# TRANSPORT AND FATE OF AMMONIUM AT A RIVERBANK FILTRATION SITE IN DELHI (INDIA)

## Assessment of the Groundwater Contamination, Treatment Strategies and Recommendations for an Adapted Management

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# Summary

At a riverbank filtration site in central Delhi elevated ammonium ($NH_4^+$) concentrations were measured in the past decade. At one of the production wells measured $NH_4^+$ concentrations were more than tenfold higher than the Indian drinking water requirement of 0.5 mg/L $NH_4^+$-N. Elevated $NH_4^+$concentrations in raw water interfere with the chlorination step at water treatment plants, making it difficult to ensure a safe disinfection. In case of water quality problems individual wells might be taken off the network. However, due to the high water stress in the Delhi metropolis, it is hardly feasible to abandon an entire well field and not use available groundwater resources.

The studied riverbank filtration site is located on the eastern bank of the Yamuna River, in the Delhi-section of the river. This section has a length of 22 km and is bounded by two barrages, which are only opened during monsoon times (July−September). During non-monsoon times, the river is mostly fed by treated and untreated sewage water from 16 drains within the city. The river water is therefore found to be degraded. Dissolved oxygen is often not available in the water while sewage-borne $NH_4^+$ concentrations are high.

The production wells at the site are completed in the Holocene floodplain aquifer, which is the aquifer with the highest yield in Delhi. Due to the high groundwater abstraction, losing stream conditions prevail and sewage contaminated river water infiltrates into the groundwater system. In the aquifer, $NH_4^+$ does not move with average linear groundwater flow velocity but is retarded owing to cation exchange with the sediment matrix. In addition, different reactions can occur, which have an effect on the $NH_4^+$ concentrations and nitrogen mass balance in the aquifer. $NH_4^+$ can be removed from the system by way of oxidation (nitrification, anammox) or fixation in the sediment matrix while mineralization of organic matter can lead to an increase of $NH_4^+$ concentrations. Irrigation return flow might be another source of $NH_4^+$.

The goal of the present study was to make an assessment of the $NH_4^+$ contamination and to understand how $NH_4^+$ concentrations in the drinking water production wells will develop in the future. Recommendations for suitable remediation and water treatment options are given to provide a basis for the development of an adapted groundwater management.

A groundwater study along a W−E transect in the Yamuna floodplain was conducted. The transect was 2.4 km long and reached from the eastern riverbank to the border of the undeveloped floodplain. Water samples were taken from handpumps, bore wells, observation wells and large production wells during five sampling campaigns in 2012−13. Six deep drillings with depths between 8 and 27 m were conducted to determine the local geological and hydrogeological situation and to obtain sediment samples from the saturated zone. Six shallow drillings up to 4 m deep were carried out to study the unsaturated zone in detail. Three cross sections of the river were chosen to measure the water depth and sample riverbed sediments.

The sediment parameters necessary for sediment characterization were obtained through standard laboratory analyses. To study the transport of $NH_4^+$ in aquifer material, laboratory column

experiments were conducted under anoxic/suboxic and partly under oxic conditions with six sediment samples from the saturated zone and two samples from the unsaturated zone. Tracer tests were carried out to determine transport parameters of the sediments. Reactive transport models have been set up to model the column experiments. Cation exchange was implemented in the models with adapted selectivity coefficients for the different sediments. Two 1D flow paths have been modeled with PHREEQC at field scale to obtain a first estimation of the time periods that the contamination can still prevail in the aquifer after the $NH_4^+$ source was removed.

A catalogue of remediation and post-treatment measures was compiled. The options have been evaluated concerning their applicability under conditions found in Delhi.

In the study area the floodplain aquifer has a thickness of about 15 m. A several m thick clay layer forms the lower boundary of the aquifer. This clay layer is overlain by an about 1 m thick kankar layer. Kankar particles are calcareous-bound nodules made up of clay and silt. The size of the nodules varies from several mm to several cm. The kankar horizon is covered by well sorted medium sand. The sequence ends with the 3−4 m thick unsaturated zone, consisting of fine sand and clayey silt. Towards the river, the kankar layer is thinner, and clay lenses were encountered in the medium sand. The mean hydraulic conductivities in the kankar layer ($3.7\times10^{-3}$ m/s) are about one magnitude greater than in the medium sand ($2.9\times10^{-4}$ m/s). The hydraulic properties of the kankar are similar to those of gravel. Preferential flow through the kankar layer can be expected.

$NH_4^+$ concentrations show a high temporal variability in the sampling points located within 500 m from the riverbank (e.g. between 4.5 and 35 mg/L). These can partly be explained by the varying $NH_4^+$ loads in the infiltrating river water. Regarding the transport of $NH_4^+$, the medium sand and the kankar show distinct characteristics. In both units, cation exchange was the main process. While it took about 10−12 flushed pore volumes to reach a 100% $NH_4^+$ breakthrough in the sand, it took 30−35 pore volumes in the kankar. Similar results were obtained when flushing out the $NH_4^+$. Regarding solute transport, the kankar layer has characteristics similar to clay. 1D modeling at field scale revealed that it will take 19 years to flush the sorbed $NH_4^+$ out of the medium sand layer and 61 years to flush it out of the kankar within the first 500 m from the river. These are conservative estimates that do not consider the biological degradation of $NH_4^+$. In the column experiments, oxidation or fixation of $NH_4^+$ was only observed in the sediments of the unsaturated zone.

In case the municipality aims at a 100% water supply from the water works with no additional use of private wells, it is recommended to focus on setting up a post-treatment without installing remediation measures, which are cost-intensive. The post-treatment should be designed specifically for the well field on the floodplain, instead of mixing the water with surface water before treatment as is currently done. Biological nitrification filters or zeolites could be suitable options for conditions met in Delhi.

