



Identifying possible sources of ammonium ions and arsenic in groundwater in the Nam Du area, Vietnam

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Preface by the supervisors

High concentrations of arsenic in groundwater have been reported from different regions in the world. Well-known high-As groundwater areas have been found in Argentina, Chile, Mexico, China and Hungary, and more recently in the densely populated river deltas in S and SE Asia which contain large groundwater aquifers: West Bengal (India), Bangladesh and Vietnam. The most common cause of the high-As groundwater in these regions is due to natural occurrence of arsenic in the sediments and the right conditions for arsenic mobilisation.

The first publication on arsenic contamination of the aquifers in the densely populated Red River delta was published in 2001. Consequently, in recent years, a major concern regarding the arsenic concentration in the groundwater in the Red River delta has arisen. The process for mobilisation of arsenic in the Red River delta aquifers is believed to be due to the natural conditions. However, in order to manage the groundwater quality in the future, a deeper understanding of the prevailing conditions and the on-going processes is needed. Furthermore, the Hanoi aquifers in the Red River delta have high and increasing ammonium concentrations, of which the source, so far, have been undetermined.

The work presented in this study has been an important part of a current research project at the Swedish Geotechnical Institute (SGI): Sources and distribution of ammonium and arsenic in the Red River delta aquifers (AmonAs). AmonAs is financed by Sida/SAREC during the period 2005 – 2007 and is a co-operation between SGI, the Royal Institute of Technology (KTH) and Hanoi University of Mining and Geology (HUMG) in Vietnam.

Peter Harms-Ringdahl has made a study concerning the isotopic composition of N, O, H in ammonium, nitrate and water in order to identify possible sources to the high concentrations of ammonium and to determine the flow regime of the groundwater. The chemical composition of the groundwater was analysed and used to investigate the spatial distribution of ammonium and arsenic in the Nam Du area, south of Hanoi. In addition, the redox conditions were studied in order to identify the mobilisation process of arsenic. An extensive field campaign was carried out in Vietnam during February – March 2006, together with Johanna Moreskog. The result of this work is highly interesting for managing the groundwater quality in Hanoi, especially regarding the ammonium contamination of the groundwater. In this report, it is concluded that the ammonium in the groundwater in Nam Du, which is serving as a drinking water supply, is likely to originate from a surface source.

Peter and Johanna planned and carried out the field campaign in a highly independent manner and cooperated effectively with their Vietnamese co-students. Peter has widened his knowledge impressively and he has been deeply engaged with analysing and discussing the work during the analysis phase. It has been our pleasure to have the opportunity to work together with him.

We wish you all the best in the future!
Göteborg 2007-05-15

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Abstract

Concentrations of arsenic and ammonium ions well above drinking water standards have been detected in aquifers which supply Hanoi, the capital of Vietnam, with fresh water. Chemical analyses showed arsenic and ammonium ion concentrations varying between 27 – 264 $\mu\text{g/l}$ in freshwater and 1.8 – 34.7 mg/l in groundwater. The current Vietnamese drinking water guidelines for arsenic and ammonium are set at 10 $\mu\text{g As/l}$ and 1.5 $\text{mg NH}_4\text{/l}$.

The aim of this thesis is to investigate the fate of arsenic and nitrogen and the processes behind the mobilization of these elements in the Nam Du area, situated 10 km southeast of Hanoi. Two possible processes affecting the As concentration are investigated: (1) oxidation of arsenopyrite or (2) desorption of arsenite/arsenate bound to iron hydroxides due to iron reduction. Regarding ammonium ions, previous projects have identified two possible sources which were investigated further in this study: (a) mineralisation of organic matter in sedimentary peat layers and (b) ammonium ions derived from anthropogenic sources, such as fertilisers or leakage of waste water. The methods used in this study were: analyses of N-, O- and H-isotopes, the ionic composition and redox potential in the groundwater, combined with a conceptual model of the groundwater flow in the area.

There were large spatial variations in ammonium and arsenic levels within the Nam Du area. According to tritium (^3H) analyses the water was quite young, indicating recent mobilisation processes. The redox potential, pH and sulphate concentration in the water indicate that arsenic is mobilised by reduction of iron hydroxides rather than oxidation of arsenopyrite. Furthermore, the isotopic composition of N combined with increasing levels of ammonium ions over time, the C/N ratios and the age of the water, suggest that mineralisation of peat is not occurring to such an extent that this process could explain the currently high ammonium levels. The isotopic composition of the ammonium ions and the rising concentrations in the aquifers rather imply that the ammonium ions derive from one or several sources with a high $^{15}\text{N}/^{14}\text{N}$ ratio, such as waste water, organic fertilisers or urea.

Sammanfattning

Höga nivåer av ammoniumjoner och arsenik har rapporterats förekomma i de akvifärer som förser Vietnams huvudstad, Hanoi, med färskvatten. Resultat från detta projekt visar arsenik- och ammoniumkoncentrationer mellan 27 – 264 µg As/l respektive 1.8 – 34.7mg N/l, vilket kan jämföras med WHO's gränsvärde på 10 µg/l för arsenik, och 1.5 mg/l för ammonium.

Syftet med examensarbetet har varit att undersöka vilka processer som leder till de nivåer av ammonium och arsenik som idag förekommer i Nam Duområdet, beläget 10 km sydost om Hanoi. Två av de möjliga processerna bakom mobiliseringen av arsenik är undersökta. (1) oxidation av arsenopyrit och (2) reduktion av järnhydroxider med åtföljande mobilisering av vattenlöslig arsenik. Tidigare undersökningar visar på två möjliga ammoniumkällor: (a) kväveminalisering i torvlager som förekommer naturligt i marken och (b) antropogena källor såsom kvävegödsel och läckage av kväverikt avloppsvatten.

Metoderna som använts är N- O- och H-isotopanalyser, samt undersökningar av grundvattenflöden, redoxförhållanden och vattnets innehåll av lösta ämnen. Insamlade data har kombinerats med en konceptuell flödesmodell över området.

Resultaten visar en betydande rumslig variation både beträffande ammonium- och arsenik koncentrationerna. Tritium (³H)-analyser visar att vattnet i akvifärerna är yngre än tio år vilket tyder på att de ämnen vi finner i grundvattnet har mobiliserats under denna period. Redoxförhållanden, pH värden och sulfatkoncentrationen i grundvattnet tyder inte på att arseniken mobiliseras genom oxidation av arsenopyrit utan förmodligen genom reduktion av järnhydroxider och åtföljande frigörande av arsenik. Vidare tyder isotopsammansättningen, stigande ammoniumhalter och C/N kvoter på att kväveminaliseringen i torven inte sker i en sådan omfattning att den kan förorsaka de ammoniumkoncentrationer som observerats. Isotopsammansättningen och grundvattenflödena tyder snarare på en ytlig ammoniumkälla med höga ¹⁵N/¹⁴N kvoter. Källan utgörs sannolikt av gödselmedel eller kväverikt avloppsvatten.

Tóm tắt

Hàm lượng Asen và Amoni vượt quá mức cho phép đối với tiêu chuẩn nước ăn uống sinh hoạt được phát hiện trong các tầng chứa nước đang khai thác cho thủ đô Hà Nội - Việt Nam. Kết quả phân tích thành phần hóa học trong nước dưới đất được tiến hành trong giai đoạn này cho thấy hàm lượng Asen và Amoni tương ứng biến đổi từ 27 - 264 $\mu\text{g/l}$ và 1.8 - 3.7 mg/l , trong khi tiêu chuẩn nước ăn uống sinh hoạt của Việt Nam, Asen là 10 $\mu\text{g/l}$ và Amoni là 1.5 mg/l .

Mục tiêu của luận văn này là điều tra, khảo sát môi nguy hại của Asen và Amoni cũng như cơ chế hình thành chúng trong vùng Nam Dư, nằm ở phía Đông Nam Hà Nội.

Hai cơ chế hình thành chủ yếu của Asen trong nước dưới đất được nghiên cứu ở đây là: (1) quá trình Ô xy hóa Arsenopyrite và (2) quá trình khử Asen bám dính trên bề mặt của Hydroxyt sắt. Đối với Amoni các công trình nghiên cứu trước đây đã xác định được hai nguồn hình thành tiềm năng và sẽ được nghiên cứu chi tiết trong công trình này đó là: (a) khoáng hóa các vật liệu hữu cơ trong các lớp trầm tích chứa than bùn và (b) nguồn gốc Amoni từ các hoạt động của con người như phân hóa học hoặc từ nước thải sinh hoạt và công nghiệp. Phương pháp được nghiên cứu trong công trình này là phân tích các đồng vị của N, O và H, thành phần hóa học và điều kiện Ô xy hóa khử trong nước dưới đất kết hợp với mô hình khái niệm về dòng chảy nước dưới đất ở trong vùng.

Kết quả nghiên cứu cho thấy sự biến đổi hàm lượng của Asen và Amoni theo không gian. Kết quả phân tích Tritium cho thấy tuổi nước dưới đất ở đây hoàn toàn trẻ và cũng chỉ ra rằng quá trình giải phóng xảy ra gần đây. Điều kiện Ô xy hóa khử, pH và hàm lượng Sunphát trong nước cho thấy Asen được hình thành bởi quá trình khử Hydroxyt sắt là chủ yếu so với quá trình Ô xy hóa Arsenopyrite. Hơn nữa, thành phần các đồng vị được phân tích kết hợp với hiện tượng hàm lượng Amoni tăng theo thời gian, tỷ lệ C/N và tuổi của nước dưới đất gợi ý rằng quá trình khoáng hóa than bùn là có thể không xảy ra đến mức làm tăng hàm lượng Amoni cao như hiện nay. Thành phần đồng vị Amoni và hàm lượng của chúng thay đổi theo thời gian trong các tầng chứa nước gián tiếp chỉ ra rằng Amoni có thể được hình thành từ nguồn có tỷ lệ $^{15}\text{N}/^{14}\text{N}$ cao như là nước thải, phân bón hữu cơ hoặc phân urea.

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The planning of this thesis and the field campaign was carried out together with Johanna Moreskog. Since the field work in this project was carried out together with her, some parts are common in both reports. Chapter 3, Study area: Nam Du well field was written by Johanna Moreskog. Chapter 4, Methods and Materials, was written by Peter Harms-Ringdahl but can also be found in the report by Johanna Moreskog: Redox-conditions and distribution of ammonium and arsenic in the Nam Du well field, Hanoi, Vietnam (2007).

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Abbreviations

Universities and institutes

AmonAs – Research Programme - Sources and Distribution of Ammonium and Arsenic in the Red River Delta Aquifers

CETASD – Centre for Environmental Technology and Sustainable Development, Hanoi, Vietnam.

EAWAG – Swiss Federal Institute of Aquatic Science and Technology, Switzerland

HUMG – Hanoi University of Mining and Geology, Vietnam

HUS – Hanoi University of Science, Vietnam

INST – Institute of Nuclear Science and Technology, Hanoi, Vietnam

KTH – Royal Institute of Technology, Stockholm, Sweden

SGI – Swedish Geotechnical Institute, Sweden

SAREC – Department for Research Cooperation, SIDA.

SIDA – Swedish International Development Cooperation Agency

SLU – Swedish University of Agricultural Sciences, Sweden

SU – Stockholm University, Sweden

UMU – Umeå University, Sweden

WHO – World Health Organisation

ÅAU – Åbo Academi University, Finland

Sample Codes

Pond 1, Pond 2 and Pond 3 – Surface water in ponds

P1AB, P3AB and P86AB – Monitoring wells

B – Upper aquifer (qh)

A – Lower aquifer (qp)

ND3, ND 9, PY and PX – Production wells

NDT 12 – Observation well for pumping test

1RGw, 2RGw and 3RGw – River groundwater

2RSw – River surface water

Rb1, 2, 3 – River bed (for infiltration)

Equipment

AAS – Atomic Absorption Spectrophotometer

HG-AAS – Hydride Generation – Atomic Absorption Spectrophotometer

IC – Ion Chromatograph

ICP – MS Inductively Coupled Plasma – Mass Spectrometer

ICP – OES Inductively Coupled Plasma – Optical Emission Spectrometer

MS – Mass Spectrometer

1 Introduction

1.1 Background

High levels of arsenic and ammonium have recently been detected in the aquifers which supply Hanoi, the capital of Vietnam, with freshwater (Berg et al. 2001). The extraction of groundwater has increased rapidly since the beginning of the 1900s and today the city is completely dependent on ground water with an extraction rate exceeding 700 000 m³/day (Trafford et al. 1996). As a result the groundwater tables have dropped over large areas, causing depression cones and it has been suggested that the high extraction leads to increased levels of arsenic and ammonium ions (Nhan 2006). At present, the ammonium ion concentration in fresh water is high in many places and earlier studies report of alarmingly high arsenic levels in private wells around Hanoi. It has been reported that the arsenic concentration in wells in the area is 159 µg/l on an average with a peak at 3050 µg/l (Berg et al. 2001). This should be compared to the Vietnamese and WHO standards which are set to 10 µg/l.

Preceding research projects have identified three possible sources of the ammonium ions: Nitrogen mineralization in peat layers, ammonium ion leaching from agriculture and other surface activities and induced infiltration from the Red River delta. According to a master thesis Andersson & Norrman published in 1998, the Red River can be excluded as the total nitrogen concentration in the river is too low (Andersson et al. 1998). However, the other sources mentioned, need to be investigated. The Red River delta contains sediments of Quaternary origin, which are a likely to be a natural source of some of the arsenic. According to a study by Berg et al. (2001) anthropogenic arsenic sources cannot be excluded, but the naturally occurring arsenic in the sediments seems to be a more likely source. Figure 1-1 shows an overview of the distribution of arsenic, ammonium ions and peat in the Hanoi area.

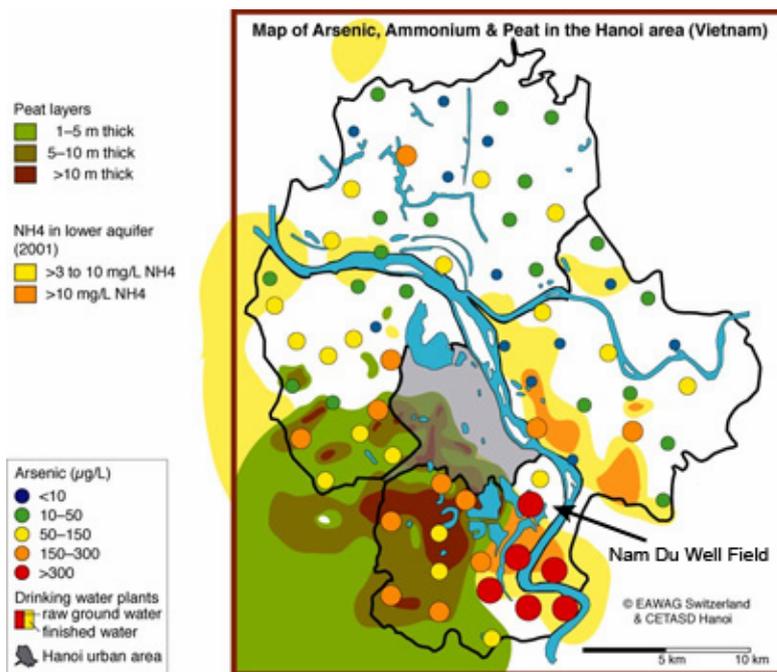


Figure 1-1 Map over the distribution of arsenic, ammonium and peat in the Hanoi area. The map is a combination of the results from Trafford et al. 1996 and Berg et al. 2001 compiled by Michael Berg and received by email 2007.

Nam Du, situated on the shores of the Red River south of Hanoi city, is one of the larger areas with wells in Hanoi and a further expansion of the field is under way. The pumping started in 2005 and the raw water passes a treatment plant before distribution. Since the well field started recently it provides an opportunity to follow how it affects the ground water flow and water quality. It may also give a possibility to observe trends and develop the understanding of the processes that lead to increasing ammonium ion and arsenic levels.

In order to preserve water quality, the sources of ammonium ions and arsenic should be identified and the processes leading to the observed ammonium ion and arsenic concentrations should be better understood.

1.2 Objectives

This master's thesis has two objectives:

1. To investigate the fate of nitrogen species, including a study of the isotopic composition of nitrogen in order to trace nitrogen sources in groundwater, surface water and aquifer sediments in the Nam Du Area.
2. To relate the distribution of arsenic with the prevailing redox conditions and water chemistry in the Nam Du area, in order to identify the processes behind the mobilisation of arsenic.

1.3 Hypotheses

Based on Andersson and Norrman (1998), there should be mainly two potential sources of ammonium ions in Nam Du: (1) Nitrogen mineralisation in peat layers that are buried in the soil profile, and (2) ammonium ions derived from anthropogenic activities, such as leaching of nitrogen rich sewage water and farming activities (fertiliser and waste water applications on the fields). Isotopic fractionation of nitrogen results in different $^{15}\text{N}/^{14}\text{N}$ ratios in different nitrogen compounds. Mineralisation of peat should create a different $^{15}\text{N}/^{14}\text{N}$ ratio in the ammonium ions released due to this process, compared to ammonium ions derived from surface based activities. Comparisons of the isotopic composition of organic nitrogen in the peat and ammonium ions in the groundwater may indicate the ammonium ion source. Isotope studies combined with a conceptual flow model and measured redox conditions should give an indication of the main process that leads to high ammonium ion concentrations in the Nam Du area.

Mobilization of arsenic in ground water is mainly driven by two processes (Bhattacharya et al. 1997):

- (1) Oxidation of pyrite and/or arsenopyrite which occurs in clayey intercalations;
 - (2) Reduction of ferric coatings on sand grains releasing adsorbed arsenite/arsenate
- Investigations of redox conditions and chemical composition of the water may therefore indicate the processes behind arsenic mobilisation.

1.4 Scope of work/limitations

This work will focus on the processes that may lead to high ammonium levels, while processes associated with the mobilisation of arsenic will be discussed more briefly. There are two reasons for this, one is that the AmonAs project (see below) will focus more on arsenic in the second phase and the other reason is the time limitation of this master project.

1.5 Outline of project

This thesis is a part of the AmonAs project, initiated 2005 with the purpose to investigate the distribution of ammonium ions and arsenic in the Nam Du area and the processes of mobilisation. The project is carried out in collaboration between Swedish Geotechnical Institute, Royal Institute of Technology, Hanoi University of Science and Geology and Swiss Federal Institute of Aquatic Science and Technology and is financed by the Department of Research Co-operation at the Swedish International Development Cooperation Agency. Two field campaigns were planned within AmonAs. The first field campaign was carried out in February – March, 2006, and the results from this campaign are reported in this Master's thesis. The main purpose was to investigate the distribution of ammonium ions. The second field campaign of AmonAs should be carried out during March – April 2007 with a stronger emphasis on arsenic.

Before the field work started a literature study was made, including results reported from similar projects and similar local conditions as at the field site. The literature study was followed by a project design phase performed in collaboration with the Swedish and Vietnamese supervisors. The field work took place in Vietnam in February and March 2006, in collaboration with Vietnamese students from HUMG.

In order to get an overview of the spatial distribution of ammonium ions and arsenic, transects along the ground water flow direction were designed. The transects consisted of sampling points where groundwater could be sampled in wells, while points for collecting surface water were chosen afterwards to fit into the selected transects. Field data combined with literature studies were used to create a flow model describing one of the transects (no. 2). At all points samples were taken and sent to laboratories for chemical and isotopic composition. All data have then been analysed and compared with similar studies in order to understand the prevailing processes in Nam Du.

2 Theory

2.1 Nitrogen

The N content of the planet earth is 0.03%, out of which 97.76% is located in rocks, 2.01% in the atmosphere and the remaining 0.23% in the hydro- and biospheres (Kendall et al. 2000). Nitrogen compounds could have oxidation numbers extending from -III (NH_4^+) to +V (NO_3^-). All living organisms contain nitrogen, which is one of the main building blocks of DNA and proteins. More than 99% of the nitrogen in the hydro- and biosphere occurs as nitrogen gas (N_2) but it is the remaining smaller part that plays an essential role for life on earth (Hoefs 1997).

The nitrogen cycle

There is a continuous flow of nitrogen between, atmosphere, soil, water and organisms, which is described graphically in Figure 2-1. Nitrogen transformations in soil are mediated by micro-organisms. The main N inputs to the soil system originate from atmospheric N_2 via biological nitrogen fixation, application of mineral fertilisers (which are manufactured by using the Haber-Bosch method) or emission and fallout of gaseous NO_x compounds formed during combustion processes in factories and motor vehicles.

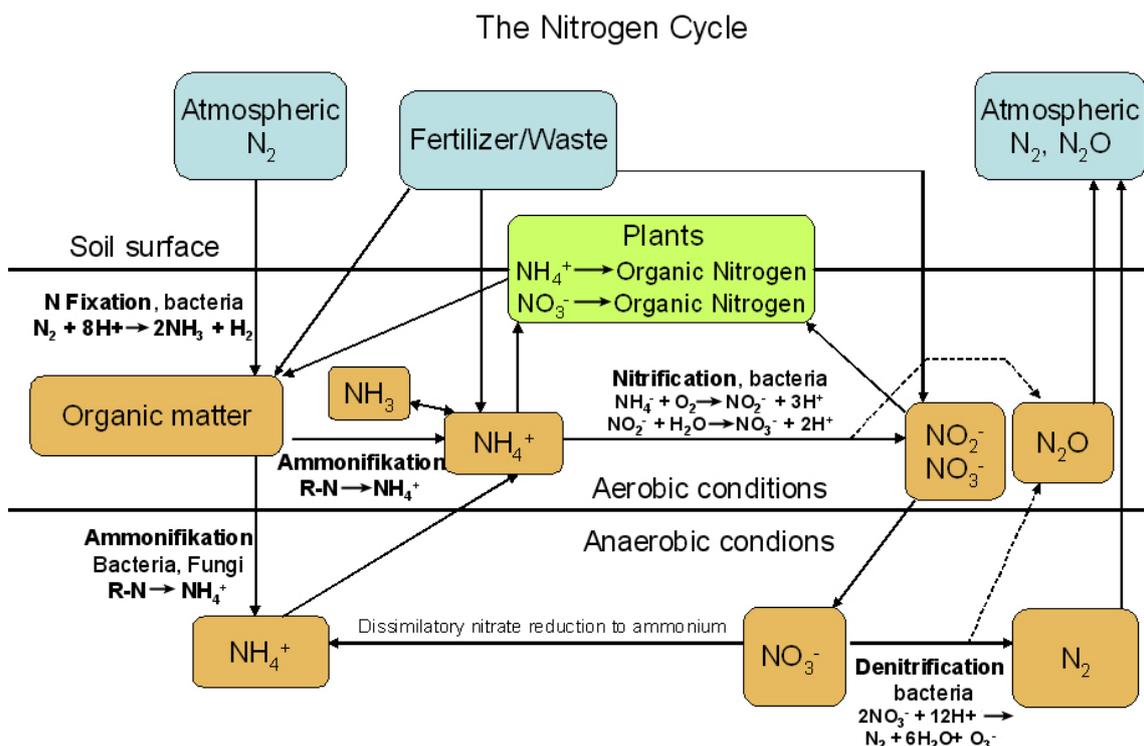
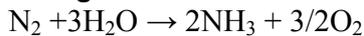


Figure 2-1 A simplified graphical description of the nitrogen cycle, which covers the processes that are considered in this thesis (Schlesinger 1997).

