increasing NH_4^+ concentrations; this could be a sign that in some locations NH_4^+ originates from a source rich in B, probably wastewater. However since B is also a micronutrient for plants it might be possible that B is mineralized at the same time as NH_4^+. The average concentrations of NH_4^+, B and coliform bacteria are also higher in the Holocene aquifer than in the Pleistocene. $\delta^{15}N$ and $\delta^{11}B$ values are also higher on average in the Holocene aquifer. This indicates that the Holocene aquifer at least locally is affected by anthropogenic activities and/or that NH_4^+ is mineralized to a larger extent in the Holocene sediments. The lowest NH_4^+ concentrations in groundwater are found in the deep ND-wells close to the Red River while highest are found in the shallower P-boreholes further inland. The ND-wells are located close to the Red River and therefore receives more recharge from the Red River compared to the Pleistocene aquifer further inland which receives a larger amount recharge as seepage from the Holocene aquifer.

The sampled wastewaters in this study usually show lower concentrations of NH_4^+ than most groundwater, implying that the wastewater is not a likely source. The binary mixing model constructed (Figure 15) does however suggest that the wastewaters sampled in this study might be heavily diluted. As such it might be possible that undiluted wastewater is directly infiltrating to the Holocene aquifer from leaking sewage pipes or septic tanks which could produce the high $\delta^{15}N$-values and NH_4^+ concentrations found in for example the P2B borehole.

The sampled wastewater and ponds contain more NO_3^- than NH_4^+ and as such DNRA from infiltrating wastewater is another process that could possibly increase NH_4^+ concentrations to the levels found in some groundwater samples. The process of denitrification is usually more important than that of DNRA which would cause NO_3^- to be lost as N_2-gas. However, under strongly reducing and NO_3^- limited conditions DNRA might be more efficient than denitrification since more electrons can be transferred per mole NO_3^- (Rutting et al., 2011). This means that conditions in Nam Du are likely to favor DNRA. Since NO_3^- concentrations were below the LOD in all groundwater samples but present in all wastewaters and ponds this means that either:

i. Wastewater is not infiltrating to the groundwater

ii. Wastewater infiltrates to the groundwater but the NO_3^- is transformed to N_2 by denitrification or NH_4^+ by DNRA

Interestingly this means that if the amount of nitrification or DNRA in the aquifers can be quantified, it can be used as a proxy to evaluate whether infiltration of wastewater or water from ponds is reaching the groundwater or not. NO_2^- or N_2O is produced as intermediate forms in both denitrification and DNRA, and may as such be used as proof that these processes occur (Rutting et al., 2011; Smith et al., 1991). Denitrification can also be measured by quantifying the amount of dissolved N_2 gas in groundwater (Smith et al., 1991). All samples in this study were analyzed for NO_2^- by EAWAG but were below the LOD in all samples. NO_2^- is however a very unstable species and may as such be hard to detect before it reacts to form NH_4^+ or N_2. This should however be further investigated in future studies.

To summarize, most of the sampled groundwater does not show any clear signs of anthropogenic influence though there are results suggesting that the elevated NH_4^+ levels in sevral locations can be attributed to anthropogenic sources, probably wastewater or animal manure. It should be stressed that there probably is no simple truth about the NH_4^+ in groundwater in Nam Du. In all, the high NH_4^+ concentrations is a result of both natural and anthropogenic sources which's relative importance vary both spatially and temporally.

6.3 Sources of error

One problem with this type of study is the relatively small number of samples taken due to high costs associated with the different chemical analyzes. This makes it hard to statistically verify or reject different hypotheses. It is also a problem that samples have only been taken once from each location during this study. While some locations have been investigated before during other studies (Baric and Sigvardsson, 2007; Harms-Ringdal, 2007), all these studies (including this one) has been performed during the same time of the year. Several samples taken at different times from the same location would increase the chance of identifying random errors such as contamination of samples during field work or in the laboratory. Taking samples from the same location at different times of the year would also make it possible to see if the different parameters vary annually. If this is the case, the samples taken now (i.e. only during the dry season) might not be fully representative, which could cause incorrect conclusions to be drawn. This is especially true with the surface waters (wastewaters, rivers and ponds) since concentrations of different compounds could vary significantly depending on the amount of precipitation, evaporation, run-off or which crops that are being cultivated at the specific time (different types of manure may be used for different crops).

It can also be questioned whether the sampled wastewater is representative of actual sewage water transported in the sewage systems. Since the wastewater sampled in this study was taken from canals and sedimentation ponds/lakes it is probably heavily diluted by precipitation and run-off. A more correct estimate of wastewater characteristics might have been given if the samples had been taken directly from sewer pipes. The B-concentrations measured in the wastewaters in this study are very low compared to studies from other parts of the world (USA, Switzerland and France) (Bassett et al., 1995; Vengosh et al., 1999; Widory et al., 2004) which could be an effect of dilution, but may also reflect differences in the usage of detergents and washing powders. In that case boron may not be a good tracer of wastewater in this area.

The low B concentrations make it hard to accurately measure $\delta^{11}B$ as seen by the quite large standard deviations of some samples, see Appendix 2. Boron isotope data are hard to interpret due to the large differences in $\delta^{11}B$-values between the two natural sources of recharge; rainwater and the Red River.