# Zusammenfassung

An dem untersuchten Uferfiltrationsstandort in Delhi (Indien) sind in den vergangenen Jahren stark erhöhte Ammoniumkonzentrationen ermittelt worden, wobei an einem der Versorgungsbrunnen der von der indischen Trinkwasserverordnung festgelegte Grenzwert von 0,5 mg/L Ammonium-N um mehr als das Zehnfache überschritten wurde. Erhöhte Ammoniumkonzentrationen stellen in der Wasseraufbereitung ein Problem dar, da eine zuverlässige Chlorung erschwert wird. Gleichzeitig ist der Wasserstress in der Millionenmetropole Delhi hoch. Das Abschalten einzelner Brunnen wegen schlechter Rohwasserqualität ist zwar möglich, die Nichtnutzung einer Brunnengalerie oder eines Grundwasserleiters aufgrund von Qualitätsproblemen ist jedoch wegen des ständig steigenden Wasserbedarfs nicht bzw. kaum umsetzbar.

Der Uferfiltrationsstandort befindet sich im Zentrum Delhis auf der Ostseite des Yamuna-Flusses, an dem Flussabschnitt, der als Delhi section bekannt ist. Dieser 22 km lange Abschnitt wird durch zwei Stauwerke begrenzt, die in der Regel nur während des Monsuns (Juli-September) geöffnet sind. Während des Rests des Jahres wird der Flussabschnitt fast ausschließlich durch den Zufluss von geklärtem und ungeklärtem Abwasser gespeist. Die Wasserqualität ist daher besonders kritisch. Während gelöster Sauerstoff oft nicht vorhanden ist, sind die Konzentrationen abwasserbürtiger Stoffe (z.B. Ammonium) im Fluss hoch.

Die Uferfiltrationsbrunnen sind im holozänen Flussaue-Grundwasserleiter verfiltert, welcher der Grundwasserleiter mit der höchsten Ergiebigkeit in Delhi ist. Aufgrund der hohen Grundwasserförderung herrschen im Untersuchungsgebiet influente Verhältnisse, d.h. abwasserkontaminiertes Flusswasser infiltriert in den Grundwasserleiter. Dabei breitet sich Ammonium jedoch nicht mit der Grundwasserfließgeschwindigkeit aus, sondern wird infolge von Kationenaustausch retardiert. Zusätzlich können verschiedene Reaktionen stattfinden, bei denen Ammonium abgebaut (Nitrifikation, Anammox), dauerhaft im Sediment fixiert oder neu gebildet wird (Mineralisierung von organischem Stickstoff). Gleichzeitig kann es weitere Ammoniumquellen wie z.B. Bewässerungsrücklauf geben.

Um die Gefährdung des Grundwasserleiters zu beurteilen und die zukünftige Entwicklung der Ammoniumkonzentration abzuschätzen, wurde die Ammoniumkontamination umfassend untersucht. Empfehlungen für Grundwassersanierungsmaßnahmen und Wasseraufbereitung wurden erarbeitet, um eine Basis für angepasstes Grundwassermanagement zu schaffen.

An dem Uferfiltrationsstandort wurde eine 2,4 km lange Transekte vom östlichen Ufer bis zur Grenze der unbebauten Flussaue untersucht. In fünf Geländekampagnen wurden Handpumpen, Grundwassermessstellen und Horizontalfilterbrunnen der Brunnengalerie beprobt. Zusätzlich wurden Oberflächenwasserproben genommen. Zur Ermittlung der geologisch-hydrogeologischen Verhältnisse und zur Gewinnung von Sedimentproben aus der gesättigten Zone konnten sechs Bohrungen mit Tiefen zwischen 8 und 27 m abgeteuft werden. Sechs weitere Bohrungen bis zu einer Tiefe von 4 m dienten der näheren Untersuchung der oberflächennahen ungesättigten Zone. Zusätzlich wurden drei Profile durch den Yamuna aufgenommen.

Die notwendigen sedimentologischen Parameter wurden im Labor ermittelt. Der Transport von Ammonium wurde mittels Säulenexperimenten (suboxisch/anoxisch und teilweise oxisch) mit sechs Sedimenten aus der gesättigten und zwei Sedimenten aus der ungesättigten Zone untersucht. Zur Ermittlung von Transportparametern wurden konservative Tracertests durchgeführt. Die Ergebnisse der Säulenversuche wurden in 1D und 2D mit dem reaktiven multikomponenten Transportmodell PHT3D modelliert. In den Modellen wurde Kationenaustausch implementiert und die unterschiedlichen Selektivitätskoeffizienten der Sedimente berücksichtigt. Im Geländemaßstab wurden zwei 1D Fließpfade im Geländemaßstab mit PHREEQC modelliert, um den Dekontaminationszeitraum abschätzen zu können. Weiterhin wurde ein Katalog mit Sanierungsmaßnahmen und Aufbereitungsoptionen erarbeitet.

Der Flussaue-Grundwasserleiter ist im Untersuchungsgebiet etwa 15 m mächtig. Über einem tonigen Grundwasserstauer liegt ein etwa 1 m mächtiges Lockersediment, welches aus karbonatisch gebundenen siltig-tonigen Konkretionen, Kankar genannt, besteht. Die Größe der Konkretionen schwankt vom Sand- bis Kiesbereich. Darüber folgt ein gut sortierter Mittelsand. Zum Hangenden hin wird das Sediment feinkörniger und die Abfolge endet mit der c.a. 3−4 m mächtigen ungesättigten Zone, die aus Feinsanden und Silt-Ton besteht. Zum Ufer hin schalten sich Tonlinsen in den Mittelsand ein und die Kankarschicht ist geringer mächtig. Die Durchlässigkeitsbeiwerte in der Kankarschicht ($3.7\times10^{-3}$ m/s) sind etwa um eine Größenordnung größer als im Mittelsand ($2.9\times10^{-4}$ m/s). Der Kankar wirkt hydraulisch wie ein sandiger Kies und ist somit der Hauptfließweg des Wassers.