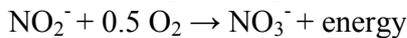
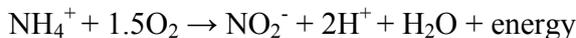
Nitrogen fixation



Cyanobacteria are the only soil organisms which can convert nitrogen gas to organic nitrogen (Hoefs 1997). An important part of the nitrogen fixation takes place in root nodules and is mediated by bacteria which either stay in symbiosis with vascular plants or are free living (Erikson et al. 2005). Under favourable growth conditions the organic nitrogen in dead bacterial cells will eventually be assimilated by other bacteria. A surplus of soil organic N favours net mineralisation of N to NH_4^+ which is available to plants (Hoefs 1997).

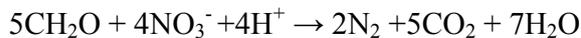
Nitrification

Nitrification is mostly carried out by autotrophic bacteria. The process can be divided into two steps.



The process takes place in soils under aerobic conditions. Even though nitrite (NO_2^-) is one of the products in the reaction chain from NH_4^+ to NO_3^- , it is generally not accumulated to any great extent. Nitrite seems to be converted to nitrate at the same rate as it is produced. Nitrification processes in soils with lower pH than 4.5 are often quite slow since most nitrifying bacteria grow best at neutral pH (Sylvia et al. 1999).

Denitrification



Under anaerobic conditions nitrate can be transformed to nitrogen gas (N_2) by micro-organisms which use nitrogen species instead of oxygen to oxidise organic matter (Sylvia et al. 1999). Denitrification is seen as a sink for soil nitrogen as there is an exchange between the produced nitrogen gas in the soil and the atmosphere. During partly anaerobic conditions, gaseous nitrogen compounds such as N_2O (laughing gas) can be formed (Erikson et al. 2005).

Dissimilatory reduction of nitrate to ammonium (DRNA)



Under anaerobic conditions dissimilatory reduction of NO_3^- ions to NH_4^+ ions (DRNA) may occur. The quantitative significance of DRNA seems to depend on factors such as nitrate and carbon availability and redox conditions (Sylvia et al. 1999). In solutions with high concentrations of nitrate, denitrification is the dominating process, while in solutions where organisms have access to carbon, and have a limited nitrate supply, DRNA is dominating (Bonin 1996). Strongly reducing conditions also seem to favour DRNA before denitrification (Kelso et al. 1997)

Ammonium ions

The following chapter is based on WHO reports EHC 54 (WHO 1986) and Guidelines for drinking water quality 3d ed. (WHO 2004).

The ammonium ion (NH_4^+) is positively charged and is formed by protonation of ammonia (NH_3). Usually it occurs in large amounts only under anoxic (reducing) conditions or after addition of farmyard manure. Ammonium ions are less mobile in the soil than are nitrate ions since ammonium ions bind electrostatically to negatively charged clay mineral or humic matter surfaces. Even though the presence of ammonium ions in groundwater is not a severe health problem, high amounts often indicate a water contamination.

Ammonium levels in unpolluted groundwater are usually below 0.2 mg N/l but can be higher in cultivated areas and in areas with an intensive animal production. Even though ammonium in groundwater is not directly a health problem, a high concentration often indicates water contamination from animal waste or sewage sludge. However, ammonium ions can be oxidised to nitrite ions that are known to cause Methemoglobinemia, or Blue baby disease. Therefore, carefulness should be practiced. The suggested threshold concentration regarding odour in drinking water is around 1.5 mg N/l and regarding taste the threshold is 35 mg N/l. However these values are only guidelines. As ammonia does not have any direct relevance to health at these levels no standard has been set.

2.2 Arsenic

The arsenic (As) content of the earth's crust is about 2 mg/kg. It is mainly found as a component in pyrite minerals or adsorbed to Al and Fe oxides as arsenite (As(III)) or arsenate (As(V)) ions. The speciation of arsenic is strongly dependent on pH and redox potential (Eh). Arsenopyrite, FeAsS , is the most common arsenic mineral. Elementary arsenic (As^0), forms small hard crystals but is very uncommon. Arsenic occurs in a variety of products such as fertilisers, pesticides and mine deposits. Generally, arsenic compounds have no specific taste or smell. The toxic effects are unspecific and involve the blocking of various enzymes that are essential for cell metabolism. Acute poisoning of humans leads to vomiting and diarrhea. Chronic exposure over ten years or more may cause skin or bladder cancer. Poisoning is usually treated with an antidote that binds As and increases its secretion (WHO 2001).

Mobilization of arsenic in ground water is mainly driven by two processes (Bhattacharya et al. 1997):

- (1) Oxidation of pyrite and/or arsenopyrite which occurs in clayey intercalations;
- (2) Reduction of Fe(III) in ferric coatings on sand grains, which results in a release of adsorbed arsenite/arsenate

2.3 Isotopes and fractionation processes

Isotopes of an element have the same number of protons but differ in their number of neutrons. Isotopes thus have the same atomic number but different masses. The number of protons decides the element, and the number of neutrons describes the isotope, illustrated as ${}^m_n\text{E}$, where: E is the element, m is the mass number, and n is the atomic number (Clark et al. 1997). Differences in the number of neutrons have effects on both chemical and physical properties, but effects on physical properties are more important for the lighter elements. For instance the deuterium molecule (${}^2\text{H}$) has almost twice the weight of an ordinary hydrogen molecule (Hoefs 1997).

Isotopes are divided into two major groups; stable and unstable, where the unstable isotopes are classified as radioactive. The stability depends on the proportion of neutrons compared to protons (Clark et al. 1997). Most compounds consist of a mixture of isotopes, where one isotope (the basic element) is dominating. The proportion between a basic element and other isotopes is described as Z/N, where Z is the amount of an isotope and the N is the amount of the basic element. The different properties of the isotopes make them react and behave differently, e.g. during chemical reactions and diffusion (Hoefs 1997). In general, the lighter isotopes react faster than the heavier ones and most enzymes in organisms are adapted to the basic elements (Kendall et al. 2000). The Z/N relation can therefore indicate the importance of an isotope as an analytical tool for tracing the origin and reaction pathways of many elements (Hoefs 1997). A change in the Z/N ratio indicates an isotopic fractionation.

N-fractionation

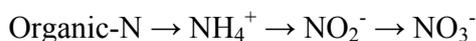
Nitrogen has two stable isotopes, ^{14}N and ^{15}N . The $^{15}\text{N}/^{14}\text{N}$ ratio in the atmosphere is constant and equals about 1/272 (Kendall et al. 2000). This gives an atmospheric nitrogen composition of 99.64% ^{14}N and 0.36% ^{15}N . ^{15}N values in investigated media are often expressed as per mille of N_2 in the atmosphere (Hoefs 1997). The ratio between ^{15}N and ^{14}N is usually written as $\delta^{15}\text{N}$.

The fractionation factor for biological processes depends on temperature, concentration of products and reactants, humidity and the organisms involved. Usually, ^{14}N reacts faster than ^{15}N resulting in a product with a lower $^{15}\text{N}/^{14}\text{N}$ ratio than in the reactants. One reason for this is that bacterial enzymes are adapted to process ^{14}N rather than the heavier ^{15}N . The conversion of NH_4^+ to NO_3^- is such an example where NH_4^+ ions that have not reacted will have a higher $^{15}\text{N}/^{14}\text{N}$ ratio than the resulting NO_3^- ions (Kendall et al. 2000).

Each step in the nitrogen cycle where NH_4^+ is either a product or a reactant will change the isotopic composition. The four processes in the nitrogen cycle that affect the $^{15}\text{N}/^{14}\text{N}$ ratio of NH_4^+ are volatilisation, mineralisation, nitrification, and DRNA. Different nitrogen sources will also have their characteristic $^{15}\text{N}/^{14}\text{N}$ ratios which is useful for the tracing of nitrogen pathways (Hoefs 1997).

Mineralisation and Nitrification

There are three steps in which fractionation can take place during N mineralisation and nitrification, as illustrated below.



When organic nitrogen is mineralised to NH_4^+ there is usually no or very little fractionation (Hoefs 1997). If a comparatively large amount of NH_4^+ is available most of the fractionation takes place in the last two steps. The resulting NO_3^- ions will be depleted in ^{15}N by 25-35% compared to NH_4^+ which is enriched with respect to ^{15}N . This is what usually happens when mineral fertiliser or manure is applied to a field (Kendall et al. 2000). If there is no nitrification, mineralisation will produce NH_4^+ with a similar $^{15}\text{N}/^{14}\text{N}$ ratio as that in organic matter. In many soils organic nitrogen is mineralised at a slow rate. The, the first step ($\text{Organic-N} \rightarrow \text{NH}_4^+$) is rate limiting, and the resulting NO_3^- will have an isotope composition similar to that of the organic nitrogen source (Hoefs 1997). The

oxygen in the nitrate ion will also be fractionated. For the tracing of nitrate a $\delta^{18}\text{O}/\delta^{15}\text{N}$ diagram is very useful (Figure 2-2). This is of less importance in the present study, which focuses on ammonium ions, but the origin of nitrate could indicate the ammonium source.

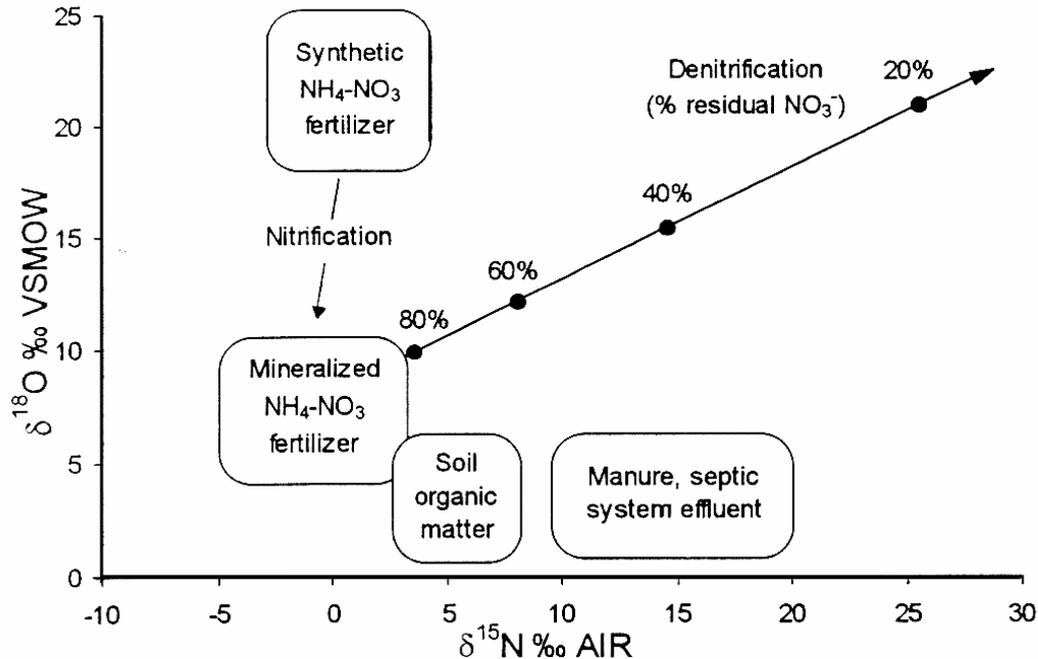


Figure 2-2 Different sources have different $^{18}\text{O}/^{15}\text{N}$ ratio in nitrate. The process of denitrification will make a positive correlation ammonium (Clark et al. 1997). Note that the figure refers to nitrate and not ammonium.

Volatilisation

Fractioning during ammonium volatilisation will result in a depletion of ^{15}N in the emitted NH_3 gas while the remaining NH_4^+ ions in the soil solution will be enriched. The $^{15}\text{N}/^{14}\text{N}$ ratio in the residual NH_4^+ ions may be well above 20‰. Isotopic fractionation takes place both during the conversion of $\text{NH}_4^+(\text{aq})$ to $\text{NH}_3(\text{aq})$, and the conversion of the latter to $\text{NH}_3(\text{g})$ (Kendall et al. 2000).

Dissimilatory reduction of nitrate to ammonium (DRNA)

The fractioning during DRNA can be seen as a reverse nitrification and is considered to have the same effect as denitrification (Lehmann et al. 2003). The produced NH_4^+ ions will have a lower ^{15}N content than the residual NO_3^- ions (Cline et al. 1975).

Sulphur

When SO_4^{2-} is reduced by bacteria to H_2S , sulphur fractionation is typically taking place. The heavy ^{34}S isotope will be enriched in the residual SO_4^{2-} ions while ^{32}S will be depleted. The isotopic composition of SO_4^{2-} gives an indication of the prevailing redox conditions. Some of the SO_4^{2-} reducing bacteria can also be expected to reduce NO_3^- to NH_4^+ (Dalsgaard et al. 1994).

Deuterium and ^{18}O

Deuterium (^2H) and ^{18}O are used for tracing water in the hydrogeological cycle. The fractionation of deuterium and ^{18}O takes place during evaporation and rainfall. A higher

temperature (implying a higher evaporation) will result in a linear enrichment of the heavy isotopes deuterium and ^{18}O in rainfall. Water masses within the hydrogeological cycle, that have a similar $^{18}\text{O}/^2\text{H}$ ratio, usually have an hydraulic connection. Apart from indicating the circulation of the water, fractionation of deuterium and ^{18}O can, to some extent, be used for dating water and revealing climate changes (Clark et al. 1997).

Tritium

Tritium ^3H has a radioactive half life of 12.3 years. It is one of the most common isotopes used for dating the age of water, because of its incorporation in water molecules which are transported throughout the hydrogeological cycle (Lucas et al. 2000). A background level in precipitation is always present and maintained by cosmic radiation in the upper atmosphere. Hydrogen bomb tests during the 1950s to the 80s created a tritium “peak” which can still be traced, although the level in the current precipitation is very close to the background level. Since water older than the bomb tests will have a very low tritium level, it is difficult to date water recharge originating from the period before 1951. Tritium levels are measured as Tritium units (TU) (Clark et al. 1997).

The following data are valid for coastal and low latitude regions (Clark et al. 1997). The current values will be somewhat lower due to the decay of tritium.

<0.8 TU	Submodern recharged before 1952
0.8 to 2 TU	Mixture between submodern and recent recharge
2 to 8 TU	Modern (<5 to 10 years)
10 to 20 TU	Residual ^3H from bombs is present, recharge 10-40 years.
>20 TU	Considerable component of recharge from 1960 and 1970.

2.4 Redox reactions

Redox reactions occur due to the movement of electrons from one atom to another and the order in which these reactions proceed can be predicted from thermodynamic theory. As a result the involved atoms will change their oxidation number (Spocito 1989). Reduction implies a gain of electrons and is defined as a decrease in oxidation number. Oxidation is the opposite process, i.e. a loss of electrons, defined as an increase in oxidation number. The process always involves one oxidized chemical species which donates electrons and a reduced species which accepts these electrons.

It is convenient to describe redox reactions by splitting them into two half reactions, one involving the electron donor and the other the electron acceptor (Gustafsson et al. 2006). Due to kinetic constraints redox processes are often quite slow. Soil micro-organisms provide enzymes which will catalyse the reactions (Spocito 1989).

Redox processes in groundwater typically occur through the addition of an oxidant such as O_2 or NO_3^- . There is also a need of a reductant, which is usually dissolved organic carbon (Apello et al. 2005). In nature reducing environments often exist when there is plenty of organic matter and the soil is saturated with water. The oxygen is then rapidly consumed and the electron activity measured as the redox potential (Eh) decreases, which can be measured potentiometrically. The process can continue with other oxidants, see Figure 2-3, resulting in lower Eh values for each oxidation step, (Gustafsson et al. 2006).

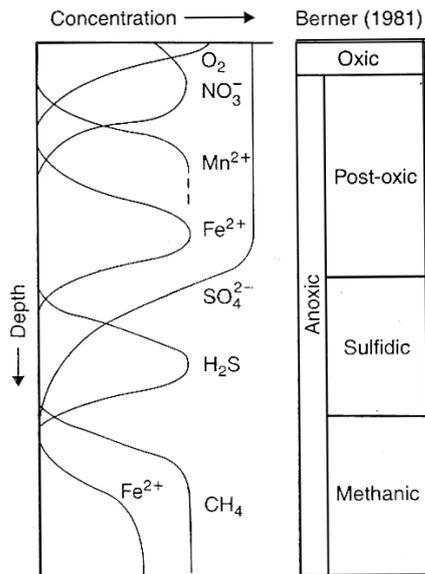


Figure 2-3 The compound reduced depends on the on the availability of oxidants. Different compounds are reduced or oxidised depending on the redox conditions (Apello et al. 2005).

In most soils, C, N, O, S, Mn, and Fe are the most important elements affected by the redox conditions. In polluted soils, the pollutant (for example arsenic) should be added to this list (Spocito 1989). The redox potential (Eh) and pH are the most important variables controlling the arsenic speciation, see Figure 2-4 (Smedley et al. 2002). Redox conditions are also to large extent controlling the processes in the nitrogen cycle (Figure 2-5). Typically the mineralisation of peat and the dissimilatory nitrate reduction should be active under different redox regimes (Binner et al. 1992).

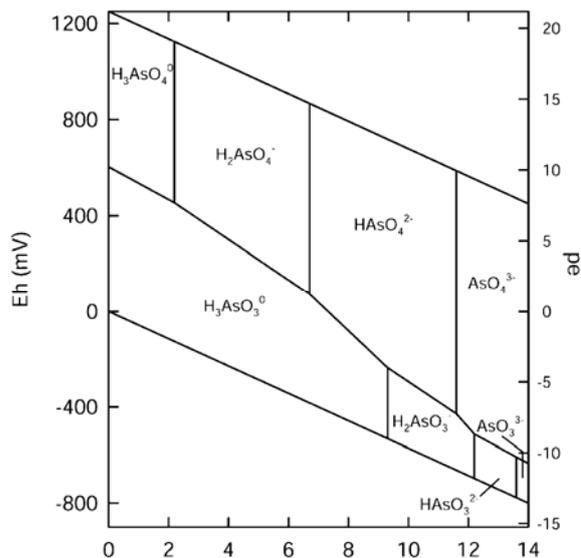


Figure 2-4 Arsenic exists in several forms depending on Eh (indication of redox conditions) and pH (from Apello et al. 2005).

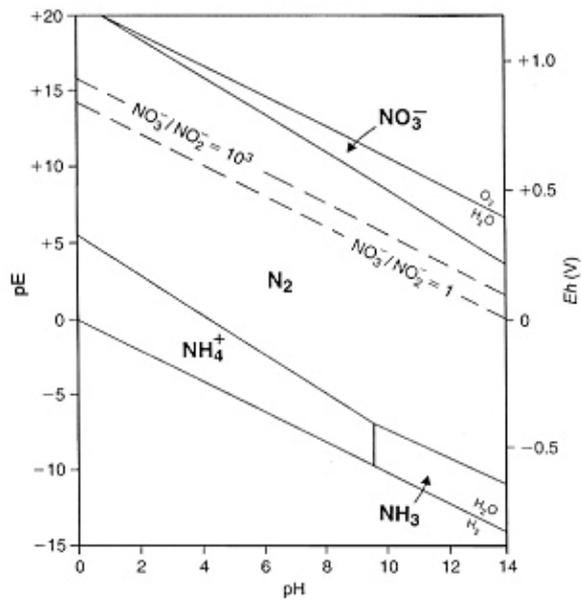


Figure 2-5 The form of nitrogen, at equilibrium, is dependent on pH and pE (description of redox conditions) (from Apello et al. 2005).

3 Study area: Nam Du well field

3.1 Geography and climate

Hanoi

Hanoi, the capital of the Socialist Republic of Vietnam, is situated in the centre of the 11 000 km² Red River delta on the Bac Bo plain in northern Vietnam, an area with approximately 11 million inhabitants (Trafford et al. 1996), (see Figure 3-1). In 2004, Hanoi was inhabited by 3.1 million people and with a growth rate of 1.5% annually, the city is expected to have around 5 million inhabitants in the year 2020 (van Horen 2005).



Figure 3-1 Map of Vietnam (CIA 2007).

In Hanoi, the treatment of sewage water is poor, liquid waste in the town is disposed through open drains which run along the edges of the streets to larger drainage canals or branches of the Red River. Every evening trucks collect the solid waste, which is swept into the streets, and transported to waste sites in the area. There is no strict border between city and farmland. However, the percentage of farmland increases in the suburbs. Animal waste, urea and waste water from the City are used as fertilisers on the fields (Trafford et al. 1996).

Extraction of groundwater began about 100 years ago during the French occupation (Dang et al. 1996). Since the 1960s, the extraction has increased rapidly (Trafford et al. 1996). Today about 500 000 m³/day is extracted according to official information (Duong et al. 2003). The extracted water mainly originates from the Hanoi aquifer system at ten major well fields (Berg et al. 2007). The water passes the eight major water treatment plants prior to distribution (Duong et al. 2003). In addition, there is an unknown number of small private tube wells for water extraction, mainly from the upper

aquifer and the total estimated extraction reaches 700 000 m³/day (Nhan 2006). In 2010, the extraction is expected to reach 1,000,000 m³/day (Dang et al. 1996).

Climate

The Hanoi area has a hot and rainy season with a mean temperature of 29°C in May – October. The annual average precipitation is 1700 mm, 80-90% of which falls in July - September. There is a cool and dry season in November – March with a mean temperature of 16°C. By the end of this season, drizzles and monsoons are frequent. Since the recharge is restricted to the rainy season and the annual evaporation is 1025 mm, the evaporation exceeds the precipitation during the dry season and causes a drawdown of the groundwater table (Trafford et al. 1996; van Horen 2005).

The Red River and its delta

The area is a flat delta landscape with only small altitude differences (1.9 – 10.6 m) and the Red River floats through the landscape. The length of river is 1150 km. It originates from the eastern Tibetan plateau in the Chinese Yunnan province (Tanabe et al. 2003). The Red River continues in a NW-SE direction through the mountainous area of north-western Vietnam down to the Gulf of Tonkin in South China Sea. The Red River received its name due to the iron-rich silt, which gives the river a red colour. The catchment area of the Red River is 170 000 km² and throughout the year the discharge varies between 700 – 23000 m³/s, with an average discharge of 3740 m³/s (Tanabe et al. 2003; Berg et al. 2007).

Nam Du well field

The Nam Du well field is located 10 km southeast of Hanoi city along the Red River (20°58'56'' N, 105°55'02'' E to 20°57'55'' N, 105°53'43'' E) in the Thanh Tri district (Figure 3-2). The area around the well field is relatively flat, with an elevation around 6.5 – 11 m above sea level.