It is also questionable if it is correct to sample possible anthropogenic sources today and directly compare them to groundwater if it takes several years for infiltrating water to reach the watertable. The concentrations of substances from anthropogenic sources found in groundwater today likely dates back several years. Sadly a precise dating of groundwater could not be obtained for this study but the tritium concentrations shows that at least some amount of water is of modern origin, thus lending some credit to sampling and comparing with present wastewater. The noble gases methods used for dating in this study are likely not suitable in these conditions as the samples were stripped.

In short, care should be taken when interpreting the results from this study and more samples would be desirable to help with the interpretation.

6.4 Water quality

The groundwater in all the sampled wells/boreholes is not suitable as drinking water according to international and national standards. The largest problem is arsenic; all groundwater samples except one exceeds, by a considerable margin, the guideline value of 10 µg/L. The high concentrations of As in groundwater have been attributed to mobilization from the Holocene sediments (Baric and Sigvardsson, 2007; Norrman et al., 2008). High concentrations are also found in ponds and wastewater; the national guideline value is exceeded in four of the sampled surface waters. This is likely a result of As-rich groundwater being pumped up and later being discharged into surface waters, but is should not be ruled out that the very high concentrations found in Pond 3 and Pond 86 (see Table 1) are the result of anthropogenic activities like spreading of pesticides. This needs to be further investigated. Even if no direct relationship can be observed between high NH_4^+ concentrations and the high As concentrations, continued degradation of organic matter in the sediments will cause the reducing conditions to prevail which means mobilization of As will continue. In this context it is also problematic if surface water rich in TOC continues to reach the groundwater.

Four wells have manganese concentrations above that of the WHO guideline value of 0.4 mg/L which is likely the result of reduction of Mn-oxides by organic matter. Ingestion of high amounts of manganese can possibly have adverse neurological effects on humans, but the number of studies are low (WHO, 2008). All surface waters, including the Red River, contained high amounts of coliform bacteria and *E. coli* showing that inflow of wastewater or animal manure to ponds and the Red River is a common occurrence. Amounts of coliform bacteria and *E. coli* exceeding the guideline values for drinking water are also found in several wells. Water quality is generally worse in the Holocene aquifer, likely due to both natural and anthropogenic causes. The increased extraction of groundwater from the Nam Du well-field is inducing higher amounts of leakage from the Holocene aquifer to Pleistocene aquifer, further degrading groundwater quality and increasing the costs associated with purifying the water to acceptable standards. Changes in wastewater management could possibly help mitigate the situation, but the degradation of peat responsible for much of the quality issues will remain a problem. Reduced abstraction rates would decrease leakage from the Holocene aquifer, which on a longer time scale might increase groundwater quality in the Pleistocene aquifer. Seeing as the groundwater in all sampled wells is of poor quality and not likely to get better without decreased groundwater abstraction, an alternate source of drinking water should strongly be considered.

7. Conclusions and recommendations

The high concentrations of ammonium in the Nam Du area mainly originate from degradation of organic-rich sediments under anoxic conditions.

There are also indications that wastewater or animal manure is infiltrating down to the groundwater in some places, locally contributing to the high ammonium concentrations.

The methods used for dating groundwater in this study (dissolved noble gases) are likely not suitable for this area due to methane gas forming in the anoxic aquifers.

The number of samples in this study is small and as such further studies are needed to confirm the results and interpretations of this study. Future studies should include more samples taken at different time over the year, especially in wastewaters to better identify their characteristics.

The amount of denitrification or DNRA in groundwater should be quantified by measuring concentrations of N_2O and N_2. If denitrification or DNRA occurs, it is strong evidence that nitrate containing water of anthropogenic origin is reaching the groundwater.

Groundwater in the Nam Du well-field is of poor quality and an alternate source of drinking water should be considered.

8. Ackowledgements

First and foremost I would like to thank my supervisor Charlotte Sparrenbom at the Department of Geology, Lund University, for entrusting me with this project and for all the help with the thesis. Much appreciated. Thanks should also be directed to my co-supervisor, pHD-student Maria Åkesson at the Department of Geology for everything from help with the sampling to proof-reading and providing enjoyable company in Vietnam.

A great many thanks also to my supervisor in Hanoi, prof. Pham Quy Nhan at the Hanoi University of Mining and Geology, for planning and arranging everything in Hanoi as well as showing great hospitality. Many thanks should also be dedicated to all the people at the Institute of Nuclear Science (INST) and Technology and the Research Center for Environmental Technology and Sustainable Development (CETASD) who helped us out with our samples. A special thanks to all the people at Hanoi University of Mining and Geology who patiently took us around and helped us with the sampling, this would never have been possible without you.

Michael Berg at the Swiss Federal Institute for Environmental Science and Technology should also be acknowledged for his help with all the chemical data and comments on the thesis.

And not to be forgotten, Rebecka Olsén from the Faculty of Engineering, Lund University , my coworker who provided invaluable support with the field -work as well as great times and good laughs in Vietnam.

This study was financed by the Swedish Research Links program (Dnr:348-2008-6215) and the Sida Minor Field Study (MFS) Scholarships program.