Auffällig sind die großen zeitlichen Schwankungen der Ammoniumkonzentrationen in den einzelnen Messstellen (z.B. zwischen 4.5 und 35 mg/L) in den ersten 500 m vom Ufer. Diese können teilweise durch den schwankenden Ammoniumeintrag aus dem Fluss erklärt werden. Der Ammoniumtransport im Sand und im Kankar ist sehr unterschiedlich, obwohl in beiden Kationenaustausch der dominierende Prozess ist. Während es im Sand 10−12 ausgetauschte Porenvolumen brauchte, um den 100% Ammoniumdurchbruch zu erreichen, brauchte es 30−35 Porenvolumen im Kankar. Bezüglich des Stofftransportes wirkt der Kankar wie ein feinkörniges Sediment mit sehr großer Oberfläche, z.B. Ton. Das kann der Grund für die noch relativ geringen Konzentrationen in den Förderbrunnen sein. Die Modellierung einer 500 m langen Transekte im Geländemaßstab ergab einen Dekontaminationszeitraum von etwa 19 Jahren im Sand-Horizont und von 61 Jahren im Kankar, für den Fall, dass kein Ammonium abgebaut wird.

Sollte eine flächendeckende Wasserversorgung der Stadtteile und Bevölkerungsgruppen, die derzeit Wasser aus dem durch die Ammoniumkontamination gefährdeten Teil des Grundwasserleiters entnehmen, gewährleistet sein, ist ein Verzicht von aufwendigen Grundwassersanierungsmaßnahmen möglich. Eine dezentrale Wasseraufbereitungsanlage speziell für das Rohwasser aus dem Flussaue-Grundwasserleiter ist empfehlenswert, sodass das Wasser nicht wie bisher vor der Aufbereitung mit dem Oberflächenwasser gemischt wird. Biologische Filter oder Zeolithe könnten für die Bedingungen in Delhi angemessene Optionen darstellen.

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# Abbreviations

| | |
|---|---|
| BF | Bank filtration, sometimes also referred to as riverbank filtration (RBF) in case the surface water body is a river |
| BOD | Biological oxygen demand |
| CEC | Cation exchange capacity |
| CGWB | Central Ground Water Board (Belongs to the Ministry of Water Resource, Government of India) |
| DJB | Delhi Jal Board (Public water supplier in NCT Delhi) |
| COD | Chemical oxygen demand |
| DO | Dissolved oxygen |
| DOC | Dissolved organic carbon |
| EC | Electric conductivity |
| GCW | Groundwater circulation well |
| K | hydraulic conductivity in [m/s] or [m/d] |
| LOI | Loss on ignition |
| MAR | Managed aquifer recharge |
| masl | Meter above sea level |
| mbgl | Meter below ground level |
| MGD | Million gallons per day. This unit commonly used in Delhi for water measurements. One imperial gallon corresponds to 4.55 L. |
| NCT | National Capital Territory |
| $n_e$ | Effective porosity (specific yield) |
| ORP | Oxidation-reduction potential |
| PRB | Permeable reactive barrier |
| RBF | see BF |
| RO | Reverse osmosis |
| STP | Sewage treatment plant |
| TKN | Total Kjeldahl nitrogen |
| WTP | Water treatment plant |

Abbreviated references (e.g. CPCB 2006) are spelled out in the references section (p. 137).

# Chapter 1

# Introduction

## 1.1 DELHI – POPULATION DEVELOPMENT, WATER SUPPLY AND SEWAGE TREATMENT

The National Capital Territory (NCT) of Delhi is a union territory situated in northern India on the banks of the Yamuna River. The NCT covers an area of almost 1500 $km^2$ and incorporates the capital New Delhi, surrounding cities and towns as well as nearby villages and rural areas, which are decreasing in number and size owing to the rapid population growth and urbanization. According to the 2011 census, about 16.8 million people are permanently resident in the area of the NCT, of which only 0.4 million are rural population (Census of India 2011a). In 1951, NCT Delhi had a population of 1.7 million people, of which 0.3 million lived in the rural areas (Town and Country Planning Organisation 2007). The predicted population in the year 2021 is 20 million people (National Capital Region Planning Board 2013). The population development of NCT Delhi is shown in Table 1.1.

The Delhi Metropolitan Area (DMA), which has been renamed Central National Capital Region (CNCR) in 2001, includes the NCT as well as neighboring cities such as Ghaziabad, Noida, Faridabad and Gurgaon, which already are indistinguishable from the metropolis Delhi (Fig. 1.1). The CNCR currently has a population of about 22 million people and is estimated to have a population of 31 million in the year 2021 (National Capital Region Planning Board 2013). Thus, it will continue to be the second largest urban agglomeration in the world after Tokyo (United Nations 2014).

**Table 1.1** Population development in NCT Delhi and Ghaziabad, Noida, Faridabad and Gurgaon (summarized as contiguous cities).

| Year | 1951 | 1971 | 1991 | 2001 | 2011 |
|---|---|---|---|---|---|
| Population NCT Delhi (in millions) | 1.7* | 4.1* | 8.4* | 13.9* | 16.8** |
| Population contiguous cities (in millions) | 0.1* | 0.3* | 1.4* | 2.6* | 5.3*** |

*Town and Country Planning Organisation (2007) **Census of India (2011a) ***Census of India (2011b, c)

The National Capital Region (NCR) comprises the CNCR as well as other areas of the states Haryana, Uttar Pradesh and Rajasthan. It was put in place to reduce the population growth in the Delhi metropolis, mainly through the stimulation of migration to other cities in the region (National Capital Region Planning Board 2013).