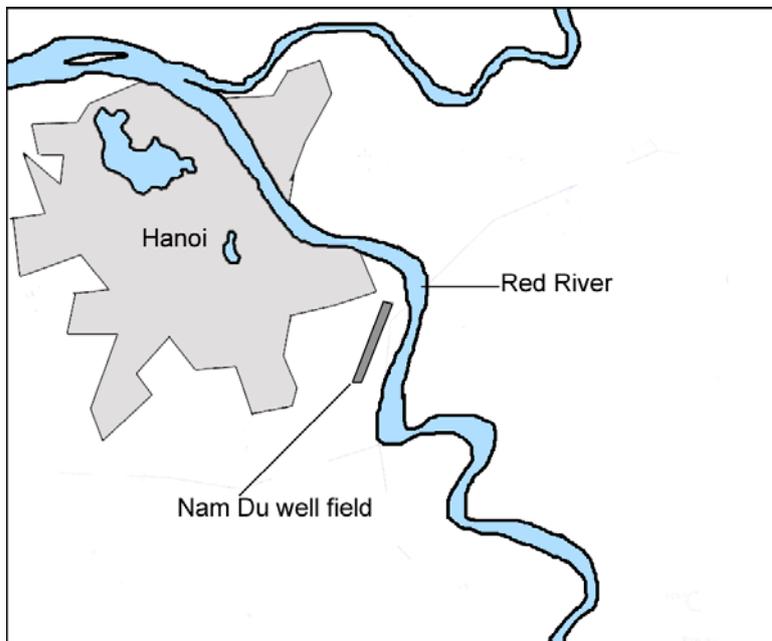


Figure 3-2 Map over the Hanoi area. The Nam Du well field is situated south east of the town centre.

There is a dyke with a road running along the river where the nine production wells (total capacity of 30.000 m³/day) are located. Water from the well field passes a treatment plant before it is distributed to the citizens of Hanoi. The distance of the production wells from the river depends on the season. At the time of sampling (dry period) they were located approximately 200 m from the river, with 250 m between each well. A second well field (Nam Du 2) was under construction during the time of the sampling campaign, and in the autumn of 2006 some of the wells were started to test the water production. Nam Du 2 is a continuation of the Nam Du 1 with nine more wells and the same total production capacity as ND1, i.e. 30,000 m³ per day. It is located in the same direction as Nam Du phase 1, continuing south along the Red River. A third phase is being planned south of the second phase. The reason for locating the wells along the Red River is to increase the

recharge and at the same time minimise ammonium ion and arsenic contamination. About 50% of the recharge is coming from the Red River (Nhan 2006).

The area of the well field is separated from the city by farmland and there are several small ponds in the area. The area is dominated by agricultural activities (Figure 3-3). Common crops are rice (paddy), banana and vegetables. During the field measurements, it was noticed that many farmers were spraying pesticides on their crops only a few meters away from the production wells. The main industries in the area are brick and sand production, and along the second phase (see below) of the well field there is a large harbour. Brick factories were situated at the shore of ponds two and three and all ponds were surrounded by farmland (Figure 3-4).



Figure 3-3 Photo with production well ND9 to the left, surrounded by farmland.



Figure 3-4 Photo of pond 2, with a small brick factory to the left (Photo: Håkan Rosquist).

3.2 Geology

The geological formations in the Nam Du area are mainly of Quaternary and Pliocene origin. The sedimentological history is complex because of transgression and regression of the sea level. This has created formations with different thickness in the area. In general, most of the formations are thinnest in the NW and thickest in SE of the Red River delta. The formations might also be discontinuously distributed, and be absent at some parts (Dang et al. 1996; Trafford et al. 1996; DTU 2005). For an overview of the geological time scale, see Figure 3-5. For an overview of the soil profile with formations and aquifers, please see Figure 3-6. If not stated otherwise the following sections are based on a report from Dang et al. (1996).

Era	Period	Epoch	Start, million years ago	
Cenozoic	Quaternary	Holocene	0.11	
		Pleistocene	1.8	
	Tertiary	Neogene	Pliocene	5.3
			Miocene	23
		Paleogene	Oligocene	34
			Eocene	56
			Palaeocene	65

Figure 3-5 Overview of the geological time scale under the cenozoic era, constructed after information from (Tarbuck et al. 2002).

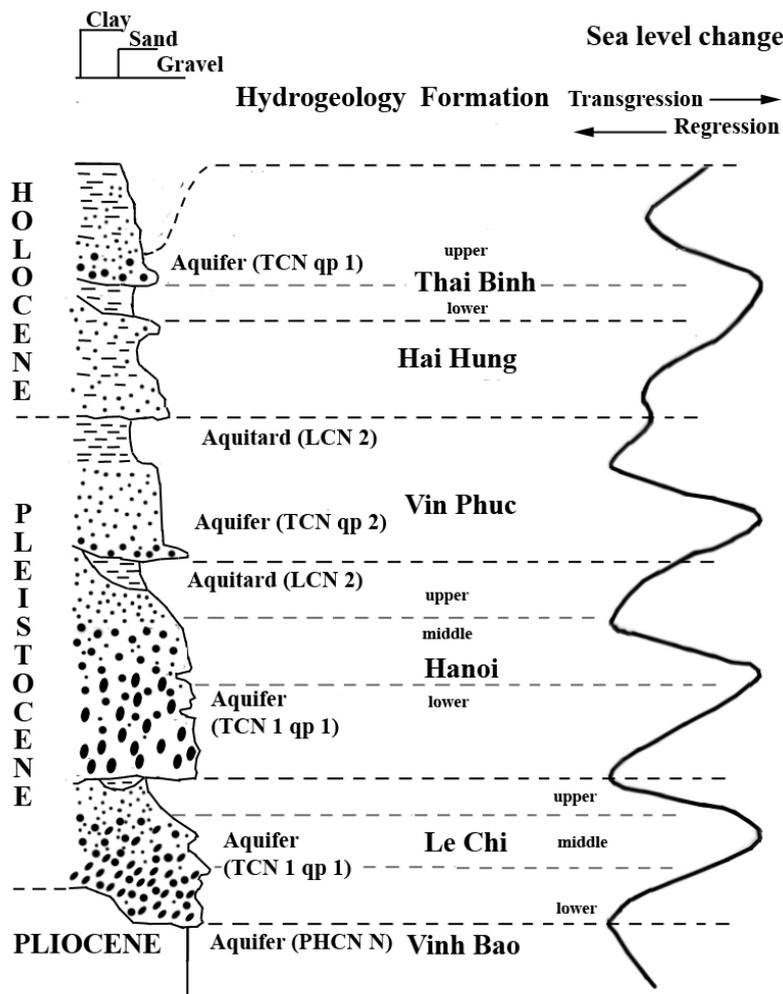


Figure 3-6 Cross section of soil profile with formation names, sea level change, aquifers, materials and time periods (Mathers et al. 1999; Nghi 2004; Dang et al. 1996).

The Holocene formations

Thai Binh ($Q_{IV}^3 tb$)

The youngest sediments are the Thai Binh formations, of late Holocene origin, which mainly consist of alluvial deposits from the Red River and were formed from 3000 years ago until present time. The upper Holocene formation can be divided into two subgroups: upper ($Q_{IV}^3 tb2$) and lower ($Q_{IV}^3 tb1$) Thai Binh formation.

The upper Thai Binh formation mainly consists of cobbles, pebbles, sand, clay, and silty clay with brown to grey-yellow colour. While the average thickness of the upper formation is 2.5 – 7 m, the thickness of the lower Thai Binh formation can reach 27 m. This formation consists mainly of grey medium grained sand mixed with silty sand, silty clay and layers with brown-grey humic material derived from plants. Thick layers of peat have been found in this formation (Trafford et al. 1996; Berg et al. 2001; UNICEF 2001).

Hai Hung (Q_{IV}^{1-2})

The Hai Hung formations, the lower Holocene subdivisions, are formed from lacustrine, palustrine and marine deposits consisting of silty sand, silty clay and gravel mixed with peat and plant remains. These formations, with an average thickness of 1 – 10 m, are found at a depth of 23.5 – 37 m and consist mainly of sand.

The Pleistocene formations

Vin Phuc (aQ_{III}^2 vp)

The Vin Phuc formation in the Nam Du area has a mean thickness around 12 m, increasing towards south east.

The upper Pleistocene formation, Vin Phuc, consists of an upper clay layer mixed with sand lenses with brown and red colour. In this layer, spores and pollen grains of ferns etc. were found by Dang et al in 1996. The fractions in the lower formation are gravel, pebbles, sand, silt, and clay of yellow –yellow-grey colour. The grains are medium to well sorted and rounded. At some locations in this layer peat and fresh water algae can be found.

Hanoi formation (aQ_{II-III}^1 hn)

The Hanoi formation is from the middle Pleistocene and consists of gravel mixed with sand of alluvial origin. The higher up in the formation, the finer is the sediment and in the top, local clay lenses can occasionally be found. The average thickness in the Nam Du area is 18 m.

The uppermost part of the Hanoi formation consists of clayey - sandy silt, cobbles, mixed with clay of yellow grey or yellow brown colour that originates from flood plains. Occasionally there are lenses of black grey silty clay, mixed with humic material. The average thickness is 4 m. In the upper part there are traces from fresh water pollens.

In the middle of the Hanoi formations there are small pebbles, coarse sand and silt with a grey yellow colour, with an alluvial origin. The sediments are mainly composed of quartz, silica feldspar. In this part, the thickness varies between 1.5 – 7.3 m.

The bottom formation consists mainly of coarser fractions such as cobbles, pebbles and gravels, mixed with sand and silt of alluvial origin. The cobbles consist of quartz, silica and extrusive rocks. This is the thickest part of the Hanoi formations, between 10 – 19 m.

Le Chi (aQ_I lc)

Below the Hanoi formation is the Le Chi formation of early Pleistocene origin. The thickness varies between 0.5 – 2.5 m, and is present at depths of 60 – 63 m in the Nam Du well field.

The upper part consists mainly of sand, silt and clay mixed with organic matter. In contrast to the middle part of the formations, the grains in the upper part are of alluvial origin and are neither well sorted nor well rounded.

In the middle part the soil fractions are mainly fine sand and silty sand of grey yellow colour, also here with an alluvial, or near alluvial, origin. The lowest part consists of a mixture of well rounded cobbles, pebbles and sand, silt and clay deposited by the mountain rivers (Dang et al. 1996; DTU 2005).

The Pliocene formations

Vinh Bao (N₂ vb)

Below the quaternary system, is the Neogene formation from the Pliocene epoch. This formation starts at a depth of 64 – 71 m and continues down to approximately 100 m, but no borehole has penetrated the formation completely. This layer consists of weak conglomerates of sandstone, clay stone and well-rounded pebbles. When prospecting for the well field, fossils of organisms that lived in shallow marine environments, close to the shore were found in the Pliocene formations.

3.3 Hydrogeology

The hydrogeological features of the area such as permeability, water bearing capacity and hydrodynamic characteristics have been documented (Dang et al. 1996). Similarly to the geological formations, the extent of the geohydrological formations generally increases from NW to SE (Trafford et al. 1996). Six major geohydrological units could be distinguished see Figure 3-6. Unless stated otherwise, this chapter is based on the work of Dang et al. In 1996.

- A. Aquifer in Holocene sediments, (TCN qh)
- B. Aquiclude in Pleistocene-Holocene sediments (LCN 1)
- C. Aquifer in upper Pleistocene sediments (TCN qp 2)
- D. Aquiclude in middle-upper Pleistocene sediments (LCN 2)
- E. Aquifer in lower-upper Pleistocene sediments (TCN 1 qp 1)
- F. Water bearing formations in Neogene sediments (PHCN N)

A. Aquifer in the Holocene sediments (TCN qh).

In the Nam Du well field the thickness of this aquifer varies between 4 – 34 m, while the average thickness is 21 m. The groundwater table is normally found at a depth of 1 – 6 m, which varies with the type of landscape and throughout the year. This is a confined or locally confined aquifer and is overlain by a discontinuously distributed layer (Q_{IV}³ tb2). Pumping tests from wells in the area show that the specific capacity (Q) is 1.06 – 20.87 l/sm and the transmissivity¹ ranges from $2.31 * 10^{-4}$ – $9.14 * 10^{-3}$ m²/s. Abstraction from UAS is mainly from small private wells (DTU 2005). In the Nam Du well field this aquifer has a close hydraulic connection to the Pleistocene aquifers (qp1 and qp2), and at some points there is a vertical leakage from the Holocene aquifer and downwards.

B. Aquiclude in Pleistocene-Holocene sediments (LCN 1)

The LCN 1 aquiclude is of early Holocene and late Pleistocene origin. The thickness varies between 1 – 16 m and the average hydraulic conductivity coefficient K, is $6.13 * 10^{-7}$ m/s in LCN 1.

¹. In the reference the term transmissibility is used, but since it is stated as m²/d and describes water flow, the author assumes it is transmissivity

C. Aquifers in upper Pleistocene sediments (TCN qp 2)

Aquifer qp 2 is present in the coarser fractions of the lower Vinh Phuc formation. In Nam Du this aquifer is encountered at depths between 16 – 42 m and has an average thickness of 11 m. Q, the specific capacity, varies between 0.18 – 5.35 dm³/sm, and the transmissivity¹ coefficient varies from $1.85 * 10^{-4}$ – $5.10 * 10^{-2}$ m²/s (K $1.68 * 10^{-5}$ – $4.64 * 10^{-3}$ m/s), but has an average on $2.08 * 10^{-3}$ m²/s. In the Nam Du area, this aquifer is connected to the Red River. The static water level varies between 0.7 – 5.9 m

D. Aquiclude in middle-upper Pleistocene sediments (LCN 2)

The LCN 2, from the upper part of the Hanoi formation, is not distributed continuously over the Nam Du area. This creates a hydraulic window between qp 1 och qp 2. The average hydraulic coefficient K is $9.26 * 10^{-8}$ m/s, much lower compared to $6.13 * 10^{-7}$ m/s in LCN 1. However, due to the hydraulic windows in the aquiclude, there is a hydraulic contact between the Holocene and the upper Pleistocene aquifers.

E. Aquifer in lower-upper Pleistocene sediments (TCN 1 qp 1)

The Hanoi aquifer (qp 1) is present in materials in the lower Hanoi and the Le Chi formations, and is found at depths of 35 – 71 m. The average thickness is 21 m, but ranges from 14 – 46 m. Pumping tests from wells in the area show a specific capacity (Q) of $Q = 6.97 – 23.7$ dm³/sm. The transmissivity¹ ranges from between $9.83 * 10^{-3}$ – $3.07 * 10^{-2}$ m²/s (K is $4.68 * 10^{-4}$ – $1.46 * 10^{-3}$ m/s). The abstraction from this aquifer has increased since the 1950's and is mainly for production wells (Trafford et al. 1996). In the Nam Du well field, qp 1 is closely connected to both qh and qp2, as well as the Red River. The static water level varies between –12 and –24 m.

F. Water bearing formations in Neogene sediments (PHCN N)

Directly under qp 1, at depths of 64 – 81 m, Neogene formations with a water bearing capacity are found. The specific capacity, Q, is lower than in the upper aquifers, varies from 0.005 – 3.46 dm³/sm and the transmissivity¹ is $6.37 * 10^{-4}$ – $9.71 * 10^{-3}$ m²/s (Dang et al. 1996). The static water level is 0.3 to 12.3 m. At some locations it contains brackish water (Trafford et al. 1996).

Upper and lower aquifer system

Some authors, e.g. Trafford, 1996 and DTU, 2005 describe the hydrogeological composition of the area in terms of the upper aquifer system (UAS) and the lower aquifer system (LAS). The UAS includes the Holocene aquifer qh and the upper Pleistocene aquifer qp, which are separated discontinuously by the aquiclude LCN 1. The thickness of UAS varies from 10 – 45 m. Ground water from the UAS is primarily important as a source for recharge of the LAS, more than a direct source for drinking water (Trafford et al. 1996) The LAS is the Hanoi aquifer, qp2. LAS, like UAS increases from northwest to southeast and the thickness varies from 16 – 100 m (UNICEF 2001).

3.4 Occurrence of minerals

In the north Bac Bo plain, rock types such as conglomerate, sandstone, shale, chert siliceous limestone and shale with bauxite are abundant. In the north-east of the delta, sedimentary deposits and residuals of kaolin, feldspar, bentonite, diatomite, pozzolanic clay and coal are dominating. North of the delta, barite, tin, zink-lead and copper of post magmatic origin are present and in the northernmost districts there are large aluminium deposits and some zink-lead deposits.

In the area where the Red River flows into Vietnam, phosphates are abundant, and copper, molybdenum, uranium and dolomite are present. On its way to Hanoi, the Red River passes through areas rich in iron and kaolin. West of Hanoi, there are large amounts of post magmatic talc, asbestos and serpentine and in the western Bac Bo plain, rhyolite, orthopyre, tuff and basalt dominate.

Among elements that are present in northern Vietnam Mn, Ti, Cr, Ni, Sb, Hg, W, Be, Zr, Au, Ag, V, Mo and U should be mentioned. Non-metallic elements are found in pyrite, barite, fluorite, graphite, crystal quartz, mica, corundum, sillimanite, silica sand, quartzite gravel sand and siliceous, intermediate igneous rocks. Only at one spot in northern Vietnam, about 75 km north of Hanoi local mineral formations, containing arsenic, are present (UN 1990).

4 Materials and Methods

4.1 Sampling scheme and laboratories

The sampling sites were chosen in order to get transect lines along the groundwater flow (Figure 4-1). The sample codes are summarised in Table 4-1. Individual wells were chosen as starting points and riverbank and pond sites were chosen to fit the direction of the groundwater flow. A sketch of a transect line and sampled materials is shown in Figure 4-2. We identified transects and sampled at different depths in order to explore relationships between groundwater flow and the concentrations of As and NH₄ ions.

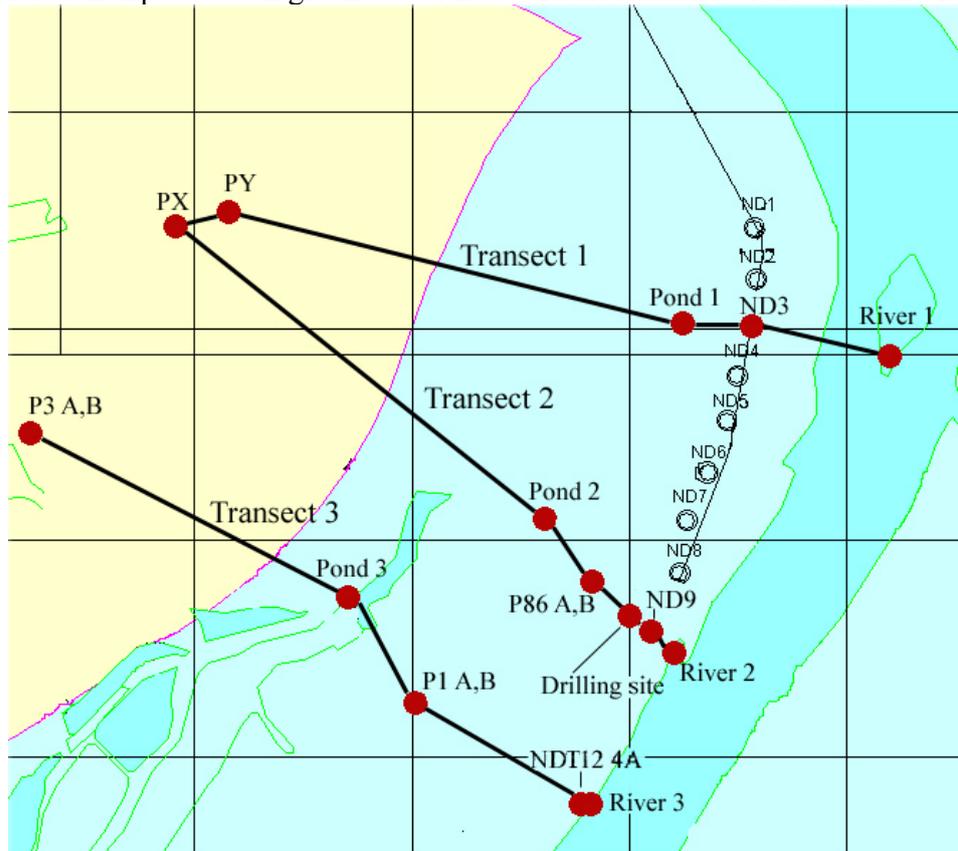


Figure 4-1 Map of the Nam Du area with sampling points and transects running perpendicular to the river. Transects run along the main flow direction of the groundwater; from the north west towards the south west.

Table 4-1 Summary of sample codes

P1AB, P3AB and P86AB	Monitoring wells
B	Upper aquifer (qh)
A	Lower aquifer (qp)
ND3, ND 9, PY and PX	Production wells
NDT 12	Observation well use for old pumping tests
Pond 1, Pond 2 and Pond 3	Ponds surface water
1RGw, 2RGw and 3RGw	River groundwater
2RSw	River surface water
Rb1, 2, 3	River bed (for infiltration measurements)

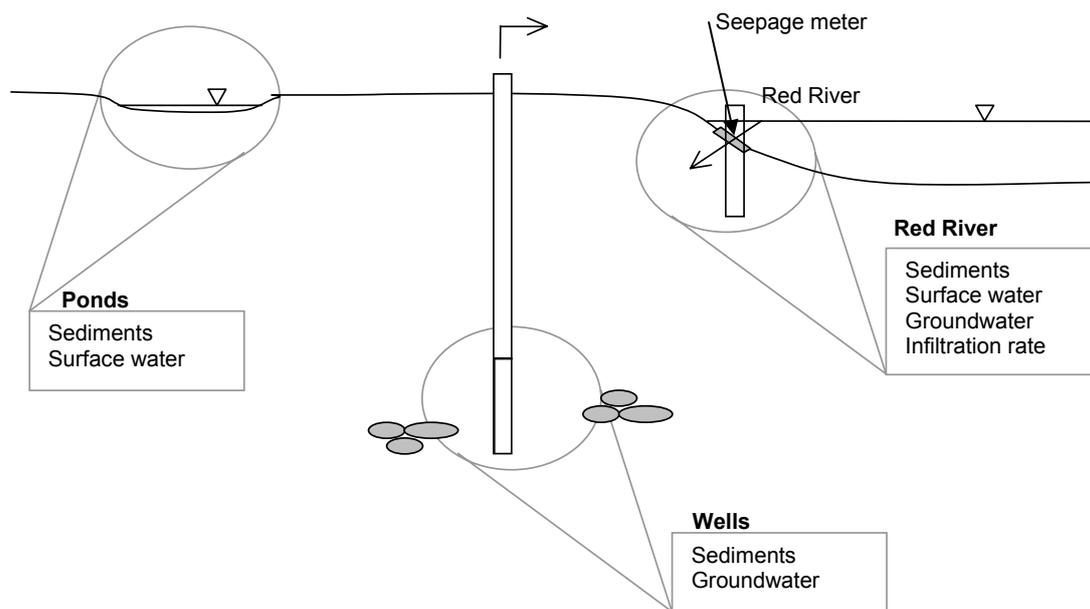


Figure 4-2 Schematic picture of locations and sampled media along a transect at the Nam Du field site.

Due to the different types of analyses and our intention to support collaboration with several laboratories, multiple samples were taken at each location and sent to different laboratories. These laboratories are listed in Table 4-2, and the analyses in each laboratory are summarised in

Table 4-3.