9. References

Appelo, C.A.J., and Postma, D., 2005, Geochemistry, groundwater and pollution: Rotterdam ; Brookfield, VT, Balkema, 649 pp.

Atkins, P.W., and Jones, L.L., 2010, The elements: The main group elements, Chemical principles: The quest for insight: New York, Clancy Marshall,786 pp.

Baric, D., and Sigvardsson, E., 2007, Distribution and mobilisation of arsenic in the Red River delta aquifers, Vietnam [Master's thesis]: Gothenburg, Göreborg University.

Barth, S., 1998, Application of boron isotopes for tracing sources of anthropogenic contamination in groundwater: *Water Resources., v. 32,* p. 685-690.

Bassett, R.L., Buszka P. M., Davidson G. R., Chong-Diaz D., 1995, Identification of groundwater solute sources using boron isotopic composition: *Environmental Science & Technology, v. 29,* p. 2915-2922

Bayer, R., Schlosser, P., Bönisch, G., Rupp, H., Zaucker, F., and Zimmek, G., 1989, Performance and blank components of a mass spectrometric system for routine measurements of helium isotopes and tritium by the 3He ingrowth method: *Sitzungsberichte der Heidelberger Akademie der Wtssenschaften, Mathematisch-naturwissenschaftliche Klasse, v. 5,* p. 241-279.

Berg, M., Pham Thi Kim, T., Stengel, C., Buschmann, J., Pham, H.V., Nguyen, V.D., Walter, G., and Stüber, D., 2008, Hydrological and sedimentary controls leading to arsenic contamination of groundwater in the Hanoi area, Vietnam: The impact of iron-arsenic ratios, peat, river bank deposits and excessive groundwater abstraction: *Chemical Geology, v. 249,* p. 91-112.

Berg, M., Tran, H.C., Nguyen, T.C., Pham, H.V., Schertenleib, R., and Giger, W., 2001, Arsenic contamination of groundwater and drinking water in Vietnam: A human health threat: *Environmental Science & Technology, v. 35*, p. 2621-2626.

Buschmann, J., and Berg, M., 2009, Impact of sulfate reduction on the scale of arsenic contamination in groundwater of the Mekong, Bengal and Red River deltas: *Applied Geochemistry, v. 24,* p. 1278-1286.

Böhlke, J.K., Smith, R.L., and Miller, D.N., 2006, Ammonium transport and reaction in contaminated groundwater: Application of isotope tracers and isotope fractionation studies: *Water Resources Research, v. 42*

Dalsgaard, T., Canfield, D.E., Petersen, J., Thamdrup, B., and Acuna-Gonzalez, J., 2003, N-2 production by the anammox reaction in the anoxic water column of Golfo Dulce, Costa Rica: *Nature, v. 422,* p. 606-608.

Fageria, N.K., Baligar, C., and Clark, R.B., 2002, Micronutrients in crop production, *Advances in Agronomy, v. 77,* p. 185-268.

Gardner, P., and Solomon, D.K., 2009, An advanced passive diffusion sampler for the determination of dissolved gas concentrations: *Water Resources Research, v. 45.*

Harms-Ringdal, P., 2007, Identifying possible sources of ammonium ions and arsenic in groundwater in the Nam Du area, Vietnam [Master's thesis]: Uppsala, Sveriges lantbruksuniversitet.

Heaton, T.H.E., 1986, Isotopic Studies of Nitrogen Pollution in the Hydrosphere and Atmosphere - a Review: *Chemical Geology, v. 59,* p. 87-102.

Hem, J.D., 1985, Study and interpretation of the chemical characteristics of natural water: Alexandria, VA, U.S. Geological Survey ;, xii, 263 pp.

Jiang, Y.J., Wu, Y.X., and Yuan, D.X., 2009, Human Impacts on Karst Groundwater Contamination Deduced by Coupled Nitrogen with Strontium Isotopes in the Nandong Underground River System in Yunan, China: *Environmental Science & Technology, v. 43,* p. 7676-7683.

Kendall, C., and Aravena, R., 2000, Nitrate isotopes in groundwater systems, *in* Cook, P.G., and Herczeg, A.L., eds., Environmental tracers in subsurface hydrology: Boston, Kluwer Academic Publishers, 529 pp.

Kendall, C., and McDonnell, J.J., 1998, Isotope tracers in catchment hydrology: Amsterdam ; New York, Elsevier, xxix, 839 pp.

Khai, N., Ha, P., and Oborn, I., 2007, Nutrient flows in small-scale peri-urban vegetable farming systems in Southeast Asia—A case study in Hanoi: *Agriculture, Ecosystems & Environment, v. 122*, p. 192-202.

Komor, S.C., 1997, Boron contents and isotopic compositions of hog manure, selected fertilizers, and water in Minnesota: *Journal of Environmental Quality, v. 26*, p. 1212-1222.

Kresic, N., 2007, Grounwater chemistry, Hydrogeology and groundwater modeling: Boca Raton, Taylor & Francis Group. 828 pp.

Lehmann, M.F., Reichert, P., Bernasconi, S.M., Barbieri, A., and McKenzie, J.A., 2003, Modelling nitrogen and oxygen isotope fractionation during denitrification in a lacustrine redox-transition zone: *Geochimica et Cosmochimica Acta, v. 67*, p. 2529-2542.