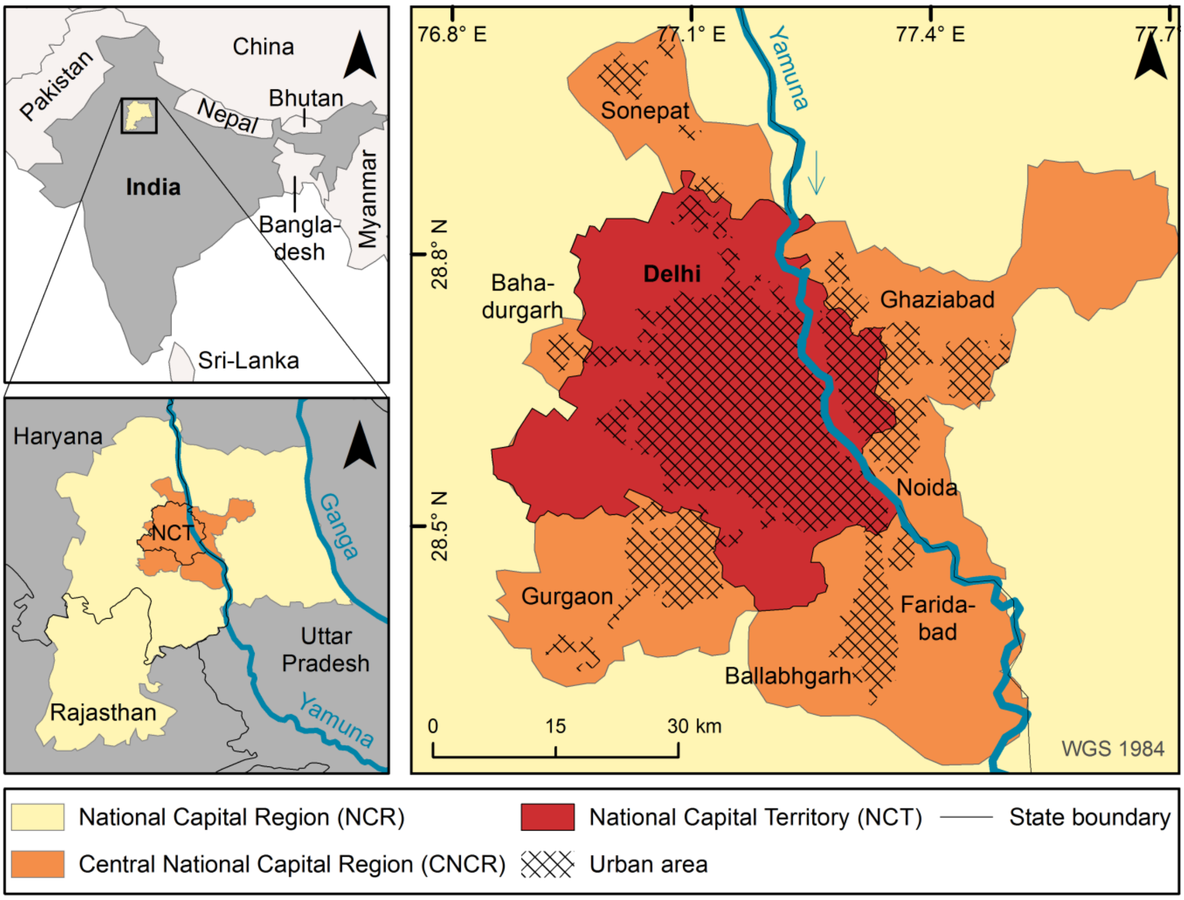

**Fig. 1.1** Location of Delhi and overview of the administrative units. Data compiled from Natural Earth (2011), Town and Country Planning Organisation (2007), National Capital Region Planning Board (2013).

In the mid-2000s, the annual water demand of the NCT Delhi was estimated to be $1435\times10^6$ m$^3$ (865 million gallons per day − MGD), of which the water supplier Delhi Jal Board (DJB) supplied $1044\times10^6$ m$^3$ (630 MGD) (CGWB 2006b, p.i, Chatterjee et al. 2009). The projected annual water demand for 2021 ranges from $1440\times10^6$ to $2588\times10^6$ m$^3$ (868−1560 MGD), depending on the supply norm and population growth applied for the calculation. The DJB would be able to provide between $1352\times10^6$ and $1990\times10^6$ m$^3$ per year (815−1200 MGD) depending on different water resources scenarios (DJB 2012, p.25). The water supplied originates to the major part from the Yamuna River and Ganga River in the neighboring states Haryana and Uttar Pradesh and from the Bhakra Storage, Satluj River, in Himachal Pradesh (DJB 2012, p.22). In January−February 2015, the DJB produced about $3.64\times10^6$ m$^3$ per day (800 MGD). Of this quantity, $136\times10^3$ to $182\times10^3$ m$^3$ (30–40 MGD) were recycled process wastewater from the water treatment plants (WTPs), $364\times10^3$ m$^3$ (80 MGD) were groundwater, and the remaining quantity was Yamuna and Ganga water (DJB 2015). Although groundwater only has a share of about 10 % in the DJBs water supply, the actual groundwater abstraction is probably higher, as many households, industries and farms have private bore wells that they use in addition to the public water supply. In their Hydrogeological Framework and Management Plan for NCT Delhi, the Central Ground Water Board (CGWB) estimated the groundwater abstraction in Delhi to be $480\times10^6$ m$^3$ per year (289 MGD) (CGWB 2006b). At the same time, the replenishable groundwater resources are estimated to be only

$280\times10^6$ m$^3$ per year (169 MGD) according to the Central Ground Water Board (CGWB 2006b, p.64-65).