Table 4-2 The laboratories used in the study.

CETASD – Centre for Environmental Technology and Sustainable Development, Hanoi
EAWAG – Swiss Federal Institute of Aquatic Science and Technology, Switzerland
INST – Institute of Nuclear Science and Technology, Hanoi
ÅAU – Åbo Akademi University, Finland
SU – Stockholm University, Sweden
SLU – Swedish University of Agricultural Sciences, Umeå

Table 4-3 A summary of all laboratories, sample type and sampled volumes.

Laboratories	Main comp + DOC.	As spec	Trace el	$\delta^{15}\text{N}$ NH_4^+	$\delta^{15}\text{N}$, $\delta^{18}\text{O}$ NO_3^-	$\delta^{18}\text{O}$, $\delta^2\text{H}$ H_2O	^3H	$\delta^{34}\text{S}$	$\delta^{15}\text{N}$ in org-N Sediments
EAWAG	120 + 25 ml	50 ml	50 ml						
CETASD	500 ml		500 ml						
INST	500 ml		500 ml	3 l	3 l	50 ml	1.5 l		
ÅAU								10 l	
SU	120 ml	50 ml	50 ml						
SLU (Umeå)									200 g

To characterize the spatial distribution of parameters supposed to affect the fate of nitrogen and arsenic, water and sediment samples were taken at different locations and at

different depths. A summary of the locations for the different analyses are given in Table 4-4.

Table 4-4 A summary over conducted analysis and the samples collected at the respective sampling sites. All were water samples except sediments. A “X” means all sites were analysed for the given parameters, however, some sites were not investigated for all parameters and for these parameters the sampled sites are named.

Sampling sites	Main comp.	As spec	Trace el	¹⁵ N/ ¹⁴ N in NH ₄ ⁺	¹⁵ N/ ¹⁴ N ¹⁸ O/ ¹⁶ O in NO ₃ ⁻	¹⁸ O/ ² H in H ₂ O	³ H	³⁶ S	C/N Ratio	¹⁵ N/ ¹⁴ N org N
Ponds (D)	X	X	X	X	X	X				
River surface water (RSw)	X	X	X	X	X	X				
Shallow groundwater (RGw)	X	X	X	RGw 1	X	X				
Production wells	X	X	X	X	X	X	ND9	X		
Monitoring wells	X	X	X	X	X	X	PX, P86A P3A	X		
Sediments	X ²	X ²	X ²						X	X

4.2 Collection of samples in the field

Surface water from the ponds and the river

The surface water samples from the ponds and river, which should be analysed at EAWAG were collected directly from the water surface at all locations. Water that should be analysed at INST or CETASD was first transferred to a bucket from which subsamples for the two laboratories could be collected.

Shallow groundwater from the riverbank

To extract shallow groundwater at the riverbank, a partly perforated, PVC tube (diameter ~30 mm) with one pointed end, was pushed down about 0.5 m into the sediment, at a distance of one to three meters from the shoreline. The open upper end of the tube was sealed with sticky tape and a hose connected to a vacuum pump was pushed through the tape. Water was extracted by creating a vacuum with the pump, (Figure 4-3). In order to minimize the amount of sediment that entered the tube, a ladies' stocking was attached over the perforated part of the tube.

² Results not yet available

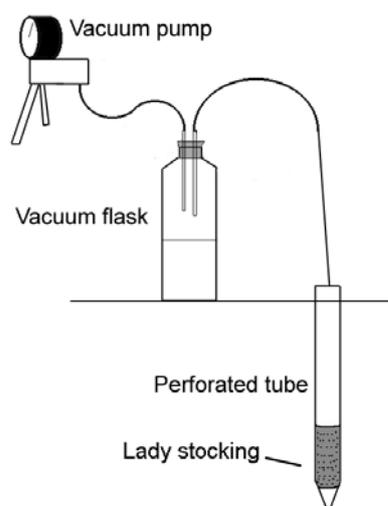


Figure 4-3 Field set-up for shallow groundwater extraction.

Production wells

At Nam Du, the production wells were between 60-70 m deep which means that they extracted water from the lower aquifer system (qp). With one exception (PX), all of the production wells had taps from which untreated water could be collected. A hose was fitted to the tap and water samples were collected directly from the hose. At the private production well, PX, there was no tap and the pipe system was dismantled before the treatment plant. A sample could be collected from a hose fitted directly to the open pipe by sticky tape. All pumps in the production wells can be submerged. Thereby the risk of oxygen introduction was low. At the private well PY the water passed an aerated sand filter before sampling. For further information concerning PY, see section 6.5, ‘Sources of error’.

Monitoring wells

The monitoring wells, P1, P3, P86 and NDT12, were situated in transect 2 and 3, see Figure 4-1. The depth of the wells and the water level were measured with a measuring tape fitted with a solder. The “P” wells had two wells at each site which covered both aquifers. The depth of the wells varied from 20 to 70 meters depending on the aquifer; see Appendix B for exact depths. The letter A after the number indicates the lower aquifer and a B indicates the upper aquifer. Before the collection of groundwater samples three well volumes of water were extracted and removed with a generator driven pump. The samples were then collected directly from the pump hose. At P86B and P1B the recharge was so slow that it was not possible to empty three volumes within the available time. These wells were totally emptied once and samples were collected on the following day. The pump was connected with a Grundfos BMI/MP1-220V to adjust the frequency/flow rate and electricity was provided by a fuel generator. The pump could be submerged and was designed to stop air entrance into the water during pumping. This was done in order not to interfere with measurements of Dissolved Oxygen and redox potential.

Deep sediments

Sediment samples from the aquifers were obtained by drilling. The drilling took place in transect two, close to ND 9 (Figure 4-1). A diesel driven rotating drill was used and the

planned depth was 60 m. The diameter of the drill was 110 mm and that of the casing was 127 mm. The cores that could be sampled with this equipment had a diameter of 91 mm. From 0 – 5.5 m and from 33.0 – 46.0 m, soil was sampled continuously. In the sandy layer (5.5 – 33.0 m), only one sample from the uppermost part could be collected and the length of the other samples that were collected varied between 0.13 – 0.50 m. The first 5.5 meter increment was drilled without a casing but when the drill entered the sandy layer, a casing had to be installed to avoid any collapsing of sand into the bore hole. After 15 m, the casing collapsed. It was not possible to withdraw it. Instead the drilling was continued through the casing. To avoid the sand fraction to collapse into the bore hole, bentonite clay was used to stabilize the profile. At 46 m, the drill reached the coarser layer of the Hanoi aquifer (LAS) and could not continue. Because of the bentonite, the outermost layer of the core was removed before taking the actual sediment sample. From each one meter increment a sample of 200 g was collected and dried at HUMG and then sent to the SLU laboratory in Umeå for analysis. No peat layers were found during the sampling campaign and therefore no information about the isotopes in fresh peat could be achieved. Instead we were provided with old peat from earlier drillings at Nam Du (ND16) carried out by Hanoi Drilling Company in 2003. These samples were sent to SLU Umeå for analysis of $\delta^{15}\text{N}$. Two samples from the drilling and two from ND16 were analysed at KTH by Gunnar Jacks, for exchangeable ammonium.

Surface sediment

Samples of about 200 g bottom sediment were collected from the three sampling points at the riverbank and at the three ponds. Samples were collected at the bottom approximately one meter from the shoreline. To take the sediment bottom samples, a 30 mm pvc tube was pressed down into the sediment and about 30 cm long cores were collected and put into plastic bags that were sealed. Before drying the samples were stored in a fridge at 8 °C. The samples from the ponds and river shoreline were dried in an oven at 30 °C, until air-dry, at SGI's laboratory in Linköping. Samples from the drilling were dried at HUMG at 70 °C until dry. Twenty-five grams of dry material were sent for analysis both to Stockholm University for total analysis and to SLU Umeå for isotope analysis of nitrogen. One sample from Pond 2 and one from Riverbed 3 were analysed at KTH by Gunnar Jacks, for exchangeable ammonium.

4.3 Analyses in the field

Analyses of pH, Eh and temperature

pH was measured in the field with a Jenway 370 pH/mV-meter fitted with a pH epoxy electrode, see Figure 4-4.



Figure 4-4 Nguyen Thi Thanh Thuy and Johanna Moreskog is measuring pH at pond 2.

At the production and monitoring wells, a flow-through cell was used (Figure 4-5). At the ponds and the river, the measurements were done directly in the water. Regarding the shallow groundwater at the riverbank, samples were measured in a 120 ml plastic bottle. The redox potential (Eh) was measured in the field with the same Jenway 370 pH/mV-meter fitted with an Eh electrode. To decrease the sample contact with oxygen the measurements were done in a flow-through cell. Temperature was measured with the same equipment..

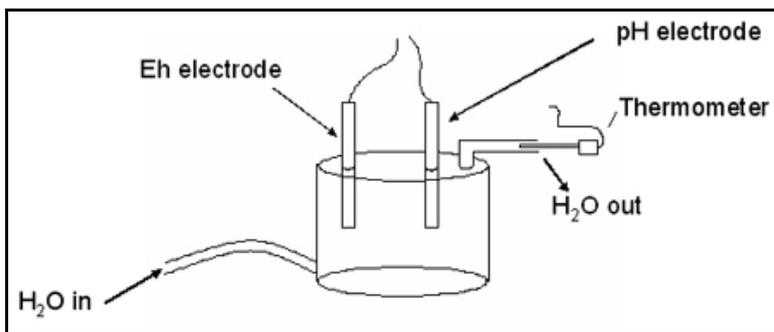


Figure 4-5 The flow-through cell which was used for measuring Eh, pH and temperature.

Infiltration capacity

To estimate the infiltration rate at the riverbank (Rb1, 2 and 3), a seepage meter was used. The seepage meter was constructed of a metal can connected to a sealable plastic bag (Figure 4-6). The can was pressed into the sediments below the water surface in the riverbank and the bag was filled with 500 ml of water. The water was allowed to pass in two directions, which means that both net infiltration *in* to the riverbank and net groundwater flow *out* from the riverbank could be measured. After 1 hour, the amount of water in the plastic bag was measured and the direction of the flow and the flow rate

could be calculated. If net infiltration was occurring there should be less than 500 ml water in the bag and if there was an outward flow the bag should contain more water. The surface area of the can was 509 cm².

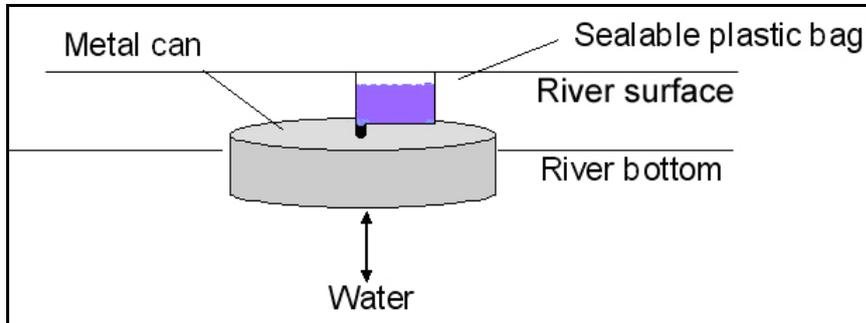


Figure 4-6 Seepage meter used for measuring the seepage at the riverbanks.

Conductivity and dissolved oxygen

The electrical conductivity (C) and dissolved oxygen (DO) were measured in the field with a WTW Multi 197i, fitted with one electrode for conductivity and one for dissolved oxygen. The conductivity and DO in surface water were measured directly in the water, whereas water from the wells was pumped into a bucket during measurements. Shallow groundwater from the riverbank could not be measured with this device since the extracted volume of water was too small. Instead Eh was measured in a small glass bottle, to give an indication of the prevailing redox conditions.

4.4 Treatment/handling of samples for laboratory analyses

The Swiss Federal Institute of Aquatic Science and Technology, Switzerland (EAWAG)

Water samples intended for the EAWAG laboratory were sucked into a 60 ml syringe. For each sample a disposable 0.45 µm Millipore filter was fitted to the syringe and the sample was injected into an acid washed plastic bottle. For the main components and DOC, 120 + 25 ml bottles were used (140 ml was needed in the laboratory). The major component samples were stored in a fridge at 8 °C to reduce microbial activity. 50 ml acid washed plastic bottles were used for trace element analysis. Each sample was acidified immediately to pH < 2 using suprapur HCl, and pH indicator paper was used to estimate the pH value. Arsenic fractionation was done in the field by fitting an anion exchange column to the filter and syringe. The column adsorbed As(V) and As(III) could leave the column. The samples that had passed through the column were collected and treated in the same way as the samples for trace elements. Both trace elements and arsenic speciation samples were stored at room temperature.

Centre for Environmental Technology and Sustainable Development, Vietnam (CETASD)

Samples intended for the CETASD laboratory, were collected with a 60 ml syringe. A disposable 0.45 µm Millipore filter was fitted to the syringe and the sample was injected into 500 ml plastic bottles. The procedure was repeated until the bottles were full. One of the bottles was used to analyse main components and the other was used for trace elements. Both samples were treated and stored in the same way as the samples for

EAWAG. However, water from the ponds contained such large amounts of sediments that the samples had to be filtered in the laboratory and not in the field.

Institute of Nuclear Sciences and Technology, Vietnam (INST)

The samples for nitrogen isotopic analysis of ammonium ions at the INST laboratory were collected in 3 L plastic bottles and acidified to pH <2 with HCL. For nitrogen isotope analysis of nitrate, 3 L of water were collected. A 500 ml sample was collected for analysis of main components. Another 500 ml sample was collected for analysis of trace elements and acidified to pH <2 with HCL. For $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (deuterium) fractionation, a 50 ml sample was collected below the water surface to prevent oxygen entering the sample. Water for the tritium (^3H) analysis was collected in three 500 ml bottles. Due to the large volumes needed, only a few of the samples were filtered in the field. Most of the samples were filtered in the laboratory about one week after sampling. All samples were stored at room temperature, about 1 month, before they were analysed. The procedures for isotope analysis are further described in section 4.5 Analyses in laboratory.

Åbo Akademi University Finland (ÅAU)

For the sulphur isotope analysis ($\delta^{34}\text{S}/^{32}\text{S}$), a 10 L water sample was collected in two 5 L bottles. The sample was passed through an ion exchange column to enrich the sulphate (see Figure 4-7). The columns were stored cool and brought to Sweden where the sulphate was eluted. The eluted samples were sent to Åbo for analysis. Unfortunately, the analyses did not succeed, either due to too small amounts of S, or incorrect treatment before sending them to ÅAU.

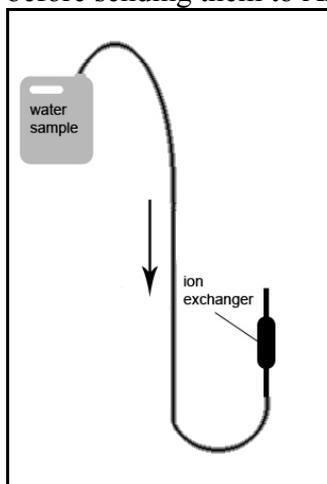


Figure 4-7 Water passed the ion exchanger by siphon.

Stockholm University (SU)

In order to get a picture of the local conditions and to be able to construct a relevant sampling schedule, samples were sent to Sweden for immediate analysis at the Stockholm University. These samples were taken only at a few easily available locations in the beginning of the field campaign. However, due to unpredictable circumstances the results were delayed and could not be used as intended.

For sampling of water for analysis at the SU laboratory, water was sucked into a 60 ml syringe. A disposable 0.45 μm filter was fitted to the syringe and the sample was injected

to acid washed plastic bottles. For the main components 120 ml bottles were used, and for DOC 20 ml bottles. For trace elements, 50 ml acid washed plastic bottles were used. Arsenic speciation was done in the field by fitting an anion exchange column to the filter and syringe. The sampled volume was 50 ml. Both trace elements and arsenic speciation samples were acidified immediately to $\text{pH} < 2$ using suprapur HCl and pH indication paper to estimate the pH. The main components and DOC samples were stored in a fridge at 8 °C to reduce microbial activity. All the other samples were stored at room temperature.

Swedish University of Agricultural Sciences, Umeå (SLU)

Dried sediment samples from surface sampling and cores from the drilling campaign were sent to Umeå for $\delta^{15}\text{N}/^{14}\text{N}$ analysis and for determining the carbon/nitrogen ratio.

4.5 Laboratory analyses

In this section the procedures in the laboratories are described. Since we only had the possibility to participate in the laboratory process at CETASD and INST, only the procedures at these laboratories are included. However, at all laboratories the samples were handled and analysed by professional laboratory staff.

Nitrogen and oxygen isotopes in NO_3^- at INST

The water samples were first filtered through a 0.45 μm filter and then passed through a column packed with 2 g of Dowex AG1-X8 anion-exchange resin. Nitrate is retained by the resin and the other anions like Cl^- and SO_4^{2-} pass through the column. Nitrate from the column were eluted with NaCl (1M). The eluate was dried using a dry freezer in order to get NaNO_3 crystals. 610 μg of NaNO_3 as a minimum was wrapped in a tin capsule and analyzed on a mass-spectrometer for $\delta^{15}\text{N}$. A part of the nitrate eluate was treated with BaCl_2 to remove any sulphate associated with nitrate during the eluation. The solution was passed through a column packed with 1 g AG 50W X8 to remove the excess Ca^{2+} . The obtained solution was dried with a dry freezer to get sulphate-free nitrate for $\delta^{18}\text{O}$ in NO_3^- analysis in a mass-spectrometer.

Nitrogen isotopes in NH_4^+ 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 NH_4^+ . The enriched ammonium was eluted from the column with 10% HCl. The excess HCl was neutralised with NaOH (0.05M) to pH 6.8. The ammonium-chloride was crystallised using a dry freezer and approximately 385 μg NH_4Cl was placed in a tin capsule for analysis of $\delta^{15}\text{N}$ in a mass-spectrometer.

Main components analysed at INST

The sample was filtered through a 0.2 μm filter and diluted 100 times with deionised water. A volume of 25 μl of the sample was then analysed by ion chromatograph (IC) to determine the concentrations of an- and cations, using two different colons.

Main components analysed at CETASD

The sample was filtered through a 0.2 μm filter and diluted 100 times with deionised water. A volume of 25 μl of the sample was then injected into an IC to determine the concentrations of an- and cations.

Trace elements analysed at INST

The sample was filtered through a 0.45 µm filter and diluted 100 times with deionised water. The filtered sample was injected into an ICP-MS and the results were displayed on a computer.

Trace elements analysed at CETASD

20 ml of sample was injected into a plastic vial and inserted the auto sampler of an atomic adsorption spectrometer (AAS).

5 Results

5.1 Abbreviations

Laboratories

CETASD – Centre for Environmental Technology and Sustainable Development, Hanoi

EAWAG – Swiss Federal Institute of Aquatic Science and Technology, Switzerland

INST – Institute of Nuclear Science and Technology, Hanoi

SLU – Swedish University of Agricultural Sciences, Umeå

Sample codes

P1AB, P3AB and P86AB –	Monitoring wells
B –	Upper aquifer (qh)
A –	Lower aquifer (qp)
ND3, ND 9, PY and PX –	Production wells
NDT 12 –	Observation well
Pond 1, Pond 2 and Pond 3 –	Ponds surface water
1RGw, 2RGw and 3RGw –	River groundwater
2RSw –	River surface water

When discussing the chemical composition in the results of this report, only data from EAWAG are used. There are three reasons for this: 1) there was no delay in filtering, 2) the sampled volumes were small so it was easy to use the same standard procedure for all samples, and 3) the samples were kept cold until analysis, except for three days of transport to Switzerland. The isotopic compositions of NO₃⁻, NH₄⁺, and H₂O in water samples was measured at INST and when the isotopic composition of the samples is shown all values, including chemical composition, are taken from INST. This is because the concentrations measured at INST differed from the ones received from EAWAG. If using differing values from different labs it might give a wrong relationship between the isotopes and the chemical composition.

5.2 Drilling log

The log from the drilling that was made is shown in Figure 5-1. Note that the LCN2 aquiclude is missing at the location of the drilling. It should have appeared between D and E in the figure. This shows that there are hydraulic windows between the aquifers and that the sediment layers are not continuous and of different thickness.

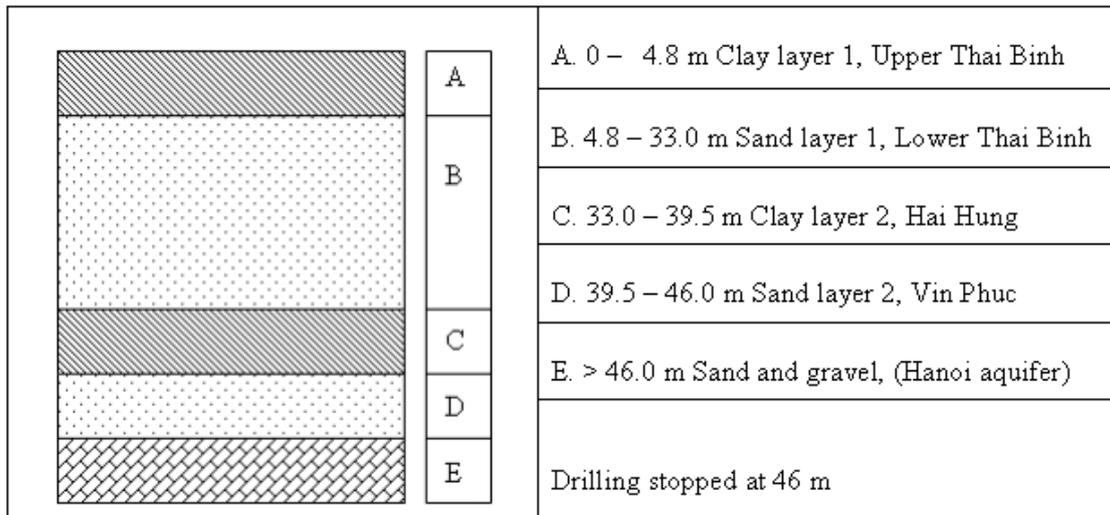


Figure 5-1 The sediment layers according to the drilling carried out close to ND9 in transect 2.

5.3 Recharge and groundwater flow in the aquifers

The Red River has a similar deuterium/¹⁸O ratio as most samples from the qp aquifer, which indicates an exchange of water (Figure 5-2). At P1A and P86A, the ratio is similar to the samples from the qh aquifer implies that there is a hydraulic connection between the qh and qp aquifers. The hydraulic contact in P86 is also indicated in the well log for P86 used for constructing the conceptual groundwater flow model, Figure 5-4.