Li, S.L., Liu, C.Q., Li, J., Liu, X.L., Chetelat, B., Wang, B.L., and Wang, F.S., 2010, Assessment of the Sources of Nitrate in the Changjiang River, China Using a Nitrogen and Oxygen Isotopic Approach: *Environmental Science & Technology, v. 44,* p. 1573-1578.

Liu, C.Q., Li, S.L., Lang, Y.C., and Xiao, H.Y., 2006, Using delta N-15- and delta O-18-values to identify nitrate sources in karst ground water, Guiyang, Southwest China: *Environmental Science & Technology, v. 40,* p. 6928-6933.

Livsmedelsverkets föreskrifter om dricksvatten, SFS 2001:30

Meng, X. and Wang, W. 1998 Speciation of arsenic by disposable cartridges: Third international conference on arsenic exposure and health effects

Moore, K.B., Ekwurzel, B., Esser, B.K., Hudson, G.B., and Moran, J.E., 2006, Sources of groundwater nitrate revealed using residence time and isotope methods: *Applied Geochemistry, v. 21,* p. 1016-1029.

Norrman, J., and Andersson, L., 1998, Ammonium contamination of groundwater in the Hanoi area, Vietnam. [Master's thesis]: Gothenburg, Chalmers University of Technology

Norrman, J., Sparrenbom, C.J., Berg, M., Nhan, D.D., Nhan, P.Q., Rosqvist, H., Jacks, G., Sigvardsson, E., Baric, D., and Moreskog, J., 2008, Arsenic mobilisation in a new well field for drinking water production along the Red River, Nam Du, Hanoi: *Applied Geochemistry, v. 23,* p. 3127-3142.

Palmer, M.R., Spivack, A.J., and Edmond, J.M., 1987, Temperature and pH controls over isotopic fractionation during adsorption of boron on marine clay: *Geochimica et Cosmochimica Acta, v. 51,* p. 2319-2323

Rutting, T., Boeckx, P., Muller, C., and Klemedtsson, L., 2011, Assessment of the importance of dissimilatory nitrate reduction to ammonium for the terrestrial nitrogen cycle: *Biogeosciences, v. 8,* p. 1779-1791.

Schlesinger, W.H., 1997, Biogeochemistry: an analyses of global change: Academic Press, 588 pp.

Smil, V., 2001, Enriching the Earth; Fritz Haber, Carl Bosch, and the transformation of world food production, Massachusetts Institute of Technology, 318 pp.

Smith, R.L., Howes, B.L., and Duff, J.H., 1991, Denitrification in Nitrate-Contaminated Groundwater - Occurrence in Steep Vertical Geochemical Gradients: *Geochimica et Cosmochimica Acta, v. 55,* p. 1815-1825.

Tanabe, S., Hori, K., Saito, Y., Haruyama, S., Doanh, L.Q., Sato, Y., and Hiraide, S., 2003, Sedimentary facies and radiocarbon dates of the Nam Dinh-1 core from the Song Hong (Red River) delta, Vietnam: *Journal of Asian Earth Sciences, v. 21,* p. 503-513.

Thapa, R., and Murayama, Y., 2008, Land evaluation for peri-urban agriculture using analytical hierarchical process and geographic information system techniques: A case study of Hanoi: *Land Use Policy, v. 25*, p. 225-239.

Tomaszek, J.A., and Rokosz, G.R., 2007, Rates of Dissimilatory Nitrate Reduction to Ammonium in Two Polish Reservoirs: Impacts of Temperature, Organic Matter Content, and Nitrate Concentration: *Environmental Technology, v.* 28, p. 771-778.

Trafford, J.M., Lawrence, A.R., Macdonald, D.M.J., Dan, N.V., Tran, D.N., and Ha, N.T., 1996, The effect of urbanisation on the groundwater quality beneath the city of Hanoi, Vietnam, BGS Technical Report WC/96/22.

Uren, N.C., 1992, Forms, Reactions, and Availability of Nickel in Soils. *Advances in Agronomy, v. 48,* p. 141-203.

Van Horen, B., 2005, Hanoi: *Cities, v. 22*, p. 161-173.

Van, N.K., Nhien, D.D., On, D.H., and Anh, N.N., 1996, On the feasibility study for groundwater exploitation of Nam Du Thuong well field with capacity 30,000 m3/d, (phase II): Hanoi, Ministry of construction, Union of Survey Companies, Construction Survey Enterprise No 1.

Vengosh, A., Barth, S., Heumann, K.G., and Eisenhut, S., 1999, Boron isotopic composition of freshwater lakes from central Europe and possible contamination sources: *Acta hydrochim, v.* 27, p 416-421.

WHO, 2008, Guidelines for drinking-water quality Vol.1, Recommendations. – 3rd ed., Volume 1.

Widory, D., Kloppmann, W., Chery, L., Bonnin, J., Rochdi, H., and Guinamant, J.L., 2004, Nitrate in groundwater: an isotopic multi-tracer approach: *Journal of Contamination Hydrology, v. 72,* p. 165-88.