In 2006, the DJB was equipped to treat $1145\times10^6$ m$^3$ per year (690 MGD) of surface water in 11 water treatment plants (WTPs) and an additional $166\times10^6$ m$^3$ per year (100 MGD) of groundwater (Department of Urban Development 2006, p.8.2-8.3). Two more WTPs are currently under construction or completed (Planning Department 2011, p.20) increasing the total supply capacity of the DJB to $1418\times10^6$ m$^3$ (855 MGD) in 2011 (Planning Department 2011, p.23). The treatment plants are of different ages and designed for capacities between 909000 m$^3$/d (200 MGD) in Haiderpur I & II (Department of Urban Development 2006, p.8.7) and 4545 m$^3$/d (1 MGD) in the Commonwealth Games Village WTP (Comptroller and Auditor General of India 2012, p.379-382). The technologies vary from conventional treatment with a sequence of coagulant addition, coagulation, flocculation, sedimentation, filtration and disinfection by chlorination (CPCB year unknown, p.81) to the use of membrane ultra-filtration and UV-disinfection at the Commonwealth Games Village (VA TECH WABAG GmbH year unknown). Due to ageing infrastructure, a discontinuous water supply and subsequent storage of water in 500–1000 L tanks, as well as the additional use of private wells, the water used by households is often not of drinking water quality (Dasgupta 2004, Walsh et al. 2011). The use of filter systems in homes or the purchase of bottled drinking water is, therefore, the common practice. However, three pilot projects for a 24/7 water supply are currently in progress, and an improvement of water supply can be expected.

Sewage treatment capacity and quantity have improved considerably over the past years. In 2006, the sewage generated was estimated to be $2.98\times10^6$ m$^3$/d (656 MGD), while sewage treatment plants (STPs) with a total capacity of $1.44\times10^6$ m$^3$/d (317 MGD) operated at 17 locations in Delhi (Jamwal and Mittal 2010). However, due to problems with the sewerage network, many STPs were not always operating at full capacity (Jamwal et al. 2011), meaning that less than 50 % of the sewage generated was treated while the rest was discharged into the river untreated. Today the sewage generated is $3.09\times10^6$ m$^3$/d (680 MGD) according to the Delhi Jal Board, who estimated the amount to be 80 % of the water supplied. STPs can be found at 21 locations, and the total treatment capacity was increased to $2.70\times10^6$ m$^3$/d (595 MGD) (DJB 2014). However, the Delhi Jal Board does not consider the amount of water from private bore wells in their calculations, which was estimated to be $480\times10^6$ m$^3$ per year ($1.32\times10^6$ m$^3$/d, 289 MGD). Applying the calculation of the DJB, another $384\times10^6$ m$^3$ per year (231 MGD) would have to be treated. Thus between 65 and 87 % of sewage generated is presently treated, depending on the estimations of water supply.

## 1.2 GEOLOGY, HYDROGEOLOGY AND HYDROLOGY OF THE REGION

### Overview

Delhi is located in the Indo-Gangetic plain, an alluvial plain that stretches from the Indus in Pakistan to the Brahmaputra valley in the Indian state Assam. It is part of the Himalayan foreland basin (Singh 1996) and is bound by the Himalayan foothills in the North and by the Precambrian cratonic provinces of the Indian peninsula in the South. The Shillong Plateau and the northern Indo-Burman ranges (Naga and Miso Hills) mark the Eastern boundaries, and the Kirthar-Sulaiman ranges in Pakistan constitute the western boundary (Fig. 1.2). The Himalayas are the primary source of the plain's major rivers and alluvial sediments while the Indian Peninsula in the South does not contribute significantly to runoff and sedimentary deposit (Geddes 1960, Singh 1996).