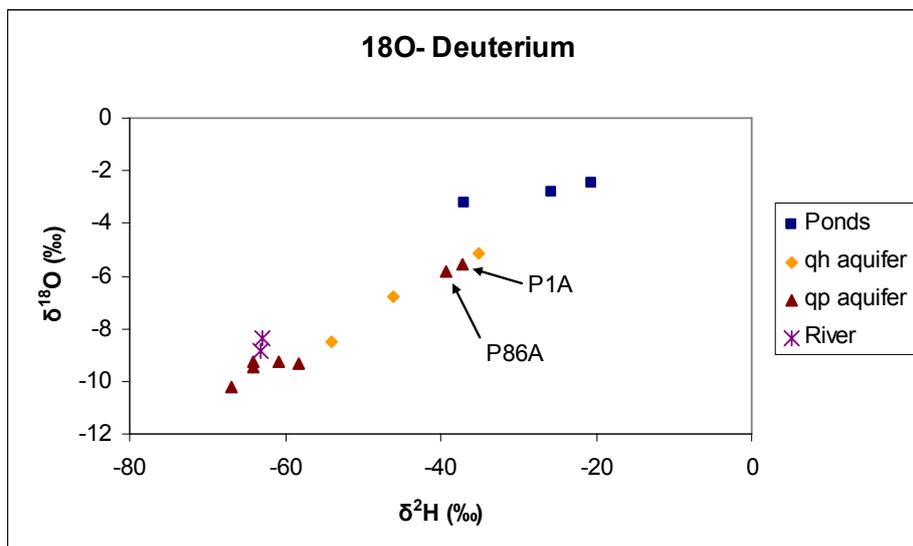


Figure 5-2 Observed $\delta^2\text{H}$ and $\delta^{18}\text{O}$ levels in surface water and groundwater

Tritium was analysed for dating the water in the qp aquifer. In Figure 5-3 it is shown that the observed tritium levels of this project are in the same range as the tritium levels measured in precipitation in Hong Kong from the end of the 1990's (IAEA 2004). The tritium levels at Nam Du therefore suggest the groundwater to be relatively young (within the range of a few years only).

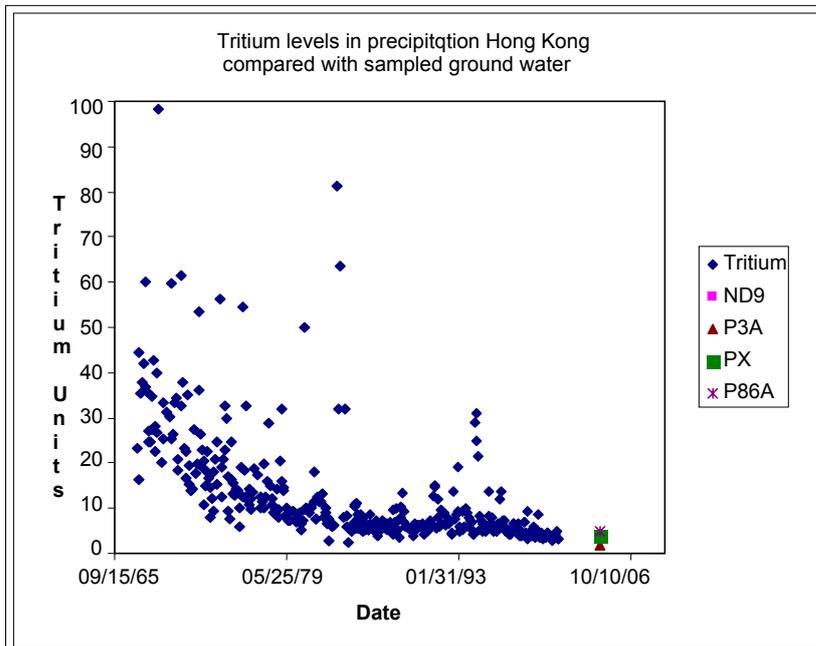


Figure 5-3 Observed tritium levels in the Nam du qp aquifer compared with tritium data in precipitation in Hong Kong during the period 1967-2002 (IAEA 2004)

Seepage measurements indicated an infiltration of river water at the shoreline of the Red River at transects 1 and 2. At riverbed one (Rb1) the infiltration was $2.4 \text{ dm}^3/\text{m}^2\text{h}$ and at riverbed two (Rb2) $0.4 \text{ dm}^3/\text{m}^2\text{h}$. At riverbed three (Rb3) however, a groundwater flow into the river could be observed with a rate of $\text{dm}^3/\text{m}^2\text{h}$.

An outline of the hydrogeological conditions at transect 2 is shown in Figure 5-4. This conceptual flow model is constructed from well logging data, modelling carried out by Pham Quy Nhan and from measurements of seepage. The aquifers and aquicludes are displayed together with sampling sites and groundwater flows. Displayed formations are only to be seen as conceptual as there could be large variations in the thickness of the layers in the described area. The formations close to the river are probably very irregular which will affect the seepage from the river, therefore the formations under the river are displayed with bleached colours. Measurements of seepage at the shoreline of the Red river, (transect two), showed an infiltration rate of $0.4 \text{ l}/\text{m}^2$ and hour. The transport of water between the Red River and the qp aquifer must be quite fast as the tritium analysis dates the age of the water in the second aquifer to less than ten years.

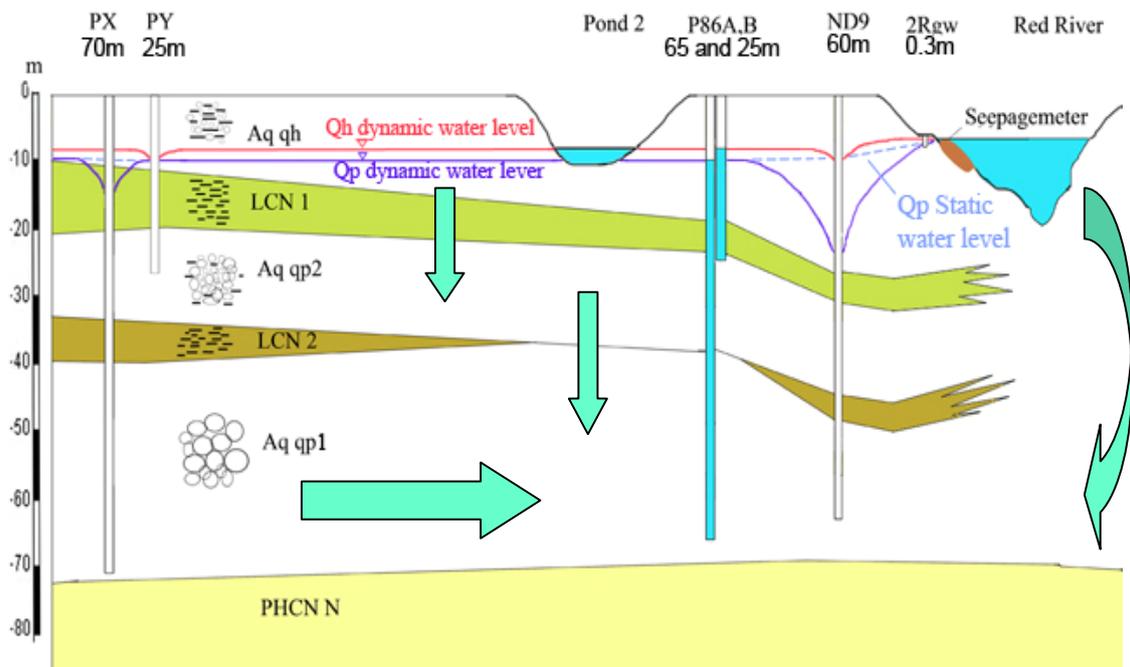


Figure 5-4 Flow model based on field measurements and literature studies. Qh is the Holocene aquifer, Qp the Pleistocene aquifer, LCN are the aquicludes and PHCN is the Neogene formation.

The groundwater flow is illustrated with green arrows. The flow direction is both vertical and horizontal, but the main flow is along the transect from left to right. The ND9 well extracts about 3300 m³/day and about 50 % of the recharge is expected to come from the Red River (Nhan 2006). Depression cones caused by the extraction of groundwater can be seen from the dynamic water levels around the production wells. Note the difference between the static water levels, which was before the pumping started and the dynamic water levels. A hydraulic connection between aquifer qp2 and qp 1 can be seen next to P86, with results from well log (Figure 5-1). It is interesting to note that the analysis of deuterium and ¹⁸O, Figure 5-2, also implies a hydraulic connection between the upper and lower aquifers at P86, which also is confirmed by the well log.

5.4 Redox conditions

As can be seen in Figure 5-5, both dissolved oxygen (DO) and the redox potential (pE) are low in the groundwater, indicating reducing conditions. The conditions in the surface water are more oxidising. Dissolved oxygen should correlate well with the measured pE, since pE will decrease when oxygen becomes less available. The correlation gives an indication of the error associated with the two methods as the measuring devices used should give proportional results. However it cannot indicate an introduction of oxygen as both measurements took place in field and in the same medium.

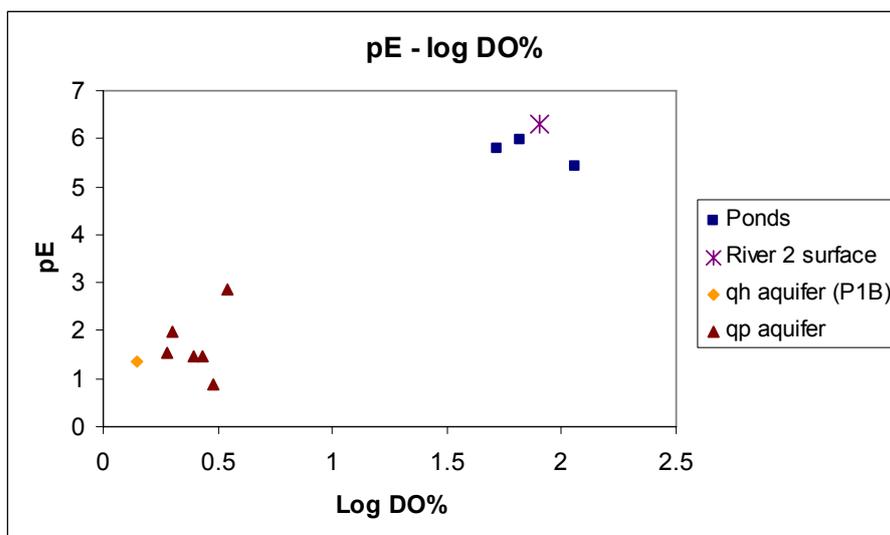


Figure 5-5 Field measurements of pE and DO% in surface and groundwater.

5.5 Water chemistry

Table 5-1 summarises the results from the chemical water analyses. The $\text{NH}_4\text{-N}$ concentration in ground water was high when the sampling depth was taken into account. Normal concentrations in ground water are in the order of 0.2 mg/l (WHO 2004). The $\text{NH}_4^+\text{-N}$ concentration varied within a range extending from < the analytical detection limit via 0.2 mg/l in the river water to 34.7 mg/l in P1B. Nitrate-N concentrations were low at all sites. The maximum concentration (0.6 mg N/l) was observed in shallow groundwater at RGW2.

Arsenic concentrations varied from 0.4 $\mu\text{g/l}$ in shallow groundwater at RGW2 to 312 $\mu\text{g/l}$ in P86A (a monitoring well in transect 2). Most of the arsenic occurred as As(III). The sulphate concentration in groundwater was below EAWAG's analytical detection level (5 mg/l) while the river and ponds contained 40 mg/l as a maximum (in Pond1). The detection levels at INST and CETASD were considerable lower i.e. 0.01 and 0.5 mg/l and most groundwater samples contained sulphate concentrations below these detection levels as well (see Appendix B). All pE values were > 0. The pH values ranged from pH 6.3 at P3, A and B to 8.2 in Pond 1.

Table 5-1 Summary of selected observed results from sampling and field measurements

EAWAG RESULTS	Analysed variables and the analytical method used							
	NH4-N	NO3-N	As(tot)	As(III)	As(V)	SO4-S	pE Calc from field meas.	pH Meas. in field
	mg/L Photo	mg/L AuA	µg/L MS	µg/L MS	µg/L Calculated	mg/L AuA		AuA
Pond 1	1.6	<0.25*	4.9	-	-	40.0	5.4	8.2
Pond 2	0.4	<0.25*	2.6	-	-	24.0	5.8	7.4
Pond 3	2.4	0.4	1.9	-	-	19.0	6.0	7.5
ND3	4.3	<0.25*	83.0	63.0	20.0	<5*	1.2	6.7
ND9	8.6	<0.25*	83.0	77.0	6.0	<5*	2.0	6.4
1 RGW	0.5	<0.25*	2.6	0.9	1.7	6.6	6.6	7.1
2 RGW	<0.2*	<0.25*	0.4	0.2	0.2	16	-	7.3
2 RSW	<0.2*	0.31	2.8	-	-	9.5	6.3	8.0
3 RGW	0.4	0.6	2.6	1.8	0.8	24.0	3.7	8.7
P1A	12.7	<0.25*	257	258	-1.0	<5*	0.9	7.1
P1B	34.7	<0.25*	264	254	10	<5*	1.3	6.7
P3A	24.0	<0.25*	152	148	4	<5*	1.5	6.3
P3B	9.8	<0.25*	39.0	34.0	5.0	<5*	1.6	6.3
PX	3.2	<0.25*	27.0	27.0	0.0	<5*	2.9	6.3
P86A	9.2	<0.25*	312	282	30	<5*	1.5	7.0
P86B	2.6	<0.25*	62.0	56.0	6.0	<5*	2.1	6.9
NDT 12-4	1.8	<0.25*	44	39	5	<5*	1.5	7.1

5.6 Ammonium

The distribution of ammonium-N and the $\delta^{15}\text{N}$ -ratio in transect 2 are shown in Figure 5-6. Surface water had low concentrations of ammonium-N while the highest concentrations were found in the qp1 aquifer. There was a large spatial variation. The N-isotopic composition of ammonium-N in the ponds was similar to the composition in the deeper aquifer.

The covariation between ammonium-N and the distance to the Red River is shown in Figure 5-7. The maximum concentrations were found in wells connected with the qp aquifer, the minimum concentrations were found in the river, while the concentrations in ND wells were in between those of the qp aquifer and the river.

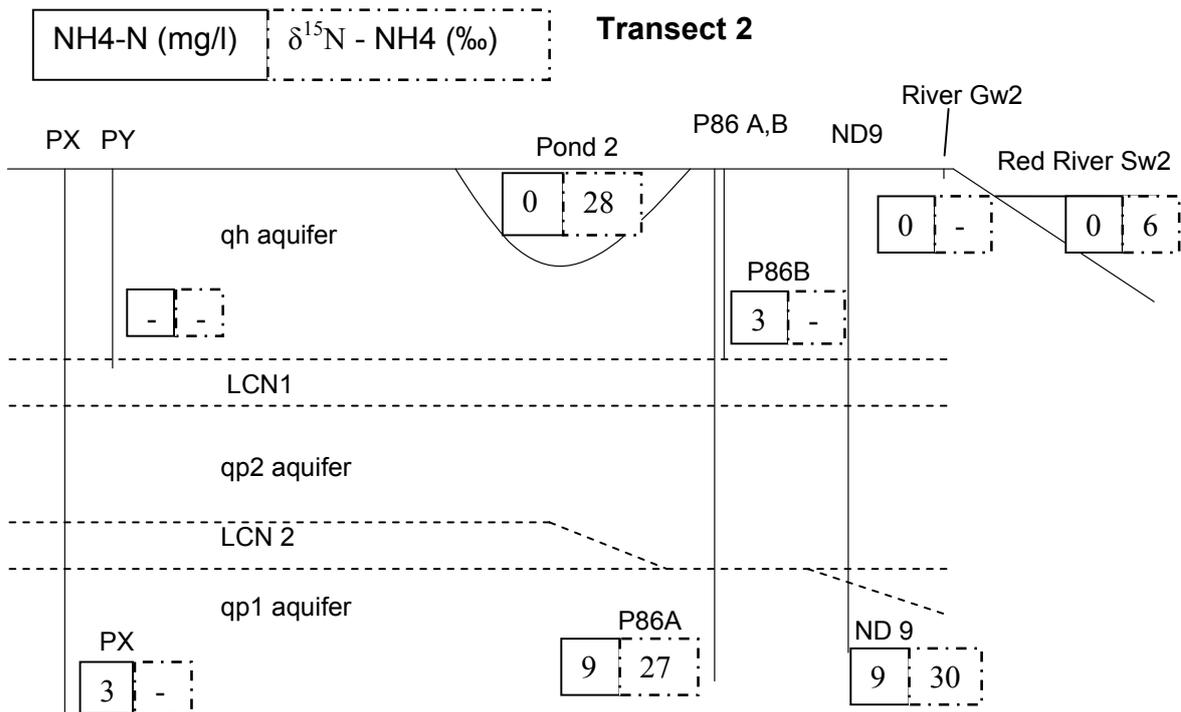


Figure 5-6 Schematic description of the ammonium-N distribution (analytical data from EAWAG) and $\delta^{15}\text{N}$ (analytical data from INST) in transect 2. At some sampling points the isotopic composition of ammonium-N is shown although the ammonium-N concentrations are marked as 0. This is because the ammonium-N concentrations were obtained from EAWAG and the isotopic composition was obtained from INST (see chapter 5.8, comparison of laboratories for further information).

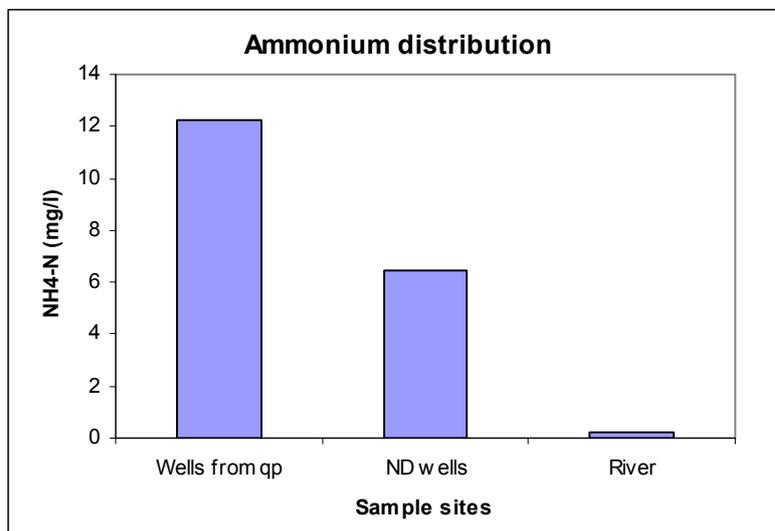


Figure 5-7 Ammonium-N concentrations in the wells from the qp aquifer, the Nam Du production wells and in the river water. The wells from qp are P1A, P3A, P86A, PX, the Nam Du production wells are ND3 and ND9. River water includes both surface water and ground water.

According to Figure 5-8, NH_4^+ -N was enriched with ^{15}N in pond water as well as in ground water,, while water from the Red River had a lower $\delta^{15}\text{N}$ value. The average $\delta^{15}\text{N}$ value of organic N in the peat is illustrated with a horizontal line.

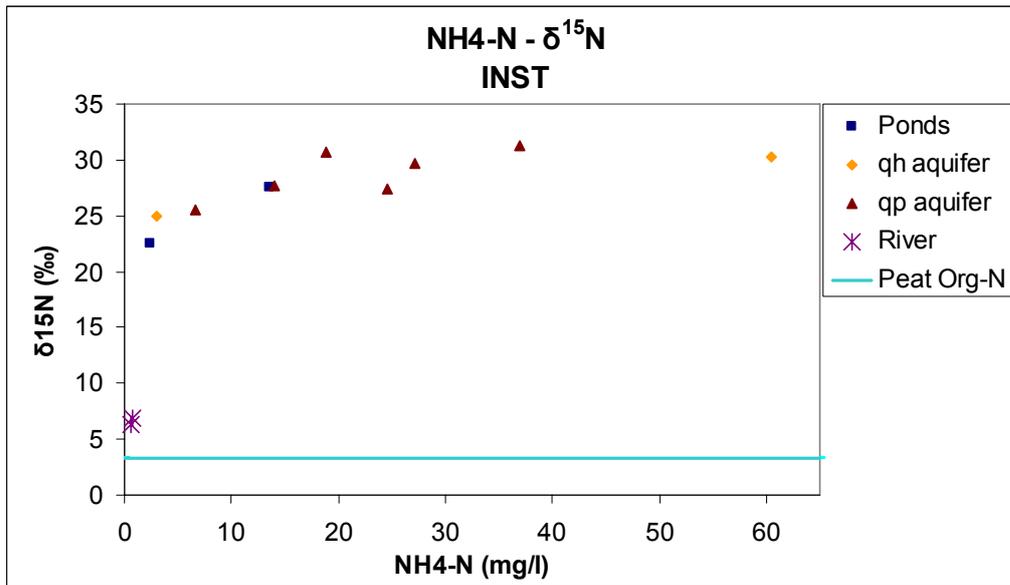


Figure 5-8 Comparison of ammonium-N concentrations and $\delta^{15}\text{N}$ values in water and sediment samples. Results are from INST.

Figure 5-9 below, indicates a weak positive relationship between the ammonium-N and DOC concentrations

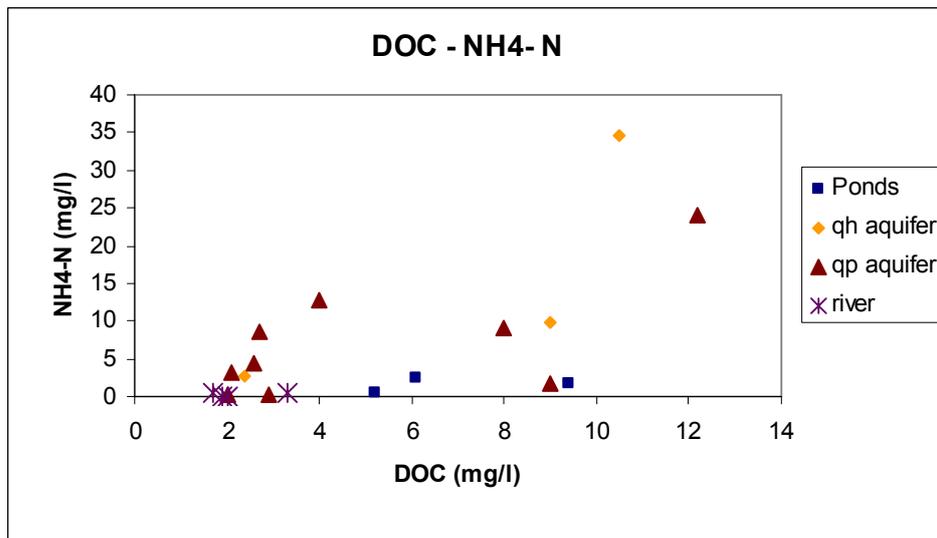


Figure 5-9 The relation between $\text{NH}_4\text{-N}$ and DOC at the sampling sites.

There was a seemingly negative relationship between ammonium-N and pE (Figure 5-10).