Widory, D., Petelet-Giraud, E., Negrel, P., and Ladouche, B., 2005, Tracking the sources of nitrate in groundwater using coupled nitrogen and boron isotopes: a synthesis: *Environmental Science & Technology, v. 39*, p. 539-48.

Winkel, L.H.E., Pham, T.K.T., Vi, M.L., Stengel, C., Amini, M., Nguyen, T.H., Pham, H.V., and Berg, M., 2011, Arsenic pollution of groundwater in Vietnam exacerbated by deep aquifer exploitation for more than a century: *Proceedings of the National Academy of Sciences of the United States of America, v. 108*, p. 1246-1251.

Visser, A., Broers, H.P., van der Grift, B., and Bierkens, M.F.P., 2007, Demonstrating trend reversal of groundwater quality in relation to time of recharge determined by 3H/3He: *Environmental Pollution, v. 148,* p. 797-807.

Yona, C., 1996, Chapter 13 - Organic Matter Reactions Involving Micronutrients in Soils and Their Effect on Plants, *in* Alessandro, P., ed., Humic Substances in Terrestrial Ecosystems: Amsterdam, Elsevier Science B.V., p. 507-529.

Younger, P.L., 2007, Groundwater in the environment : an introduction: Malden, MA ; Oxford, Blackwell Pub., xii, 318 p. p.

Appendix 1

List of all samples that were taken and which laboratory that analysed them. All results were not used in this study.

I.D.	General chemistry, As and $\delta^{18}O/\delta^{2}H$ (EAWAG)	$\delta^{11}B$ (ALS Scandinavia)	$\delta^{15}N$ (INST)	Bacteria	$^{3}H/^{3}He$ (Noble gas lab, Utah)	DOC, As (CETASD)
P1B	x	x		x	x	x
P2B	x	x	x	x		x
P3B	x	x	x	x		x
PY	x		x	x		x
DHA14	x		x	x		x
DHA18	x	x	x	x		x
DHA22	x		x	x		x
DHA30	x	x	x	x		x
DHB22	x		x	x		x
P1A	x	x	x	x	x	x
P2A	x	x	x	x	x	x
P3A	x	x	x	x		x
P86A	x	x	x			x
PX	x		x	x		x
ND3	x		x	x		x
ND9	x		x	x		x
ND13	x			x		x
DHA52	x	x	x	x		x
DHB52	x		x	x		x
Pond2	x	x	x	x		x
Pond3	x	x	x	x		x
Pond86	x	x	x	x		x
Pond DHA	x	x	x	x		x
River1	x		x	x		x
River2	x		x	x		x
River3	x		x	x		x
Riverbank	x		x	x		x
WW1	x	x	x	x		x
WPT2	x	x	x	x		x
Rainwater		x	x	x		

Appendix 2

Values for all measured parameters used in this study. Contiuned on next page.