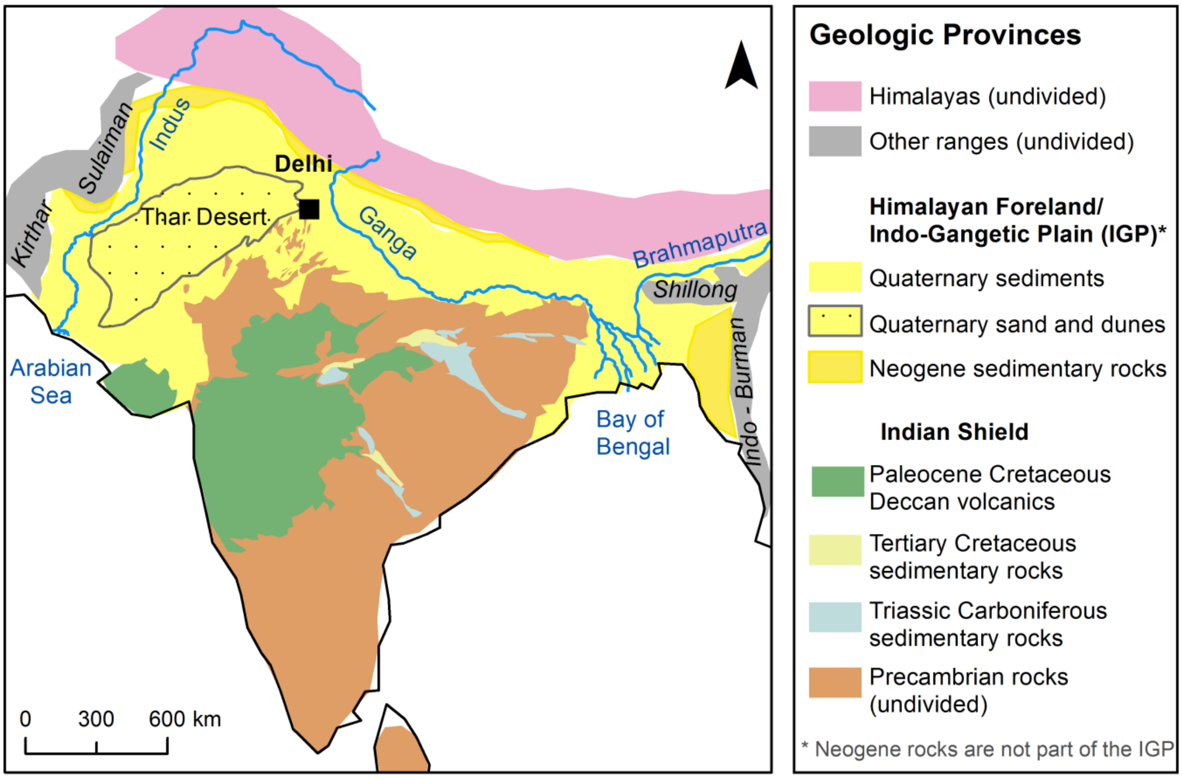

**Fig. 1.2** Simplified overview of the geologic provinces in South Asia. Delhi is located in the center of the Indo-Gangetic Plain at the Eastern edge of the Thar Desert. Modified after Wandrey and Law (1997).

The plain can be divided into the Indus basin in the West, discharging into the Arabian Sea and the Ganga-Brahmaputra Basin in the eastern part discharging into the Bay of Bengal. Although the water-divide between the two basins was formerly shifting due to changing river courses (Geddes 1960), there is no evidence for a connection between the Indus system and the Ganga system in the Holocene (Srivastava et al. 2006), except for artificial connections through irrigation systems (Geddes 1960). The current water-divide is formed by the Delhi Ridge, also known as the Delhi-Haridwar Ridge or the Aravalli-Delhi Ridge, a basement high formed by Proterozoic metamorphic basement rocks (Singh 1996, Srivastava et al. 2011). The origin of the Thar Desert on the eastern side of the Delhi Ridge is much debated; many now extinct rivers used to drain this area (Tripathi and Rajamani 1999).

## Geology

In Delhi the northernmost part of the exposed Aravalli ranges or Aravalli-Delhi surface massif can be found: Proterozoic quartzites form several NE-SW trending ridges in the south of the city (Singh 1996, Tripathi and Rajamani 2003), see Fig. 1.3. In the rest of the city area, the basement is covered by alluvial sediments of up to 300 m thickness (Chatterjee et al. 2009), depending on the depth of the basement (Shekhar and Prasad 2009). The alluvial cover can be divided into two units, the Older Alluvium of Pleistocene age and the Holocene Newer Alluvium overlying the Older Alluvium along the Yamuna River (Geological Survey of India 2006). The Older Alluvium comprises polycyclic sequences of sand and silt-clay (Kazim et al. 2008) while the Newer Alluvium consists mainly of medium to coarsely grained sands, sometimes mixed with clay, silt and gravel (Shekhar and Prasad 2009). The distinction between Older and Newer Alluvium is typical for the entire Gangetic Plain. While the Older Alluvium makes up the higher interfluves areas, the Newer Alluvium consists of the fluvial deposits of the rivers (Singh 1996). Holocene aeolian sediments can be found in the Chhatarpur basin (or Chattarpur basin), a depression in South Delhi surrounded by the hard rock of the Delhi Ridge (Geological Survey of India 2006).