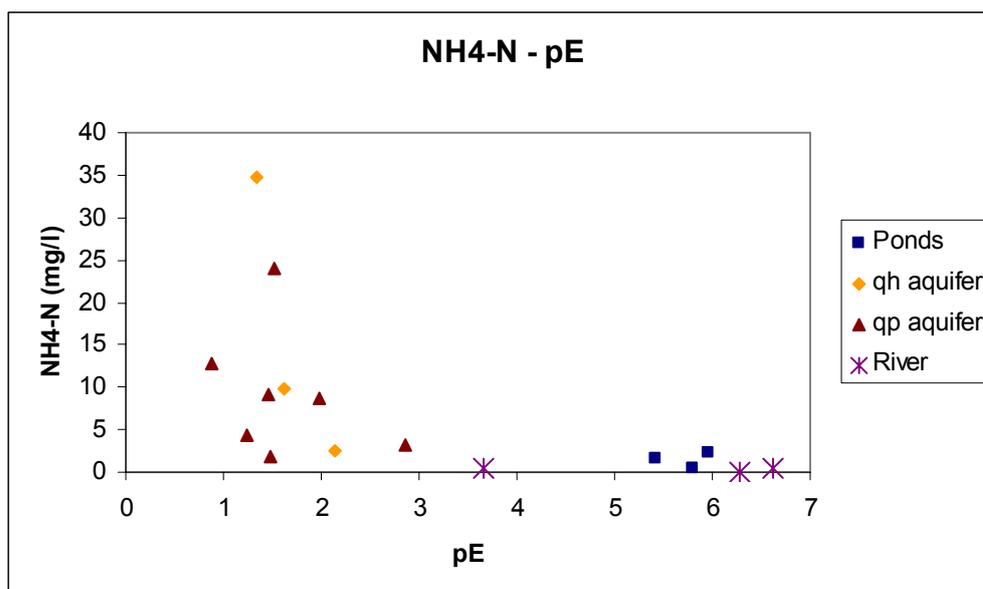


Figure 5-10 Ammonium-N concentration plotted versus pE.

Sodium (Na^+) and ammonium ions have the same charge, and may therefore compete with each other for negative surface sites on clay minerals. The relationship between sodium and ammonium ions is illustrated in Figure 5-11.

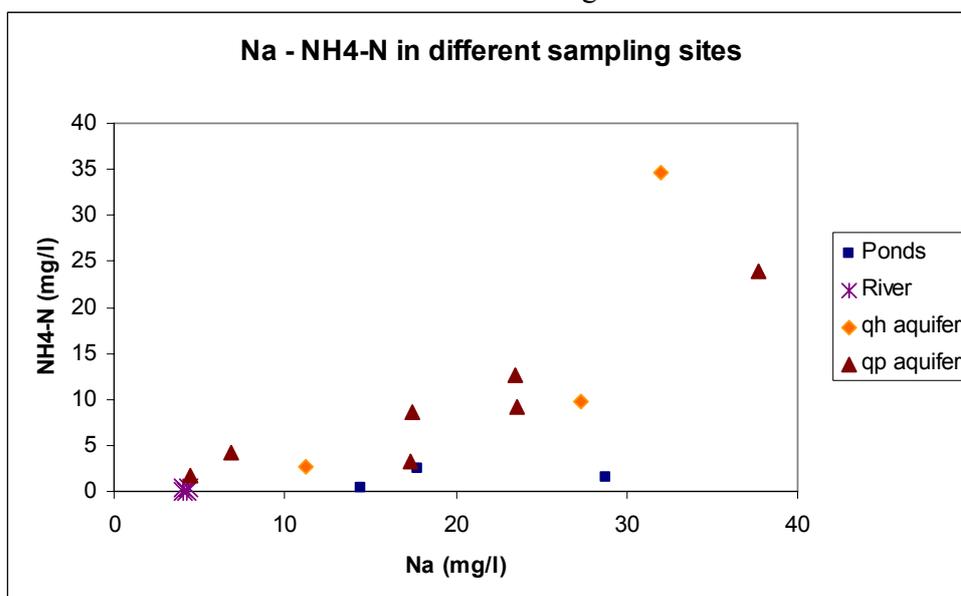


Figure 5-11 Ammonium concentrations related to sodium.

The data in Table 5-2 originate from analyses of sediment cores, which were collected in 2003 during the drilling of the monitoring well ND16, situated south of ND9. As already indicated in Figure 5-8, the $\delta^{15}\text{N}$ -ratio of ammonium-N in the water was considerably higher than the $\delta^{15}\text{N}$ -ratio of the organic N in the peat, The carbon/nitrogen ratio (C/N) was quite high, which indicated that the peat degradation had not proceeded very far..

Table 5-2 Organic nitrogen and carbon analyses in sediments.

Site	Depth (m)	C (%)	N (%)	$\delta^{15}\text{N}$	$\delta^{13}\text{C}$	C/N
ND16	23	4.5	0.1	2.4	-27.7	34.4
ND16	44	18.7	0.5	4.1	-27.5	40.3

Table 5-3 shows the amount of $\text{NH}_4^+\text{-N}$ on negatively charged surface sites in the sediments. At the depth of 46 m, this amount varied from 50 mg/kg in Pond 2 to 95 mg/kg in ND16. This means that every kg of soil contained an exchangeable pool of 50 – 95 mg $\text{NH}_4^+\text{-N}$ which was in equilibrium with $\text{NH}_4^+\text{-N}$ in the soil solution.

Table 5-3 Exchangeable ammonium-N in sediments.

Site	Year collected	Depth (m)	$\text{NH}_4\text{-N}$ (mg/kg)
Pond 2	2006	0	50
River 3	2006	0	75
ND 16	2003	23	63
ND 16	2003	46	95
2ND9	2006	4	46
2ND9	2006	6	67

As seen in Table 5-4 the average concentration of ammonium ions in the area of Nam Du had increased since 1996. The increase was evident, both in the Holocene and Pleistocene aquifers. The figure from 1996 is an average value taken from Dang et al. (1996). The data from 2004 are average concentrations in the wells that are listed in the table (Nhan, 2006). The data from 2006 are average values based on all ground water samples from the Nam Du area, which were collected in this study.

Table 5-4 Temporal variation of ammonium-N since 1996 (Dang et al. 1996, Nhan 2006)

Sampling site	$\text{NH}_4\text{-N}$		
	1996	Feb-04	Feb-06
P1A	-	4.4	12.7
P1B	-	5.1	34.7
P3A	-	6.1	24.0
P3B	-	4.1	9.8
PX	-	0.0	3.2
NDT 12-4	-	1.03	1.8
Average Nam Du area	1.6	3.5	11.1

5.7 Arsenic

The distribution of arsenic in transect 2 is shown in Figure 5-12. Surface water had a low arsenic concentration, while the highest concentrations were found in the qp1 aquifer. There was a large spatial variation.

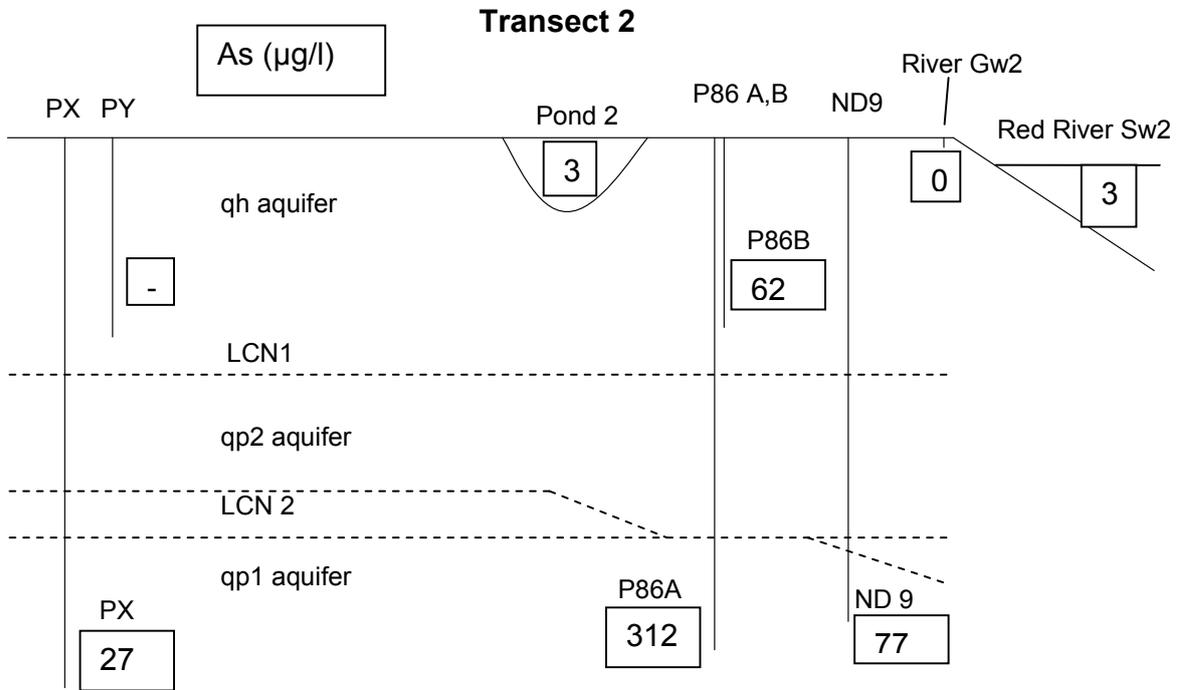


Figure 5-12 Schematic sketch over arsenic occurrence in transect 2.

Regarding the qp aquifer and the river, the arsenic concentration showed a spatial pattern that was similar to that of the ammonium concentration (Figure 5-13). There were high arsenic concentrations in the monitoring wells that were situated far away from the Red River, lower concentrations in the ND wells, and very low concentrations in the river.

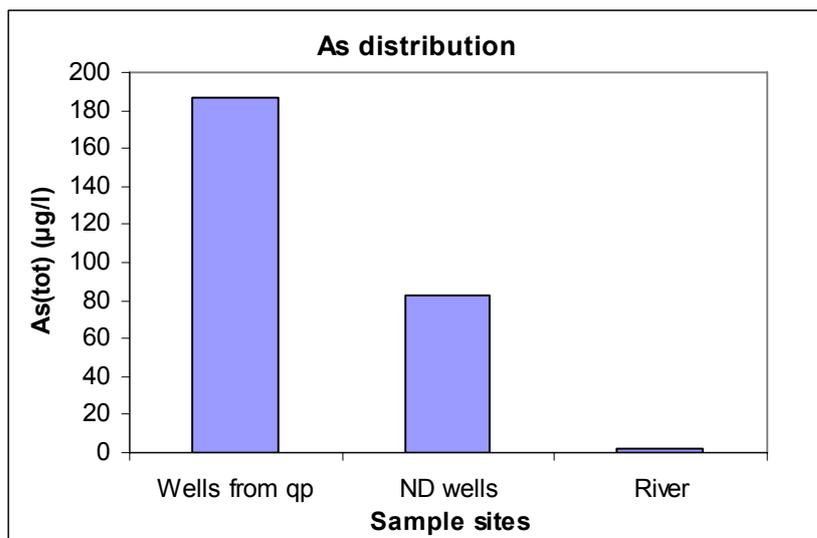


Figure 5-13 Arsenic concentrations in the wells from the qp aquifer, the Nam Du production wells and in the river water. Data are from P1A, P3A, P86A, PX, the Nam Du production wells are ND3 and ND9, river water is from both river surface and groundwater.

Figure 5-14 indicates a negative relationship between the arsenic concentration and pE, which points to the fact that the arsenic mobilisation is dependent on the ambient redox conditions.

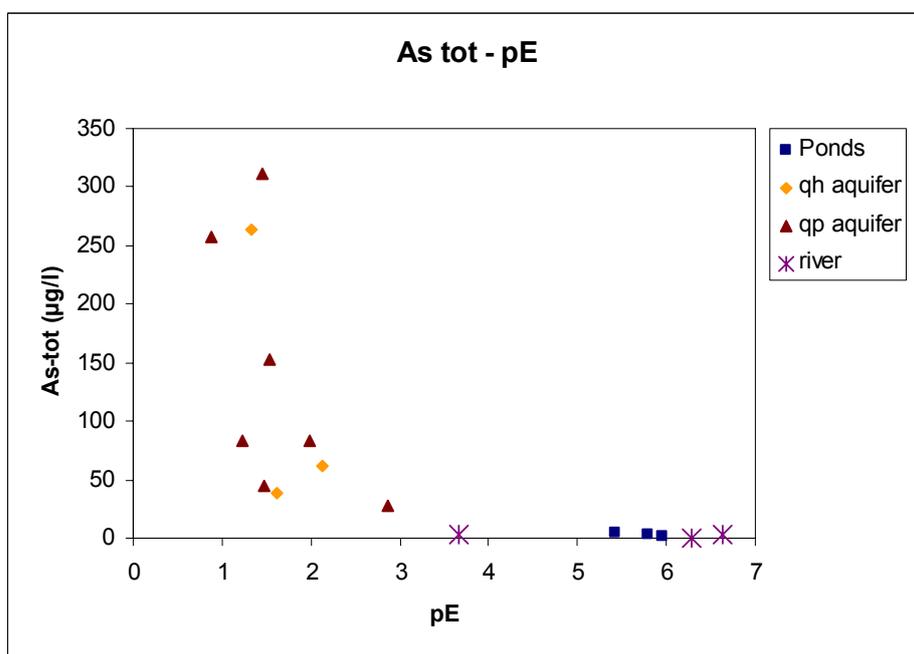


Figure 5-14 Diagram of pE – As(tot).

Figure 5-15 demonstrates that most of the arsenic occurred as arsenite (As(III)), which is the more toxic form of arsenic and occurs under reducing conditions. Typically, As(III) starts to dominate at pH 7 when pE < 0 (most of the samples had a pH around 7).

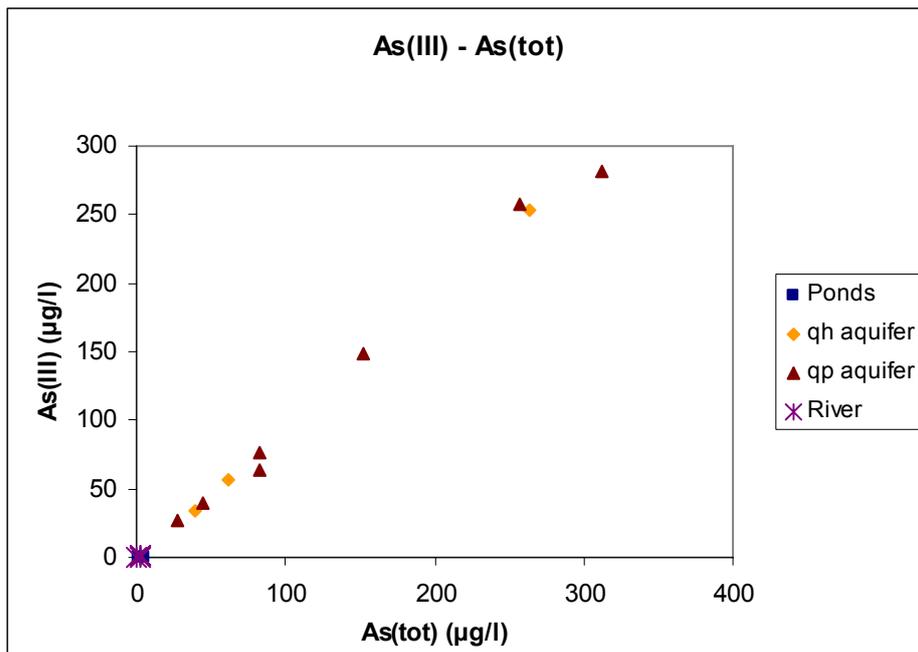


Figure 5-15 Relation between arsenite and total arsenic at different sampling points.

Figure 5-16 indicates that there is no correlation between Fe and As(tot) in the samples and Figure 5-17 indicates that there is a positive correlation between As(tot) and HCO_3^- and arsenic.

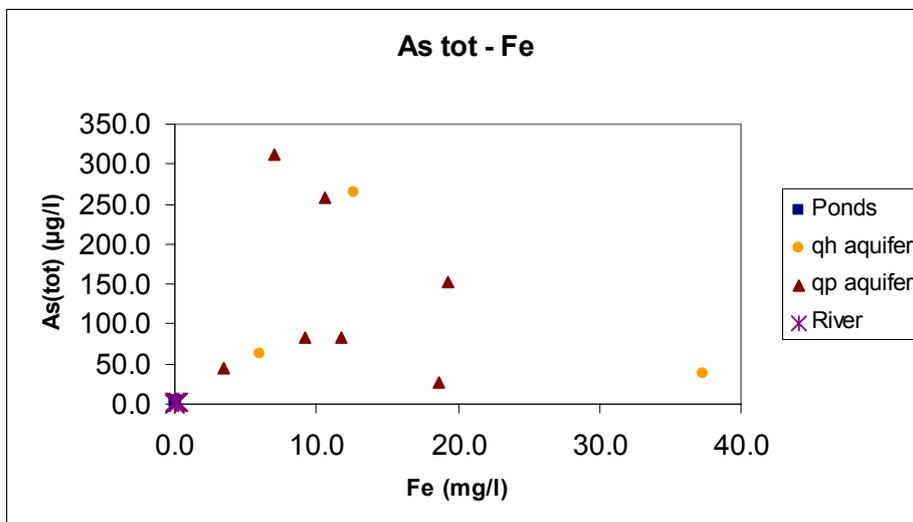


Figure 5-16 Iron concentration versus total arsenic concentration.

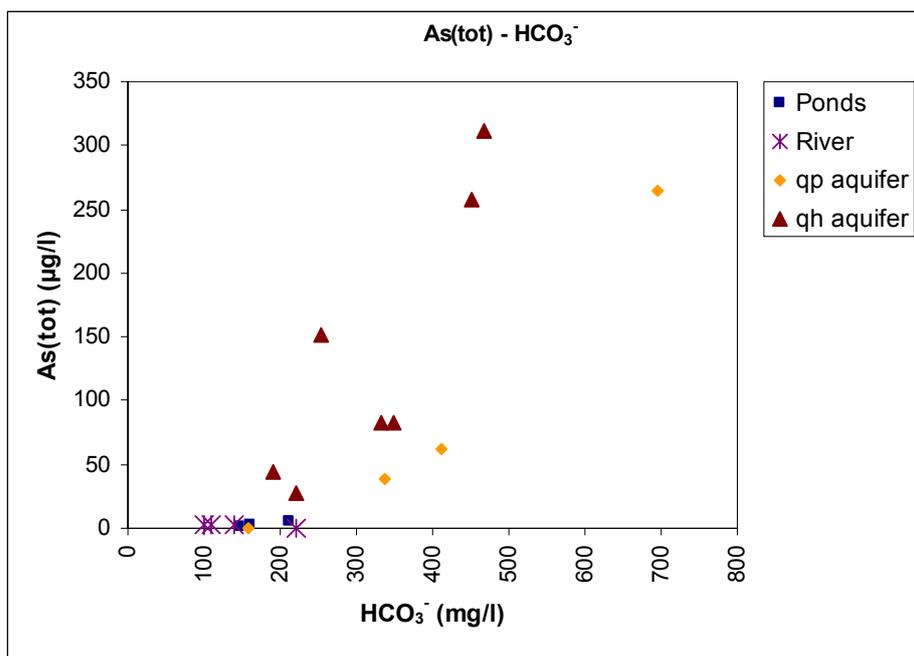


Figure 5-17 HCO_3^- concentration versus total arsenic concentration

The average arsenic concentration in the Nam Du area had increased since 1996. The data in Table 5.5 were obtained in the same way as the ammonium-N concentrations treated above.

Table 5-5. Temporal variation of arsenic concentration since 1996 (Dang et al. 1996; Nhan, 2006).

Sampling Site	As		
	1996	Feb-04	Feb-06
P1A	-	-	257.0
P1B	-	4.5	264.0
P3A	-	-	152.0
P3B	-	6.5	39.0
PX	-	-	27.0
NDT 12-4	-	-	44.0
Average Nam Du area	0.0	5.5	132.3

5.8 Interlaboratory comparison

As already mentioned, samples were sent to several laboratories. The results from the laboratories differ somewhat which leads to the problem that the results from one lab has to be selected as base for the discussion. As can be seen in Figure 5-18, Figure 5-19 and Figure 5-20, the values differ between the laboratories, especially between INST and the other two laboratories, EAWAG and CETASD. A probable reason could be the delay in filtering at INST, another could be different laboratory methods. CETASD and EAWAG have similar equipment and practices.

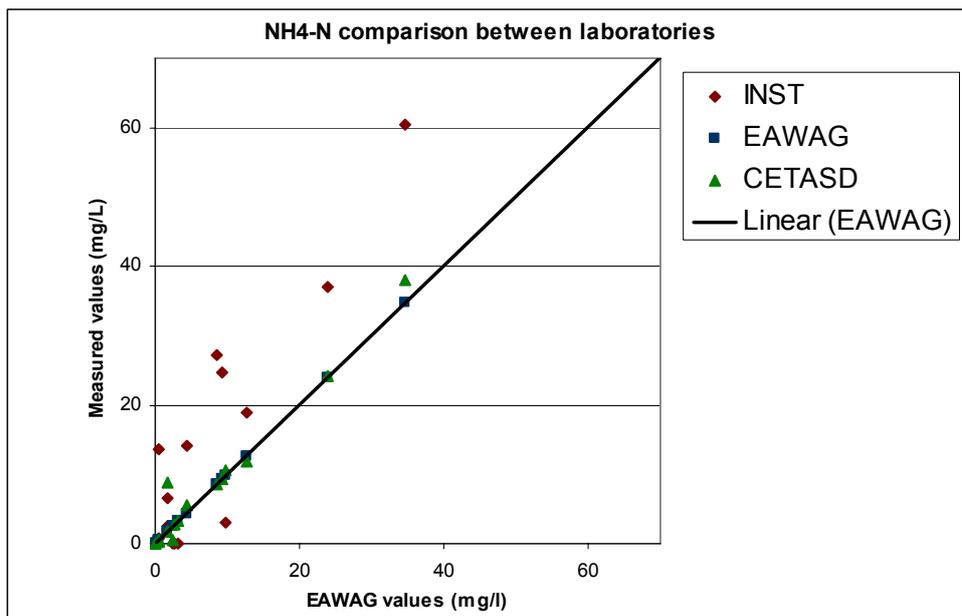


Figure 5-18 Different ammonium levels obtained from the laboratories. EAWAG values are displayed on the x axis and EAWAG, INST and CETASD values on the y-axis, where also the difference is displayed.