ID	Type	Depth	pH	DO	Eh	d2H	d18O	As(tot)	As(III)	Fe	Ni	Mn	Na	K	Ca	Mg	Mg	HCO3-	Cl-
		m		%	mV	‰	‰	µg/L	µg/L	mg/L	µg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
DHA14	Holocene	14.00	7.29	1.20	-205.0	-32.3	-4.1	594	523	12.4	0.72	0.28	25.2	4.9	70	31	31	526	7.0
DHA18	Holocene	18.00	7.18	1.40	-179.0	-34.0	-4.5	504	488	11.9	1.5	0.21	18.8	5.0	72	30	30	519	13.8
DHA22	Holocene	22.00	7.09	1.80	-182.0	-24.7	-3.2	420	397	11.9	<0.1*	0.22	26.9	3.9	88	24	24	498	17.2
DHA30	Holocene	30.00	6.83	1.90	-135.6	-48.0	-6.7	200	186	6.6	<0.1*	0.22	14.2	3.5	76	33	33	496	9.1
DHB22	Holocene	22.00	7.08	1.70	-173.3	-21.7	-2.8	375	356	10.3	<0.1*	0.36	16.1	3.8	88	23	23	407	6.9
P1B	Holocene	-	6.96	1.00	-176.3	-45.8	-6.6	374	330	13.2	15	0.34	24.7	8.2	93	36	36	687	11.0
P2B	Holocene	28.30	6.92	0.60	-152.7	-39.4	-5.5	95	17	0.8	6.2	0.11	48.3	6.8	40	18	18	527	11.2
P3B	Holocene	20.00	6.33	1.20	-92.4	-28.0	-3.5	40	38	27.6	0.9	0.36	30.5	1.5	68	25	25	271	70.7
PY	Holocene	46.00	6.68	2.60	-131.3	-52.3	-7.3	11	11	20.9	0.14	0.17	29.8	2.3	14	9.9	9.9	142	20.4
Riverbank	Holocene	-	7.64	1.2	-43.2	-63.3	-9.0	9.3	7.1	0.04	<0.1*	0.51	3.6	2.3	48	7.9	7.9	206	2.3
DHA52	Pleistocene	52.00	6.96	0.70	-154.4	-57.8	-8.1	114	102	9.8	1.6	0.17	17.7	3.7	23	12	12	212	7.9
DHB52	Pleistocene	52.00	6.96	1.90	-145.6	-39.3	-5.4	80	78	12.5	1.9	0.11	19.8	6.1	36	18	18	298	13.2
ND13	Pleistocene	67.00	6.99	6.50	-134.2	-59.9	-8.7	91	88	6.1	0.20	0.22	7.2	3.2	27	13	13	152	2.6
ND3	Pleistocene	70.00	6.93	1.60	-139.6	-57.8	-8.4	72	72	6.2	<0.1*	0.41	6.0	2.8	33	14	14	194	2.3
ND9	Pleistocene	80.00	6.78	1.30	-109.4	-59.1	-8.5	85	84	6.6	0.32	0.39	10.7	3.7	25	14	14	197	4.4
P1A	Pleistocene	59.80	7.06	0.10	-173.4	-33.3	-4.5	412	388	7.4	<0.1*	0.37	19.1	6.3	82	30	30	471	15.3
P2A	Pleistocene	48.10	6.85	0.40	-148.3	-37.5	-5.2	152	145	11.8	2.2	0.07	23.5	6.2	56	25	25	417	15.1
P3A	Pleistocene	47.50	6.65	1.00	-132.3	-53.6	-7.8	139	132	22.5	3.2	0.08	36.1	4.2	16	12	12	243	31.5
P86A	Pleistocene	58.75	7.02	0.40	-179.8	-42.7	-5.9	299	-	10.1	<0.1*	0.19	23.1	3.2	99	26	26	463	17.9
PX	Pleistocene	70.00	6.51	-	-61.1	-57.7	-8.2	22	21	15.3	<0.1*	0.63	17.5	4.3	19	13	13	186	4.4
Pond DHA	Pond	-	-	-	-	-25.3	-2.2	4.5	1.7	0.17	3.0	0.01	26.3	13.6	26	9.5	9.5	134	24.2
Pond2	Pond	-	-	-	-	-19.8	-1.3	9.3	1.6	0.09	2.6	0.01	48.6	17.7	21	11	11	168	46.3
Pond3	Pond	-	-	-	-	-30.7	-3.6	172	5.4	0.12	2.3	0.02	55.6	25.4	37	14	14	278	67.8
Pond86	Pond	-	-	-	-	-68.7	-9.2	80	4.3	0.13	2.1	0.51	25.2	20.1	41	12	12	166	27.3
River1	River	-	-	-	-	-61.6	-8.7	3.6	0.7	0.05	0.33	<0.01*	4.1	1.6	25	5.3	5.3	108	2.7
River2	River	-	-	-	-	-61.7	-8.7	3.4	<0.5*	0.04	0.38	<0.01*	4.1	1.6	25	5.4	5.4	109	2.6
River3	River	-	-	-	-	-63.5	-8.6	3.3	<0.5*	0.02	<0.1*	<0.01*	4.2	1.7	25	5.4	5.4	108	2.8
WPT2	Wastewater	-	-	-	-	-49.3	-6.5	19	16	0.28	3.3	0.20	51.0	14.8	34	12	12	155	45.7
WW1	Wastewater	-	-	-	-	-43.3	-5.4	10	1.6	0.12	3.7	0.14	44.9	15.3	51	14	14	246	40.2

Appendix 2 (continued)

ID	SO_4^{2-}	DOC	TOC	B	d11B	NO_3^-	NH_4^+	d15N	N-tot	Colifrom	E-coli	3H
	mg/L	mg/L	mg/L	µg/L	‰ (±2SD)	mg/L	mg/L	‰	mg/L	MPN/100 mL	MPN/100 mL	TU
DHA14	<0.15*	3.2	3.7	12.0	-	<0.25*	14.5	8,59	14.5	0	0	-
DHA18	0.77	3.4	3.7	16.0	-10.2±4.8	<0.25*	18.0	7,46	18.0	9	4	-
DHA22	<0.15*	2.0	2.1	16.0	-	<0.25*	7.5	6,84	7.5	-	-	-
DHA30	<0.15*	4.7	5.0	27.0	11.5±2.4	<0.25*	29.0	4,15	29.0	4	0	-
DHB22	<0.15*	2.1	2.8	16.0	-	<0.25*	5.7	6,85	5.7	7	0	-
P1B	<0.15*	11.9	12.6	47.0	11.5±2.6	<0.25*	35.2	-	35.2	23	9	0.81
P2B	<0.15*	19.6	19.9	40.0	18.4±1.2	<0.25*	69.8	13,09	69.8	43	7	-
P3B	<0.15*	9.4	10.9	15.0	-2.7±3.2	<0.25*	8.3	0,42	8.3	150	9	-
PY	2.07	1.5	1.9	7.7	-	<0.25*	1.2	3,87	1.2	0	0	-
Riverbank	1.03	1.0	1.2	<1.3*	-	<0.25*	0.1	-	0.1	4	0	-
DHA52	0.64	8.3	8.5	12.0	7.9±5.2	<0.25*	27.0	2,14	27.0	43	7	-
DHB52	<0.15*	2.8	3.2	12.0	-	<0.25*	10.8	4,13	10.8	9	4	-
ND13	1.26	1.9	2.0	6.2	-	<0.25*	4.1	-	4.1	0	0	-
ND3	1.27	1.5	1.8	5.2	-	<0.25*	2.4	1,39	2.4	0	0	-
ND9	0.80	1.8	1.9	5.1	-	<0.25*	5.3	5,84	5.3	0	0	-
P1A	<0.15*	4.3	4.7	18.0	20.9±3.3	<0.25*	18.3	4,17	18.3	9	4	1.62
P2A	<0.15*	3.9	4.0	15.0	5.0±1.2	<0.25*	13.5	4,42	13.5	23	4	1.99
P3A	<0.15*	10.0	10.5	10.0	-0.6±2.2	<0.25*	22.5	6,5	22.5	0	0	-
P86A	0.18	3.2	3.9	17.0	19.2±3.6	<0.25*	6.0	5,51	6.0	-	-	-
PX	<0.15*	1.4	1.9	5.4	-	<0.25*	4.1	-	4.1	0	0	-
Pond DHA	7.52	7.3	9.1	31.0	8.9±4.4	1.9	0.7	-	2.6	>2400	1100	-
Pond2	5.18	10.9	13.4	53.0	10.0±1.2	2.2	0.9	-	3.1	>2400	>2400	-
Pond3	3.96	13.2	17.8	74.0	6.5±3.0	2.1	1.5	-	3.6	>2400	460	-
Pond86	8.77	4.8	6.3	36.0	5.4±1.8	9.8	0.6	13,85	10.4	>2400	1100	-
Rainwater				13.0	15.4±2.6							
River1	3.63	2.0	2.5	3.9	-1.3±4.1	<0.25*	0.4	-	0.4	>2400	460	-
River2	3.59	1.4	1.6	2.4	-	<0.25*	0.3	-	0.3	>2400	>2400	-
River3	3.59	1.2	1.2	2.4	-	0.3	0.1	-	0.4	>2400	460	-
WPT2	10.5	6.9	12.3	46	4.6±0.8	6.9	5.2	13,05	12.1	>2400	460	-
WW1	33.9	10.6	15.4	42	-0.9±1.0	6.1	1.1	12,4	7.2	>2400	460	-