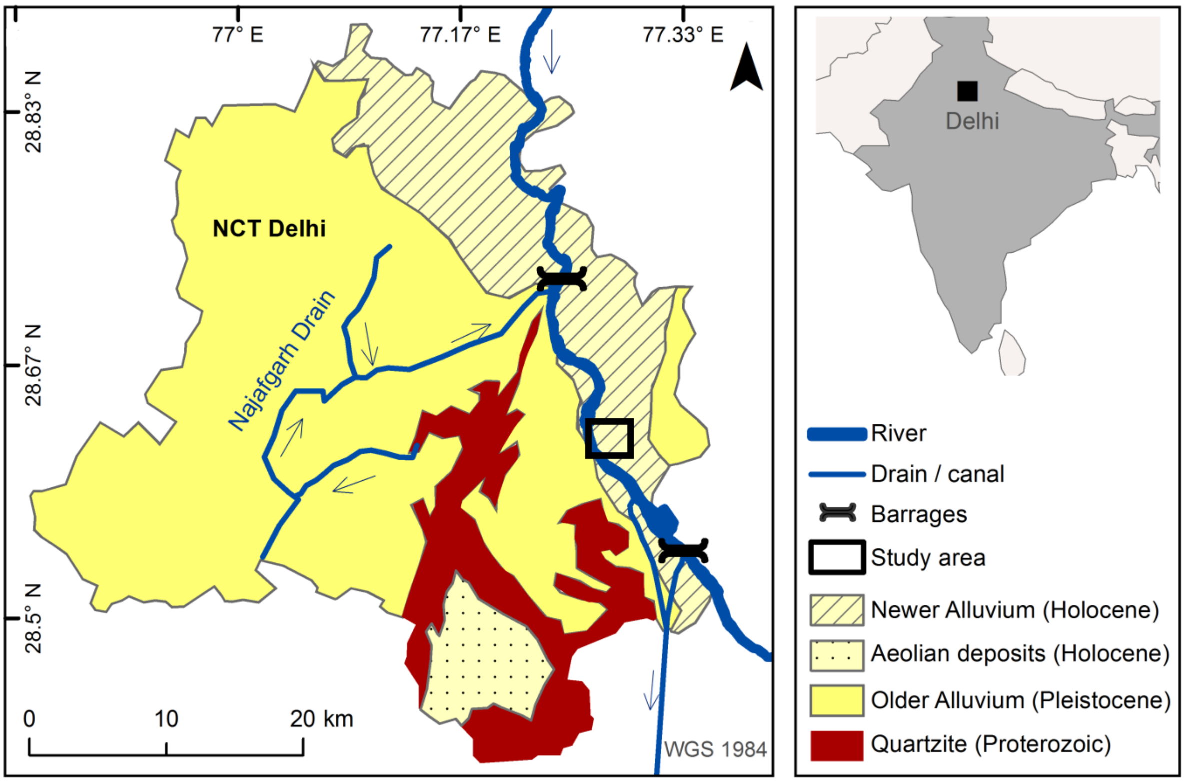

**Fig. 1.3** Geology of NCT Delhi. Modified after Geological Survey of India (2006).

## Hydrogeology

Three hydrogeological units can be discerned, which correspond to the geology: the quartzite, the Older Alluvium and the Newer Alluvium. The overall groundwater potential of the quartzite is limited (Kumar et al. 2006) and strongly varies regionally depending on number and quantity of fractures in the rock. In fractured areas, the ridges act as recharge structures (Chatterjee et al. 2009). The Older Alluvium has several water-bearing horizons made up of fine to coarse grained sand and kankar, which are separated by silt-clay layers. The formation is characterized by low hydraulic conductivities between $3\times10^{-5}$ and $5\times10^{-5}$ m/s (3−4 m/d) (Chatterjee et al. 2009) as secondary carbonates reduce the permeability of the water-bearing horizons (Chaterji and Seth 1961, p.3). Deeper groundwater in this aquifer is saline. The depth of fresh-saline water interface varies widely.

In some parts of the city it is at 22–40 m below ground level (mbgl), at other places it can be found at 70–100 mbgl, and in some parts of the city, fresh water can be found throughout the explored depth (CGWB 2006b, p.ii-iii, 26). An overview of possible sources of the salinity is given in Chapter 2 (State of the Art).

The Newer Alluvium constitutes the aquifer with the highest fresh water potential in Delhi (Kumar et al. 2006). It is commonly referred to as the floodplain aquifer. The thickness of the aquifer varies from 70 m in the north to 30–40 m in the southern part of the floodplain according to Shekhar and Prasad (2009). However, Kazim et al. (2008, p.13) only reported a thickness of 14 m in central Delhi. The aquifer is unconfined, and depth to water is very shallow (between 2.5–7.0 mbgl) (CGWB 2006b, p.45). Groundwater level fluctuations (pre−post monsoon or compared to the same time the previous year or compared to the decadal mean) are only moderate in the floodplain aquifer (between 0.5 and 1.5 m - CGWB 2006b, p.45, ±2 m - CGWB 2012, maps p.46−50). The hydraulic conductivities of this unit vary between 13–60 m/day ($2\times10^{-4}$ to $7\times10^{-4}$ m/s) (CGWB 2006b, p.45, Chatterjee et al. 2009).

The largest well field used for Delhi's water supply is located in the northernmost part of NCT Delhi at Palla village on the west bank of the Yamuna River. It comprises about 80 tube wells and five radial collector wells (Ranney wells) constructed on the floodplain (Mutiyar et al. 2011), making use of the principle of riverbank filtration (RBF) (Lorenzen et al. 2010, Mutiyar et al. 2013). In addition, the DJB operates numerous tube wells and some 11 (DWSSP 2004) or 16 (DJB 2012) Ranney wells on the floodplain in the central part of the city, drawing water from the floodplain aquifer. Although these wells were probably not specifically designed for RBF, it can be assumed that the wells located on the East bank of the river, where losing stream conditions prevail, draw high shares of bank filtrate (Lorenzen et al. 2010, Kumar et al. 2011). The recorded discharge of the wells in the floodplain aquifer is about 150–300 $m^3$/h according to Chatterjee et al. (2009), while the Central Groundwater Board reports a discharge between 18 and 144 $m^3$/h for tube wells located on the Yamuna floodplain (CGWB 2012).

### Hydrology

The Yamuna River flows through Delhi in north-southerly direction. The Yamuna is the largest tributary of the Ganga River. The main stream of the Yamuna originates from the Yamunotri glacier in the lower Himalayas at about 6300 masl. After 120 km, it enters the Indo-Gangetic Plain and after a total of 1376 km it meets the Ganga at Allahabad (CPCB 2006, p.1). The river water is mainly used for drinking water supply and irrigation; several barrages dam the water to divert it into canals or to WTPs.

Three main barrages divide the river into four segments (Fig. 1.4). The first, 157 km long segment is the part of the river from the source to Hathnikund barrage, where the Yamuna water is diverted into Western and Eastern Yamuna Canals. The second segment is 224 km long and reaches from Hathnikund barrage to Wazirabad barrage right upstream Delhi, where water is stored in the Wazirabad reservoir for the city's water supply. The third segment is the 22 km long Delhi segment between Wazirabad barrage and Okhla barrage in southern Delhi, at which water is diverted to the

Agra Canal. The fourth segment is the 973 km long section from Okhla barrage to Allahabad (CPCB 2006, p.7–9).

80 % of the river flow occurs during monsoon season (July – September), which is the only time when the barrages are open. In this time, almost the entire sediment load is carried by the river (Jha et al. 1988). During the rest of the year the barrages are closed: No or little water passes through, and the segments receive water only from their sub-catchment areas and from various drains and canals. This includes the treated and untreated sewage water from the urban centers along the river. In the Delhi segment, treated and untreated sewage water is discharged into the river through 17 drains. Furthermore, this segment receives water from the Upper Ganga Canal and the Western Yamuna Canal through the Hindon cut canal and the Najafgarh drain (CPCB 2006, p.7–9).