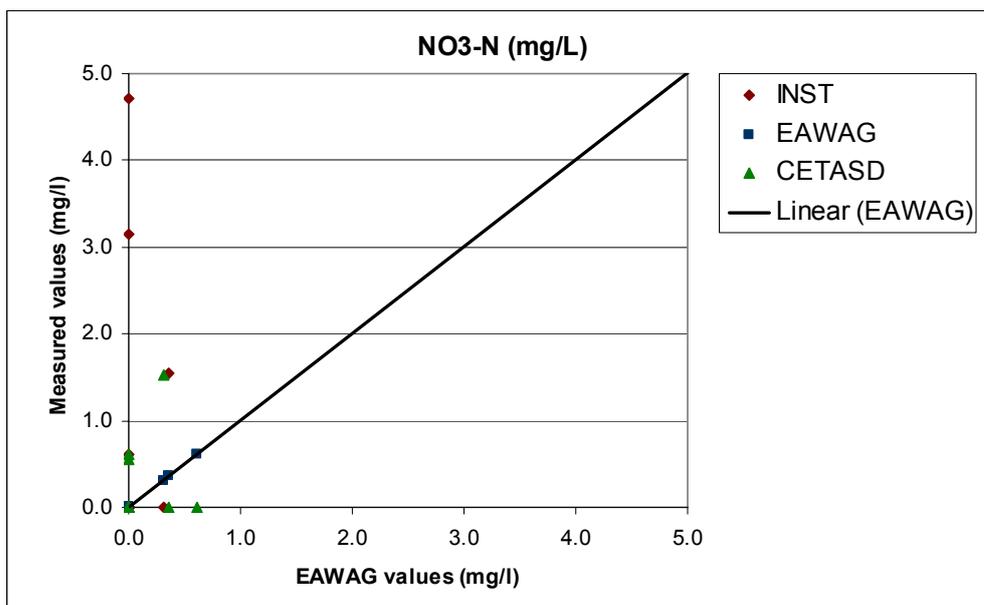


Figure 5-19 A comparison between the laboratories show large variations of nitrate.

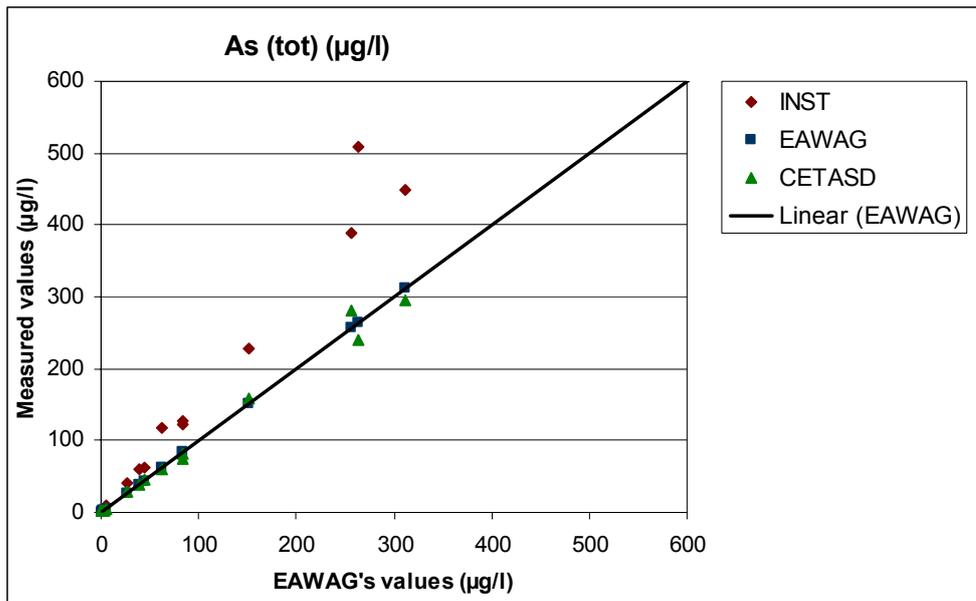


Figure 5-20. Different arsenic levels obtained from the laboratories. EAWAG values are displayed on the x axis and EAWAG, INST and CETASD values on the y-axis, where also the difference is displayed.

6 Discussion

6.1 Recharge and groundwater flow in the aquifers

According to the deuterium- ^{18}O analyses, there seems to be an exchange of water between the river and the qp aquifer, which can be seen at the points where water from different aquifers have a similar $^{18}\text{O}/^2\text{H}$ ratio. This is in agreement with the modelling carried out by Pham Quy Nhan at HUMG (Nhan 2006), and also according to Trafford et al. (1996). Interestingly enough the deuterium - ^{18}O composition in P3A and P86A, is similar to the values in the qh aquifer. This may indicate a hydraulic connection where water from the qh aquifer leaches to the qp aquifer. This could happen due to leakage through non-maintained wells. Alternatively, the LCN 1 aquiclude which separates the two aquifers could be absent. A leakage implies that pollutants could be transported from the surface to deeper aquifers.

Based on tritium measurements in precipitation collected in Hong Kong by the end of the 1990's (IAEA 2004), the tritium level in our water samples indicated that the age of the water in the deeper aquifer was less than 30 years. Values in the qp aquifer ranged from 1 to 4 TU which, according to Clark and Fritz (1997), should date the recharge to 5-10 years back. Trafford et al. (1996), concluded that increased pumping has decreased the turnover time drastically, which was confirmed by the tritium data collected in the present study. Moreover, tritium analyses carried out by Berg et al. (2001) dates the water in the aquifers to 5 to 15 years old.

At transects 1 and 2, the seepage meter showed that the aquifers were recharged by water from the Red River. At transect 3 however, the direction of flow was reversed, i.e. water flowed from the aquifer to the Red River. Extraction of groundwater at Nam Du should affect the flow direction and it will be interesting to see if the flow direction at transect 3 will reverse when the extraction at Nam Du phase 2 will be started. It should be pointed out that the measurements were made by the end of the dry season, which probably influenced the direction of the water-flow. During the rainy season the Red River is likely to recharge the aquifers, even prior to the large extraction of groundwater in Nam Du. The groundwater flow occurs both in a horizontal and a vertical direction which makes conclusions about compound origin and main transportation direction rather difficult.

6.2 Redox

To measure Eh accurately is difficult and consequently, the results are often unreliable. The relationship between pE and DO (Dissolved Oxygen), indicates that the equipment we used was probably unpolluted but this comparison did not show whether there was an introduction of oxygen or not..

Iron concentrations were fairly high, and pH was around 7. This would indicate a pE below 0, otherwise Fe^{2+} should precipitate as trivalent iron hydroxide. The speciation of As could provide another indication of the correctness of the measured pE values. In this study, As(III) was the most dominating species and As(V) occurred in smaller quantities. The expected equilibrium pE for a dominance of As(III) within the range of measured pH values would be less than 0.

As pH seems to be easier to measure in the field than pE, this implies (not surprisingly) that the field measurements of pE are too high (around two units), probably due to an introduction of oxygen or a disequilibrium. Therefore, it is possible that the redox conditions were such that reduction of sulphate to H₂S could take place, however we could not observe the typical sulphite smell. The isotopic composition of sulphate would have been a useful tool to determine if this process took place but unfortunately the analyses of the sulphur isotopes were not successful.

The peat buried in the sediments might be the ultimate reason for a low redox potential. In addition, the extensive cropping of rice may be an important factor as large areas are water saturated during most of the year. More information about the prevailing redox conditions is given by Moreskog 2007.

6.3 Ammonium ions

In general, the ammonium concentrations in the analysed samples were higher than would be expected in groundwater not affected by anthropogenic activities. The concentrations were higher in 2004 than in 1996 (Dang et al. 1996, Nhan 2006). As there might be temporal variations this could be due to normal fluctuations, but the increase was quite drastic. In the monitoring well PIB the concentration had increased from 5.1 mg N/l in 2004 to 34.7 mg N/l in 2006.

The slightly positive relationship between the $\delta^{15}\text{N}$ values and ammonium concentrations indicated a process where ¹⁵N was enriched with respect to ammonium ions. Moreover, the high ¹⁵N/¹⁴N ratios implied that the ammonium ions in the upper and lower aquifer were derived from a source enriched in ¹⁵N or alternatively, from a source where either evaporation of ammonia gas or nitrification took place. The reducing conditions in the groundwater made nitrification a less likely alternative. The ¹⁵N/¹⁴N ratios in the groundwater therefore suggested another source where nitrification or volatilisation processes could take place. As the peat was likely to have been buried in the soil under reducing conditions, a more likely source would be organic fertilisers, urea or sewage water leaching down to the qp aquifer. The fertilisers are used to a large extent on farmland around Hanoi, and I suggest that this problem should be addressed in future investigations. Organic fertilisers, urea and waste water are known to have high $\delta^{15}\text{N}$ values (Kendall et al. 2000).

One possibility was that nitrification of ammonium ions derived from the peat took place during previous periods in history and that the nitrate now has been washed away while some ammonium ions still remain bound to surface sites on clay minerals in the deeper aquifers. If this was the case, a decrease in ammonium concentrations could be expected as the extraction of water should deplete the bound ammonium ions. This seems not to be the case as average ammonium concentrations in 1996 were 1.6 mg N/l, 3.5 mg N/l in 2004 and 11.1 mg N/l in 2006. This trend combined with the relatively rapid circulation of nitrogen in nature makes the suggested process less likely, especially as the recharge water was quite young and the flows are complex.

Andersson and Norrman (1998) mentioned dissimilatory reduction of nitrate to ammonium ions (DRNA) as an example of a possible process. However, if DRNA took place a lower ¹⁵N/¹⁴N ratio would be expected as the produced ammonium ions should be

depleted with respect to ^{15}N (Binnerup et al. 1992). Another indication, showing that DRNA is not taking place is the observation that the $^{15}\text{N}/^{14}\text{N}$ ratio is positively correlated with the ammonium ion concentration, as DRNA should lead to a negative correlation between ^{15}N and the ammonium ion concentration, i.e. a higher the concentration of ammonium ions, the lower the $^{15}\text{N}/^{14}\text{N}$ ratio. The maximum nitrate concentration observed was 0.6 mg/l, which combined with the high $\delta^{15}\text{N}$ levels, indicates that DRNA could be expected to be of minor importance even if it takes place.

According to the hydrogeological modelling carried out by Pham Quy Nhan (Nhan 2006), about 50 % of the recharge to Nam Du originates from the Red River. This means that 50 % of the groundwater in Nam Du should contain the same nitrate and ammonium concentrations as the Red River, i.e. groundwater with high ammonium concentrations should be diluted by the water originating from the Red River which is poor in both ammonium and nitrate. The result should be that the amount of ammonium and nitrate in Nam Du should be lower than in the groundwater coming from the inland. Although there were too few sampling points for making a statistical test, this seems to be the case, which implies that the source of the ammonium ions is found further inland and not between the river and the well field.

Nitrogen mineralisation does not imply any noticeable fractionation and the produced ammonium ions would have almost the same $^{15}\text{N}/^{14}\text{N}$ ratio as the remaining organic N. One hypothesis was that if the process of mineralisation has taken place for thousands of years even a small fractionation factor could result in an enrichment of ^{15}N in the residual peat. If that was the case it should be reflected in the $\delta^{15}\text{N}$ values of the ammonium ions that are mineralised from the peat today. However, the $\delta^{15}\text{N}$ values of the ammonium ions were widely different from the $\delta^{15}\text{N}$ values in the peat. This implies that the current N mineralisation in the peat at Nam Du is not the main source for the ammonium ions. If this were the case, the $\delta^{15}\text{N}$ value of the ammonium ions should be similar to that of the organic N in the peat.

The high carbon to nitrogen ratio in the peat indicated that there was no net mineralisation of nitrogen but rather a decrease of mineral nitrogen as the bacteria would need an external nitrogen source when degrading the carbon in the peat (Sylvia et al. 1999). This is a further indication that the ammonium ions in groundwater were not derived from the peat.

The average concentration of ammonium ions in the qp aquifer was 9.1 mg N/l, which was higher than in the qh aquifer with an average of 15.7 mg N/l. As there were only three sampling points from the qh aquifer and the sources of ammonium might be quite local, it is hard to draw any conclusions from this. However if this is the general case in the Nam Du it would further support the theory that ammonium is transported from the surface downwards.

Sodium and ammonium ions have a similar hydrated radius and the same charge. This might give rise to a competition for exchange sites at negatively charged surface sites on clay minerals and organic matter. An increasing concentration of either of these ions could cause an increasing concentration of the other ion as well due to ion competition (Seitzinger et al. 1991). The results in this study indicate such a competition between

sodium and ammonium ions. If there is a large exchangeable pool of ammonium ions in the sediments, an increasing sodium concentration could result in a release of ammonium ions. If there should exist an external ammonium ion source the increased ammonium concentration in the water could probably be maintained. The exchangeable ammonium ions in the deeper sediments ranged from 46 – 95 mg N/kg, which means that large amounts of ammonium ions would be available from the sediments. Older data from Dang et al. (1996) and Nhan (2006) indicate an increasing ammonium concentration in the Nam Du area since 2004, i.e. the time before establishing Nam Du. However, there were no data available to support whether the concentration of Na has increased or not. It is known is that the Neogene formations below the qp aquifer locally contains high levels of sodium. An increased extraction of groundwater from the Hanoi aquifer could therefore cause an upward flow of more saline water from the Neogene formations. Another explanation for the observed relationship is that the source of both ammonium and sodium ions is sewage water which often is enriched with respect to both ions. Sewage water should also have a $\delta^{15}\text{N}$ value similar to that observed in groundwater.

It is not likely that the observed ammonium concentrations have any hazardous effects, not least because the water from Nam Du passes a treatment plant. However, high ammonium concentrations might be a problem in smaller private wells and an indication of other pollutants such as water born diseases.

6.4 Arsenic

The observed arsenic concentrations seemed to follow the same pattern as the ammonium concentrations, i.e. there were lower concentrations close to the river than in the ND wells. As half of the recharge in the ND wells derives from the Red River and the river contains very low concentrations of arsenic this could be a dilution effect. Another possibility is that recharge water from the river may be less reducing and therefore the mobilisation of arsenic will be lower.

Low concentrations of sulphur were reported for bedrock and sediments and the abundance of arsenic-containing sulphide minerals in the sediments was low as well. (Berg et al., 2001). Therefore, arsenopyrite, could be excluded as a primary arsenic source in this area. In the present study, the sulphate concentrations in the groundwater were low and sometimes even below the detection limit (see Table 5-1). Combined with the neutral pH values this suggests that oxidation of pyrite does not occur. However, the low sulphate concentration does not necessarily show that there are no sulphur containing minerals at all, as the reducing conditions may lead to a reduction of sulphate to form gaseous H_2S . If so, this would give an isotopic signal of ^{34}S in the remaining sulphate because residual sulphate will be enriched with respect to the heavier isotope. Unfortunately the sulphate concentrations in the groundwater were too low to permit an analysis of ^{34}S . None of the samples could be processed even though the samples were concentrated in an anion exchanger.

There was a negative correlation between pE and arsenic concentration in the groundwater. If oxidation of arsenopyrite was the main mechanism accounting for the arsenic mobilisation an opposite correlation should be expected. A more likely explanation to the mobilisation of arsenic seems to be a reduction of iron in iron hydroxides (oxides), to which arsenic is adsorbed, followed by an arsenic release.

Furthermore, when plotting arsenic against bicarbonate it seems to correlate quite well, whereas arsenic and iron do not correlate at all.

It is possible that Arsenopyrite has weathered far upstream, at the Tibetan Plateau, and the released arsenic has been bound as inner-sphere-complexes on iron oxides. The oxides could then have been transported along the Red River and deposited in the delta. As the sediments are buried and the conditions become anoxic, the arseniferous iron oxides will be reduced, and a mobilisation of arsenic will be initiated. The reducing conditions in the aquifers of Nam Du, which are likely to be created in the peat layers or due to leakage of DOC from the soil surface, may lead to reductive dissolution of the iron oxides and mobilisation of arsenic. The process involves microbial oxidation of organic carbon, which generates HCO_3^- ions. It is similar to that observed in the Bengal delta (Bhattacharya et al. 1997). However there are several processes that will generate HCO_3^- which should be seen more as an indicator of reducing conditions. The reason for the poor correlation between arsenic and dissolved iron might be precipitation of Fe^{2+} and HCO_3^- to form solid FeCO_3 (Sracek et al. 2004). It is therefore suggested that the arsenic originates from reductive dissolution of iron hydroxides (Nickson et al. 2000).

Based on the data obtained during the field campaign it is difficult to understand the reason for the rising levels of arsenic. One possibility might be that the rate of the groundwater flow has increased which might lead to a faster transport of DOC from the peat or an increased leaching of waste water and dissolved fertilisers. This could maintain the anoxic conditions in the deeper aquifers and increase the reduction of iron hydroxides and mobilisation of arsenic. Arsenic deriving from surface activities could also be one explanation, though this needs to be investigated further. Another possibility is that the pumping creates larger fluctuations of the ground water level and thus leads to shifting redox conditions, which also could mobilise the arsenic.

In all groundwater samples, the observed arsenic concentrations were well above Vietnamese and WHO standards (10 $\mu\text{g}/\text{l}$). Most of the arsenic occurred as arsenite, which is considered to be more toxic than arsenate. However, health risks should be drastically reduced when water from the Nam Du well field is aerated in a treatment plant before distribution.

6.5 Sources of error

To measure Eh is problematic. The electrodes tend to be polluted with oxygen and the obtained readings are often unstable. Redox couples in the water are rarely at equilibrium, which means that the redox measurement will give a mixed potential for the different redox couples. It is only at thermodynamic equilibrium that measured values represent the actual redox potential in water. The risk of introducing oxygen into the samples is another problem. If oxygen is introduced, Eh will raise to values that are unrealistically high (Back 2001). A flow through-cell decreases the risk of oxygen introduction and creates an even flow of water around the electrode. Unfortunately, the flow-through cell could not be used at all locations. It was not possible to use it for measuring the Eh of surface water or shallow ground water at the riverbank. However, the redox conditions in surface water were of less interest as oxygen was freely available. However, even a flow-through cell, could give erroneous Eh-values, which was indicated by the chemical ion speciation.

Measurements of infiltration were only done on one occasion at each site. This means the values should only be seen as indicators of the flow directions.

Due to the large sample volumes needed for the samples sent to CETASD and INST, some of samples had to be filtered in the laboratory rather than in the field. Regarding CETASD, this was only the case for samples collected in the ponds. Regarding INST, most of the samples (except for ND3 and ND9) were filtered in the laboratory. After filtration, small particles and most of the bacteria were removed, but as long as some bacteria were left in the sample, the analytical results might have been affected. For example, when the samples were collected under anaerobic conditions, and brought to the aerobic conditions at the water surface, nitrification process might start, if the micro-organisms were present. However, acidification of the samples should minimise the bacterial activity.

There were samples, from Pond 2, for which the results of analysed ammonium and nitrate concentrations differed considerably between the INST and EAWAG laboratories (for example 13.5 mg N/l at INST and 0.4 mg N/l at EAWAG). This could be due to different lab procedures or the delayed filtering. The total nitrogen concentrations also differed between the laboratories which cannot be explained by the filtering but rather by different analytical methods. Another possibility for the deviation of the results could be denitrification, i.e. that nitrogen could escape as N₂ gas, but since the samples were acidified and kept in air tight bottles this should not happen.

The use of different equipment at the laboratories could be another reason for the different analytical values. At EAWAG, arsenic was analysed on a mass spectrometer. At CETASD a hydride generating atomic absorption spectrophotometer (HG-AAS) was used, while INST used an ICP-MS. For a complete list of analytical equipment see Appendix B.

Iron and other redox sensitive elements will easily be affected by changed conditions. Iron (II) is readily oxidised to Fe³⁺, which forms precipitates and is removed once the sample is filtered. If bacterial processes, such as nitrification, have occurred due to late filtering there is a risk that the ammonium ions will be somewhat enriched with respect to ¹⁵N. However, this should result in higher concentrations of nitrate and therefore it should be detectable.

The drilling was associated with practical problems since the samples were disturbed, the casing collapsed and at times surficial fresh plant material must have fallen down into the deeper sediments. Due to the disturbed samples and the mixing with bentonite it was difficult to make conclusions regarding the particle size distribution, However, it was possible to distinguish between sand and clay.

PY was a privately owned production well where the water passed a sand filter and was thus aerated before sampling. Due to the aeration, the data obtained at the PY well were likely to differ rather much from the observed trends at the other locations. Therefore, PY has not been included in the results and discussion sections of this report. However, the obtained values are shown in Appendix B.

7 Conclusions

- The deuterium and ^{18}O compositions suggest that an important part of the recharge in the qp aquifer originates from the Red River and that there are hydraulic windows between the qp and qh aquifer.
- The reducing conditions will both maintain the ammonium concentrations and trigger a dissolution of ironhydroxides.
- The isotopic composition of the ammonium ions and peat combined with the pattern of groundwater flow implies that the ammonium ions are not derived from the peat. Human activities, such as farming or release of sewage water are more likely explanations of the high ammonium ion concentrations.
- Dissimilatory nitrate reduction to ammonium ions (DRNA) does not take place to such an extent that it could explain the ammonium concentrations observed in this study.
- Taken together, the negative covariation of pE and the total arsenic concentration, and the positive covariation between the arsenic and HCO_3^- concentration, indicate that reduction of ironhydroxides is the driving process behind the mobilisation of dissolved arsenic.

8 Recommendations for future studies

- Additional seepage measurements along the Red River will give a more detailed and accurate picture of the seepage.
- Further studies of isotopic composition are needed to determine possible sources of ammonium. I suggest that ammonium ions in sewage water as well as in organic fertilisers should be investigated.
- Localisation of possible sources, such as major sewage canals, close to the Nam Du area.
- Investigation of how increased groundwater extraction rates affect the Neogene aquifers and the sodium content in the qp aquifer.
- Studies of $\delta^{34}\text{S}$ in sulphate ions will give further information about the redox conditions and possible sources of arsenic.
- The likelihood of anthropogenic arsenic sources should be evaluated. It should be investigated to what extent arsenic is used in agriculture. Moreover, are there any mining or land filling sites which could leach arsenic?
- Investigation of the possibilities for other pollutants, deriving from surface activities, to reach the ground water in the Nam Du area

9 References

- Andersson, L. and J. Norrman (1998). Ammonium contamination of groundwater in the Hanoi area, Vietnam. Geologiska institutionen. Gothenburg, Chalmers Teknologiska Högskola.
- Apello, C. A. J. and D. Postma (2005). Geochemistry, groundwater and pollution. Leiden, Great Brittain, A.A. Balkema Publishers.
- Back, P.-E. (2001). "How to measure the redox potential and why it often fails (In Swedish)." Vatten **57**: 153-160.
- Berg, M., C. Stengel, P. T. K. Trang, P. H. Viet, M. L. Sampson, M. Leng, S. Samreth and D. Fredericks (2007). "Magnitude of arsenic pollution in the Mekong and Red River delta, Cambodja and Vietnam." Science of the Total Environment **372**: 413-425.
- Berg, M., H. C. Tran, T. C. Nguyen, H. V. Pham, R. Schertenleib and W. Giger (2001). "Arsenic Contamination of Groundwater and Drinking Water in Vietnam: A Human Health Threat." Environmental Science & Technology **35**(13): 2621-2626.
- Bhattacharya, P., G. Jacks and D. Chatterjee (1997). "As safe aquifers in the Bengal delta aquifers." Journal of Water resources development **13**(1): 79-92.
- Binnerup, S. J., K. Jensen, N. P. Revsbech, M. Hjorth Jensen and J. Sørensen (1992). "Denitrification, dissimilatory reduction of nitrate to ammonium and nitrification in a bioturbated estuarine sediment as measured with ¹⁵N and microsensor techniques." Applied and environmental microbiology **58**: 303-313.
- Bonin, P. (1996). "Anaerobic nitrate reduction to ammonium in two strains isolated from coastal marine sediments: A dissimilatory pathway." FEMS Microbiology Ecology **19**: 27-38.
- CIA. (2007). "Worldfact book." Retrieved 2007-03-01, from <https://www.cia.gov/cia/publications/factbook/geos/vm.html>.
- Clark, I. and P. Fritz (1997). Environmental isotopes in hydrogeology. United States of America, Lewis Publishers.
- Cline, J. D. and I. R. Kaplan (1975). "Isotopic fractionation of dissolved nitrate during denitrification in the eastern tropical north pacific ocean." Marine Chemistry **3**: 271-299.
- Dalsgaard, T. and F. Bak (1994). "Nitrate Reduction in a Sulfate-Reducing Bacterium, *Desulfovibrio desulfuricans*, Isolated from Rice Paddy Soil: Sulfide Inhibition, Kinetics, and Regulation." Applied and environmental microbiology **60**(1): 291-297.
- Dang, H. O., N. A. Nguyen, D. N. Dao and K. V. Nguyen (1996). Report on the feasibility study for groundwater exploitation of Nam Du Thuong well field. Hanoi, Ministry of construction.