Tidigare skrifter i serien ”Examensarbeten i Geologi vid Lunds Universitet”:

252. Peetz, Romina, 2009: A geochemical characterization of the lower part of the Miocene shield-building lavas on Gran Canaria. (45 hskp)
253. Åkesson, Maria, 2010: Mass movements as contamination carriers in surface water systems – Swedish experiences and risks.
254. Löfroth, Elin, 2010: A Greenland ice core perspective on the dating of the Late Bronze Age Santorini eruption. (45 hskp)
255. Ellingsgaard, Óluva, 2009: Formation Evaluation of Interlava Volcaniclastic Rocks from the Faroe Islands and the Faroe-Shetland Basin. (45 hskp)
256. Arvidsson, Kristina, 2010: Geophysical and hydrogeological survey in a part of the Nhandugue River valley, Gorongosa National Park, Mozambique. (45 hskp)
257. Gren, Johan, 2010: Osteo-histology of Mesozoic marine tetrapods – implications for longevity, growth strategies and growth rates. (15 hskp)
258. Syversen, Fredrikke, 2010: Late Jurassic deposits in the Troll field. (15 hskp)
259. Andersson, Pontus, 2010: Hydrogeological investigation for the PEGASUS project, southern Skåne, Sweden. (30 hskp)
260. Noor, Amir, 2010: Upper Ordovician through lowermost Silurian stratigraphy and facies of the Borenshult-1 core, Östergötland, Sweden. (45 hskp)
261. Lewerentz, Alexander, 2010: On the occurrence of baddeleyite in zircon in silica-saturated rocks. (15 hskp)
262. Eriksson, Magnus, 2010: The Ordovician Orthoceratite Limestone and the Blommiga Bladet hardground complex at Horns Udde, Öland. (15 hskp)
263. Lindskog, Anders, 2010: From red to grey and back again: A detailed study of the lower Kundan (Middle Ordovician) ‘Täljsten’ interval and its enclosing strata in Västergötland, Sweden. (15 hskp)
264. Rääf, Rebecka, 2010: Changes in beyrichiid ostracode faunas during the Late Silurian Lau Event on Gotland, Sweden. (30 hskp)
265. Petersson, Andreas, 2010: Zircon U-Pb, Hf and O isotope constraints on the growth versus recycling of continental crust in the Grenville orogen, Ohio, USA. (45 hskp)
266. Stenberg, Li, 2010: Geophysical and hydrogeological survey in a part of the Nhandugue River valley, Gorongosa National Park, Mozambique – Area 1 and 2. (45 hskp)
267. Andersen, Christine, 2010: Controls of seafloor depth on hydrothermal vent temperatures - prediction, observation & 2D finite element modeling. (45 hskp)
268. März, Nadine, 2010: When did the Kalahari craton form? Constraints from baddeleyite U-Pb geochronology and geo-chemistry of mafic intrusions in the Kaapvaal and Zimbabwe cratons. (45 hp)
269. Dyck, Brendan, 2010: Metamorphic rocks in a section across a Svecnorwegian eclogite-bearing deformation zone in Halland: characteristics and regional context. (15 hp)
270. McGimpsey, Ian, 2010: Petrology and lithogeochemistry of the host rocks to the Nautanen Cu-Au deposit, Gällivare area, northern Sweden. (45 hp)
271. Ulmius, Jan, 2010: Microspherules from the lowermost Ordovician in Scania, Sweden – affinity and taphonomy. (15 hp)
272. Andersson, Josefin, Hybertsen, Frida, 2010: Geologi i Helsingborgs kommun – en geoturistkarta med beskrivning. (15 hp)
273. Barth, Kilian, 2011: Late Weichselian glacial and geomorphological reconstruction of South-Western Scania, Sweden. (45 hp)
274. Mashramah, Yaser, 2011: Maturity of kerogen, petroleum generation and the application of fossils and organic matter for paleotemperature measurements. (45 hp)
275. Vang, Ina, 2011: Amphibolites, structures and metamorphism on Flekkerøy, south Norway. (45 hp)
276. Lindvall, Hanna, 2011: A multi-proxy study of a peat sequence on Nightingale Island, South Atlantic. (45 hp)
277. Bjerg, Benjamin, 2011: Metodik för att förhindra metanemissioner från avfallsdeponier, tillämpad vid Albäcksdeponin, Trelleborg. (30 hp)
278. Pettersson, Hanna, 2011: El Hicha – en studie av saltstäppssediment. (15 hskp)
279. Dyck, Brendan, 2011: A key fold structure within a Sveconorwegian eclogite-bearing deformation zone in Halland, south-

western Sweden: geometry and tectonic implications. (45 hp)

280. Hansson, Anton, 2011: Torvstratigrafisk studie av en trädstamshorisont i Viss mosse, centrala Skåne kring 4 000 - 3 000 cal BP med avseende på klimat- och vattenståndsförändringar. (15 hp)

281. Åkesson, Christine, 2011: Vegetationsutvecklingen i nordvästra Europa under Eem och Weichsel, samt en fallstudie av en submorän, organisk avlagring i Bellinga stenbrott, Skåne. (15 hp)

282. Silveira, Eduardo M., 2011: First precise U-Pb ages of mafic dykes from the São Francisco Craton. (45 hp)

283. Holm, Johanna, 2011**:** Geofysisk utvärdering av grundvattenskydd mellan väg 11 och Vombs vattenverk. (15 hp)

284. Löfgren, Anneli, 2011: Undersökning av geofysiska metoders användbarhet vid kontroll av den omättade zonen i en infiltrationsdamm vid Vombverket. (15 hp)

285. Grenholm, Mikael, 2011: Petrology of Birimian granitoids in southern Ghana - petrography and petrogenesis. (15 hp)

286. Thorbergsson, Gunnlaugur, 2011: A sedimentological study on the formation of a hummocky moraine at Törnåkra in Småland, southern Sweden. (45 hp)

287. Lindskog, Anders, 2011: A Russian record of a Middle Ordovician meteorite shower: Extraterrestrial chromite in Volkhovian-Kundan (lower Darriwilian) strata at Lynna River, St. Petersburg region. (45 hp)

288. Gren, Johan, 2011: Dental histology of Cretaceous mosasaurs (Reptilia, Squamata): incremental growth lines in dentine and implications for tooth replacement. (45 hp)

289. Cederberg, Julia, 2011: U-Pb baddelyit dateringar av basiska gångar längs Romeleåsen i Skåne och deras påverkan av plastisk deformation i Protoginzonen (15 hp)

290. Ning, Wenxing, 2011: Testing the hypothesis of a link between Earth's magnetic field and climate change: a case study from southern Sweden focusing on the 1st millennium BC. (45 hp)

291. Holm Östergaard, Sören, 2011: Hydrogeology and groundwater regime of the Stanford Aquifer, South Africa. (45 hp)

292. Tebi, Magnus Asiboh, 2011: Metamorphosed and partially molten hydrothermal alteration zones of the Akulleq glacier area, Paamiut gold province, South-West Greenland. (45 hp)

293. Lewerentz, Alexander, 2011: Experimental zircon alteration and baddeleyite formation in silica saturated systems: implications for dating hydrothermal events. (45 hp)

294. Flodhammar, Ingrid, 2011: Lövestads åsar: En isälvsavlagring bildad vid inlandsisens kant i Weichsels slutskede. (15 hp)

295. Liu, Tianzhuo, 2012: Exploring long-term trends in hypoxia (oxygen depletion) in Western Gotland Basin, the Baltic Sea. (45 hp)

296. Samer, Bou Daher, 2012: Lithofacies analysis and heterogeneity study of the subsurface Rhaetian–Pliensbachian sequence in SW Skåne and Denmark. (45 hp)

297. Riebe, My, 2012: Cosmic ray tracks in chondritic material with focus on silicate mineral inclusions in chromite. (45 hp)

298. Hjulström, Joakim, 2012: Återfyllning av borrhål i geoenergisystem: konventioner, metod och material. (15 hp)

299. Letellier, Mattias, 2012: A practical assessment of frequency electromagnetic inversion in a near surface geological environment. (15 hp)

300. Lindenbaum, Johan, 2012: Identification of sources of ammonium in groundwater using stable nitrogen and boron isotopes in Nam Du, Hanoi. (45 hp)

LUNDS UNIVERSITET

Geologiska institutionen
Lunds universitet
Sölvegatan 12, 223 62 Lund