DTU (2005). Hydrogeological modelling in the Red River Catchment, Environment & Resources, Technical University of Denmark.

Duong, H. A., M. Berg, M. H. Hoang, H. V. Pham, H. Gallard, W. Giger and U. von Gunten (2003). "Trihalomethane formation by chlorination of ammonium- and bromide-containing groundwater in water supplies of Hanoi, Vietnam." Water Research **37**: 3242-3252.

Erikson, J., I. Nilsson and M. Simonsson (2005). Wiklanders Marklära. Lund, Studentlitteratur.

Gustafsson, J. P., G. Jacks, M. Simonsson and I. Nilsson (2006). Mark- och vattenkemi teori. Stockholm, Institutionen för mark- och vattenteknik.

Hoefs, J. (1997). Stable isotope geochemistry. Berlin Springer Verlag

IAEA. (2004). "Global Network of Isotopes in Precipitation." The GNIP Database Retrieved 2007-02-20, from <http://isohis.iaea.org>

Kelso, B. B. H., R. V. Smith, R. J. Laughlin and S. J. Lennox (1997). "Dissimilatory Nitrate Reduction in Anaerobic Sediments Leading to River Nitrite Accumulation." Applied and environmental microbiology **63**(12): 4679-4685.

Kendall, C. and R. Aravena (2000). Nitrate isotopes in groundwater systems. Environmental Tracers in Subsurface Hydrology. C. P. and A. L. Herczeg. London, Kluwer Academic Publishers: 261-297.

Lehmann, M. F., P. Reichert, S. M. Bernasconi, A. Barbieri and J. A. McKenzie (2003). "Modelling nitrogen and oxygen isotope fractionation during denitrification in a lacustrine redox-transition zone." Geochimica et Cosmochimica Acta **67**(14): 2529-2542.

Lucas, L. L. and U. M. Unterwieser (2000). "Comprehensive Review and Critical Evaluation of the Half-Life of Tritium." Journal of Research of the National Institute of Standards and Technology **105**(4): 541-549.

Mathers, S. and J. Zalasiewicz (1999). "Holocene sedimentary architecture of the Red River delta, Vietnam." Journal of Coastal Research **15**(2): 314-325.

Moreskog, J. (2007). Redox-conditions and distribution of ammonium and arsenic in the Nam Du well field, Hanoi, Vietnam. Department of Soil Chemistry Pedology. Uppsala, Swedish University of Agricultural Sciences. **Bachelor Thesis**.

Nghi, T. (2004). Quaternary sedimentation of Red River Delta in relation to groundwater potential.

Nhan, P. Q. (2006). Personal communication. P. Harms-Ringdahl and J. Moreskog. Hanoi.

Nickson, R. T., J. M. McArthur, P. Ravenscroft, B. W.G. and A. K.M. (2000). "Mechanism of arsenic release to groundwater, Bangladesh and West Bengal." Applied Geochemistry **15**(2000): 403-413.

Schlesinger, W. H. (1997). An analysis of global change. United States of America, Elsevier Science.

Seitzinger, P. S., G. W. S. and K. A. Spratt (1991). "The Effect of Salinity on Ammonium Sorption in Aquatic Sediments: Implications for Benthic Nutrient Recycling " Estuaries **14**(2): 167-174.

Smedley, P. L. and D. G. Kinniburgh (2002). "A review of the source, behaviour and distribution of arsenic in natural waters." Applied Geochemistry **17**: 517-568.

Spocito, G. (1989). The chemistry of soils. New York, Oxford university press.

Sracek, O., P. Bhattacharya, G. Jacks, J. P. Gustafsson and M. von Brömssen (2004). "Behavior of arsenic and geochemical modeling of arsenic enrichment in aqueous environments." Applied Geochemistry **19**(2): 169-180.

Sylvia, D. M., J. J. Fuhrman, P. G. Hartel and D. A. Zuberer (1999). Principles and applications of soil microbiology. Upper Saddle River, USA, Prentice Hall.

Tanabe, S., K. Hori, Y. Saito, S. Haruyama, V. P. Vu and A. Kitamura (2003). "Song Hong (Red River) delta evolution related to millenium-scale Holocene sea-level changes." Quaternary Science Review **22**: 2345-2361.

Tarback, E. J. and F. K. Lutgens (2002). Earth, An introduction to physical geology, Prentice Hall.

Trafford, J. M., A. R. Lawrence, D. M. J. Macdonald, V. D. Nguyen, N. T. Dang and T. H. Nguyen (1996). The effect of urbanisation on the groundwater quality beneath the city of Hanoi, Vietnam. British Geological Survey. Keyworth.

UN, U. N. (1990). Atlas of mineral resources of the ESCAP region, Volume 6. Viet Nam. Bangkok.

UNICEF (2001). Report on investigated results for arsenic groundwater level in Ha Noi city.

van Horen, B. (2005). "City Profile: Hanoi." Cities **22**(2): 161-173.

WHO (1986). Environmental Health Criteria 54, Ammonia Geneva, World Health Organization.

WHO (2001). Environmental Health Criteria 224, Arsenic and Arsenic compounds. Geneva, World Health Organization.

WHO (2004). Guidelines for drinking water quality, 3d ed.

10 Appendix

Appendix A

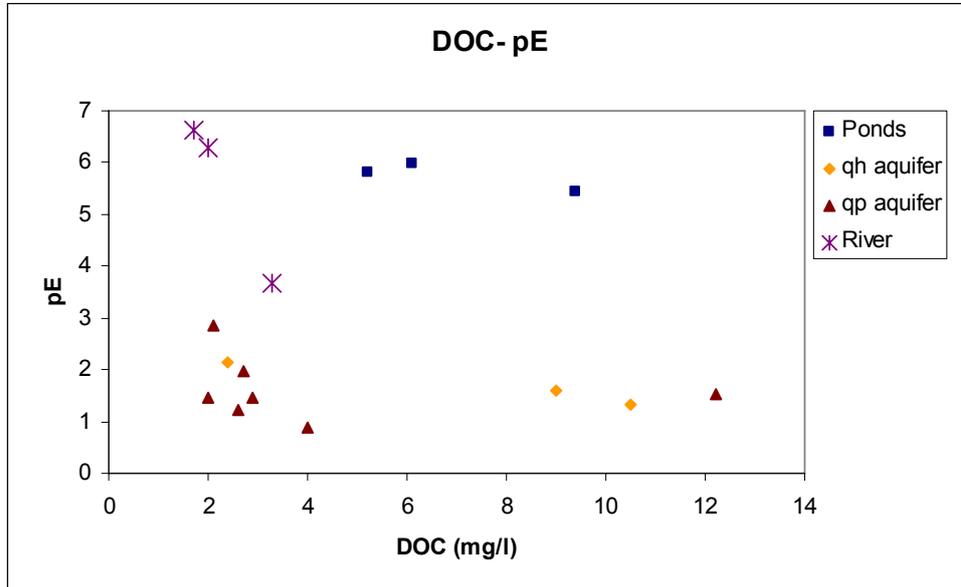


Figure 10-1 No clear pattern could be observed for DOC and measured pE.

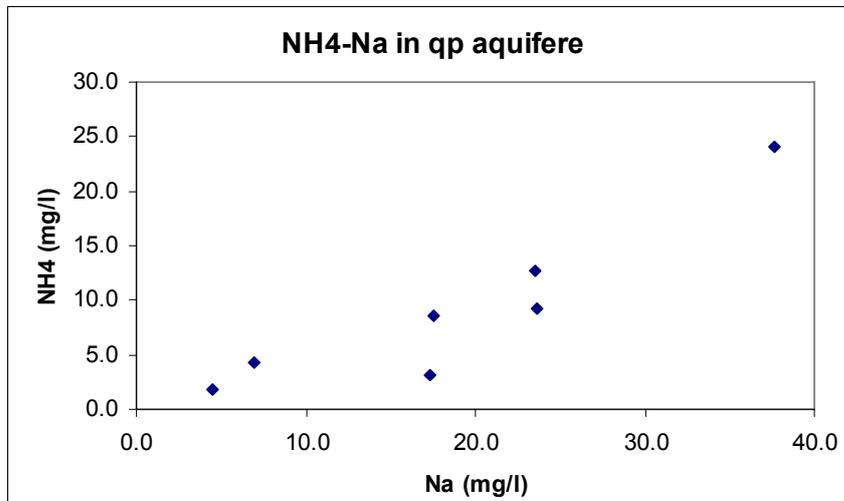


Figure 10-2 Relationship between Na and ammonium in the qp aquifer

Appendix B

Table 10-1 to 10-6 describes all obtained data from the field project.

Table 10-1

Laboratory	EAWAG	CETASD	INST	EAWAG	CETASD	INST	EAWAG	CETASD	INST	EAWAG	CETASD	INST
Element	NO3-N	NO3-N	NO3-N	NH4-N	NH4-N	NH4-N	HCO3-	HCO3-	HCO3-	SO4-S	SO4-S	SO4-S
Sampling Site	mg/L AuA	mg/L IC	mg/L IC	mg/L Photo	mg/L Photo	mg/L IC	mg/L AuA	mg/L Titration	mg/L mg l-1	mg/L AuA	mg/L IC	mg/L IC
Pond 1	<0.25*	<0,5	4.7	1.6	8.89	2.4	211	273	142	40.0	40.73	35.2
Pond 2	<0.25*	0.61	0.6	0.4	0.6	13.5	160	247	152	24.0	24.55	15.4
Pond 3	0.4	<0,5	1.6	2.4	0.61	<0,01	147	175	134	19.0	19.92	17.7
ND3	<0.25*	<0,5	<0,01	4.3	5.42	14.0	332	364	326	<5*	4.71	4.1
ND9	<0.25*	<0,5	<0,01	8.6	8.67	27.2	349	403	347	<5*	0.54	0.2
1RGw	<0.25*	<0,5	<0,01	0.5	0.27	0.8	139	195	131	6.6	7.19	6.8
2RGw	<0.25*	0.55	<0,01	<0.2*	0.03	<0,01	220	273	204	16	15.09	14
2RSw	0.31	1.52	<0,01	<0.2*	0.21	0.6	109	208	102	9.5	9.91	7
3RGw	0.6	NA	NA	0.4	NA	NA	101	NA	NA	24.0	NA	NA
P1A	<0.25*	<0,5	<0,01	12.7	11.9	19	450	520	429	<5*	<0,5	<0,01
P1B	<0.25*	<0,5	<0,01	34.7	37.95	60	696	741	714	<5*	0.78	<0,01
P3A	<0.25*	<0,5	<0,01	24.0	24.1	37	253	370	243	<5*	<0,5	<0,01
P3B	<0.25*	<0,5	<0,01	9.8	10.6	3.1	338	409	345	<5*	<0,5	1.2
PX	<0.25*	<0,5	<0,01	3.2	3.34	<0,01	222	305	163	<5*	<0,5	9.0
PY	<0.25*	<0,5	<0,01	0.3	0.22	0.5	159	227	155	8.0	8.47	10.1
P86A	<0.25*	<0,5	<0,01	9.2	9.3	25	467	578	489	<5*	<0,5	<0,01
P86B	<0.25*	<0,5	3.1	2.6	2.65	<0,01	412	455	372	<5*	0.6	0.5
NDT12	<0.25*	<0,5	<0,01	1.8	1.73	6.6	190	227	171	<5*	1.57	<0,01

Table 10-2

Laboratory	EAWAG	CETASD	INST	EAWAG	CETASD	INST	EAWAG	CETASD	INST	EAWAG	CETASD	INST
Element	As(tot)	As(tot)	As(tot)	Al	Al	Al	Ca	Ca	Ca	Cl-	Cl-	Cl-
Sampling Site	µg/L MS	µg/L HG-AAS	µg/L ICP-MS	µg/L MS		µg/L ICP-MS	mg/L ICP-OES	mg/L AAS	mg ICP-MS	mg/L AuA	mg/L IC	mg/L IC
Pond 1	4.9	4.05	9.6	30.0	NA	871.6	45.0	47.3	43.9	27.6	37.61	43.9
Pond 2	2.6	2.68	4.7	25.0	NA	569.3	41.0	42.2	38.6	14.7	14.15	37.6
Pond 3	1.9	2.43	5.8	38.0	NA	626.1	40.0	39.7	41.5	11.6	16.36	17.0
ND3	83.0	80.50	128.2	237.0	NA	12.7	68.0	69.2	67.7	2.2	4.08	3.6
ND9	83.0	74.00	121.4	16.0	NA	7.5	50.0	50.5	49.1	8.0	8.48	8.0
1RGw	2.6	3.00	5.0	99.0	NA	60.4	37.0	37.7	36.7	2.6	4.37	2.3
2RGw	0.4	1.31	2.54	24.0	NA	308.3	63	68.6	60.4	2.5	4.41	2.4
2RSw	2.8	2.51	5.76	239.0	NA	257.4	30	27.7	2.8	2.7	4.34	6.7
3RGw	2.6	NA	NA	217.0	NA	NA	31.0	NA	NA	2.7	NA	NA
P1A	257	280.30	389.40	12.0	NA	3.0	75	79.1	73.9	10.3	10.6	9.9
P1B	264	239.10	510.00	16.0	NA	253.7	99	103.5	10.2	5.8	6.94	5.6
P3A	152	157.50	228.70	54.0	NA	8.0	19	18.9	18.7	30.2	39.87	39.7
P3B	39.0	38.10	61.1	10.0	NA	55.1	73.0	77.5	71.9	41.9	57.62	4.6
PX	27.0	28.60	41.8	13.0	NA	0.9	27.0	25.9	24.9	5.1	7.03	3.9
PY	0.4	<1,00	2.1	11.0	NA	9.8	6.4	3.4	55.6	14.6	20.37	3.8
P86A	312	295.30	448.80	8.0	NA	5.4	104	105.9	10.2	16.2	24.21	25.4
P86B	62.0	59.60	117.2	6.0	NA	42.5	92.0	99.2	89.6	10.1	9.48	4.2
NDT12	44	44.90	62.9	8.0	NA	251.8	40	41.4	40.4	1.5	3.86	4.59

Table 10-3

Laboratory	EAWAG	CETASD	INST									
Element	Fe	Fe	Fe	K	K	K	Mg	Mg	Mg	Mn	Mn	Mn
Sampling	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg	mg/L	mg/L	mg/L
Site	ICP-OES	AAS	ICP-MS									
Pond 1	0.1	0.82	0.18	20.2	33.1	1.7	9.8	8.9	6.6	<0.01*	0.136	0.20
Pond 2	<0.01*	2.68	1.26	7.3	9.7	4.7	9.5	7.9	4.8	0.5	0.597	0.12
Pond 3	0.1	0.96	1.05	6.8	9.7	5.2	6.9	5.4	6.5	<0.01*	0.066	0.76
ND3	9.2	6.53	8.89	3.2	4.2	2.0	21.5	17.5	1.4	0.5	0.483	0.60
ND9	11.7	8.70	11.36	4.4	5.2	2.5	27.3	21.5	1.8	0.5	0.436	0.54
1RGw	0.1	<0.05	0.21	2.1	2.7	1.4	5.4	3.9	3.6	0.1	<0.05	0.09
2RGw	<0.01*	<0.05	1.00	2.9	5.3	1.8	9.4	8.1	6.0	<0.01*	<0.05	0.03
2RSw	0.20	<0.05	0.55	1.2	2.7	0.8	5.7	4.3	3.8	<0.01*	<0.05	0.04
3RGw	<0.01*	NA	NA	1.5	NA	NA	5.9	NA	NA	<0.01*	NA	0.00
P1A	10.6	7.07	8.96	4.6	5.4	0.3	28.1	22.2	0.2	0.38	0.333	0.43
P1B	12.6	7.54	17.98	7.4	6.7	4.1	42.7	33.9	0.3	0.84	0.832	0.92
P3A	19.3	15.90	18.98	4.1	5.2	2.3	13.3	11.6	8.7	0.05	<0.05	0.05
P3B	37.3	28.30	42.24	1.8	2.9	0.9	24.1	19.4	1.5	0.5	0.434	0.58
PX	18.7	14.90	17.66	4.3	5.1	2.5	17.6	14.0	1.1	0.7	0.740	0.81
PY	<0.01*	<0.05	0.05	1.8	2.7	0.8	6.8	4.6	4.3	1.0	0.979	1.10
P86A	7.0	5.69	6.80	3.9	4.1	2.1	30.1	24.4	1.9	0.36	0.343	0.43
P86B	6.0	5.36	9.24	1.4	1.8	0.8	22.4	18.2	0.1	0.6	0.543	0.67
NDT12	3.5	2.99	4.54	2.0	3.0	1.3	10	8.0	6.6	1.09	1.070	1.28

Table 10-4

Laboratory	EAWAG	CETASD	INST	EAWAG	CETASD	INST	EAWAG	CETASD	INST
Element	Na	Na	Na	PO4-P	PO4-P	PO4-P	SiO4-Si	SiO4-Si	SiO4-Si
Sampling	mg/L	mg/L	mg/L	mg/L	mg/L		mg/L	mg/L	
Site	ICP-OES	AAS	ICP-MS	Photo	Photo		AuA	Photo	
Pond 1	28.8	26.83	2.4	<0.2*	0.58	NA	3.9	5.3	NA
Pond 2	14.4	14.34	1.6	<0.2*	0.13	NA	5.5	6.6	NA
Pond 3	17.8	17.27	1.3	<0.2*	0.16	NA	2.2	3.3	NA
ND3	6.9	7.44	6.3	0.9	0.9	NA	16.5	15.9	NA
ND9	17.5	16.38	1.5	0.5	0.68	NA	19.8	21.3	NA
1RGw	4.1	4.35	3.9	<0.2*	0.03	NA	7.4	6.9	NA
2RGw	4.3	4.91	3.96	<0.2*	0.02	NA	3.5	2.8	NA
2RSw	4.1	4.4	3.68	<0.2*	0.03	NA	4.8	5.1	NA
3RGw	4.4	NA	NA	<0.2*	NA	NA	4.2	NA	NA
P1A	23.5	20.83	1.9	0.95	1.01	NA	17.8	18.0	NA
P1B	32.0	26.78	2.5	0.19	0.07	NA	12.5	12.1	NA
P3A	37.7	35.57	0.3	1.05	1.14	NA	15.8	17.9	NA
P3B	27.3	24.1	2.3	0.7	0.87	NA	27.7	30.2	NA
PX	17.3	16.72	1.5	0.2	0.34	NA	19.7	23.7	NA
PY	58.2	42.98	4.9	<0.2*	0.06	NA	17.9	18.4	NA
P86A	23.6	21.29	2.0	0.71	0.79	NA	14.8	15.1	NA
P86B	11.2	11.38	9.5	<0.2*	0.1	NA	13.7	15.2	NA
NDT12	4.5	4.58	4.051	<0.2*	0.17	NA	12.8	13.5	NA

Table 10-5

Sampling Site	Parameters measured in field							
	pH	Eh (mV)	Eh ref (mV)	Cond ($\mu\text{S/cm}$)	DO (mg/l)	DO (%)	Temp ($^{\circ}\text{C}$)	Infiltration
Pond 1	8.21	109	216	509	9.5	115	25.1	-
Pond 2	7.40	131	242	325	4.48	52.7	23.7	-
Pond 3	7.54	141	242	309	5.45	65.4	24.8	-
ND3	6.65	-138	217	495	0.08	0.9	26.5	-
ND9	6.35	-94	218	555	0.15	2	27	-
1RGw	7.08	180	225	-	-	-	23.9	-2,4l/m2h
2RGw	7.30	-	-	-	-	-	24.6	-0,4l/m2h
2RSw	8.00	160	219	188	6.86	80.6	23.8	-
3RGw	8.69	5	242	-	-	-	16.7	+1,2l/m2h
P1A	7.11	-159	232	1068	0.25	3	27.4	-
P1B	6.68	-132	232	692	0.12	1.4	26.5	-
P3A	6.29	43	396	572	0.15	1.9	27.4	-
P3B	6.29	48	398	777	NA	NA	24.5	-
PX	6.31	-42	238	381	0.33	3.5	27.2	-
PY	6.46	135	238	314	0.14	1.7	26.2	-
P86A	6.95	-125	234	774	0.2	2.5	26.2	-
P86B	6.90	-85	225	635	NA	NA	24.4	-
NDT12	7.10	-124	230	294	0.21	2.7	25.9	-

Table 10-6

INST RESULTS	Isotopes in samples								
	water	water		samples		samples		samples	
Element	$\delta^{18}\text{O}(\text{‰})$	$\delta^2\text{H}(\text{‰})$	^3H (TU)			$\delta^{15}\text{N}$ in NH_4	$\delta^{15}\text{N}$ in NO_3	$\delta^{18}\text{O}$ in NO_3	
Sampling Site	$\pm 0,15(\text{‰})$ (IRMS)	$\pm 1,5(\text{‰})$ (IRMS)	(IRMS)			‰ (IRMS)	‰ (IRMS)	‰ (IRMS)	
Pond 1	-2.44	-20.50				22.54	18,97 \pm 1,5	17,25 \pm 0,7	
Pond 2	-3.22	-37.00				27.6	19,20 \pm 1,7	18,37 \pm 1,2	
Pond 3	-2.83	-25.63				-	1,35 \pm 1,5	9,26 \pm 0,8	
ND3	-9.23	-64.21				27.71	-	-	
ND9	-9.24	-60.88	2.4	\pm	0.3	29.67	-	-	
Riverbank 1 GW	-8.36	-62.96				6.82	-	-	
Riverbank 2 GW	-8.87	-63.18				-	-	-	
Riverbank 2 SW						6.35	-	-	
Riverbank 3 GW									
P1A	-5.57	-37.28				30.68	-	-	
P1B	-8.52	-54.12				30.24	-	-	
P3A	-9.30	-58.35	1	\pm	0.49	31.2	-	-	
P3B	-5.12	-34.98				25.03	-	-	
PX	-9.47	-64.13	2.9	\pm	0.2	-	-	-	
PY	-6.68	-41.26				5.37	-	-	
P86A	-5.83	-39.32	4	\pm	0.22	27.35	-	-	
P86B	-6.76	-45.99				-	7,92 \pm 1,6	11,73 \pm 1,4	
ND12-4(A,C)	-10.21	-66.82				25.49	-	-	