In the Delhi stretch, the Yamuna River frequently changes the channel position and geometry of the riverbed (Khan and Bajpai 2014). Numerous dykes and embankments were constructed to control the course of the river within the city. However, the river still can shift within certain limits.

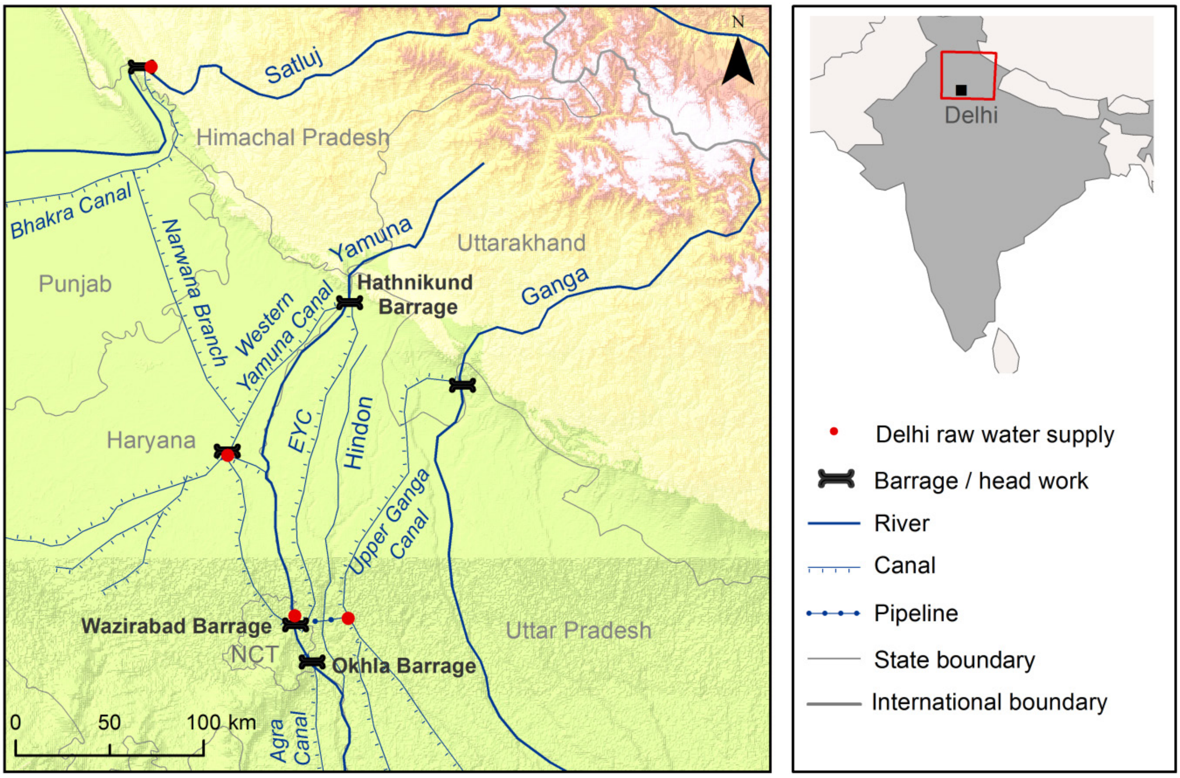

**Fig. 1.4** Hydrology of the area and raw water supply of Delhi (WYC: Western Yamuna Canal, EYC: Eastern Yamuna Canal, UGC: Upper Ganga Canal). Background image: USGS (2004), information compiled from National Atlas and Thematic Mapping Organisation (1979), CPCB (2006, p.6–9), Department of Urban Development (2006, p.8.3).

# 1.3 APPLICATION OF BANK FILTRATION IN AQUIFERS AFFECTED BY AMMONIUM0F[1]

## 1.3.1 Nitrogen – Occurrence and Effects

In aqueous solution, nitrogen is a redox-sensitive parameter that can occur in different species. The most common forms of nitrogen in the water-soil environment are, in order of decreasing oxidation state (Stumm and Morgan 1996, Metcalf & Eddy Inc., Inc. 2014):

- Nitrate ($NO_3^-$, +V)
- Nitrite ($NO_2^-$, +III)
- Nitrogen gas ($N_2$, 0)
- Ammonia and ammonium ($NH_3$ and $NH_4^+$, both −III)
- Organic nitrogen ($N_{org}$, mostly –III)

Whether the reduced form of nitrogen occurs as un-ionized ammonia ($NH_3$) or in the form of ammonium ions ($NH_4^+$) depends on the temperature and, to a stronger extent, the pH of the solution (Table 1.2).

**Table 1.2** Proportions of $NH_4^+$ and $NH_3$ at different pH values (Metcalf & Eddy, Inc. 2014, p.94).

| $NH_3 + H_2O$ | ↔ | $NH_4^+ + HO^-$ | pH | Temperature |
|---|---|---|---|---|
| 10 % | | 90 % | 8.3 | 20°C |
| 50 % | | 50% | 9.25 | 20°C |

At pH and temperature conditions commonly found in natural waters, $NH_4^+$ is the predominant species (Hem 2005). Sometimes the term “total ammonia” is being used referring to the sum of ionized and un-ionized ammonia.

Nitrogen pollution can cause problems such as eutrophication of surface water bodies (Howarth and Marino 2006), which can lead to toxic algal blooms or decreasing dissolved oxygen concentrations and related issues such as a decline in animal and plant diversity. Furthermore, ammonia ($NH_3$, un-ionized) is toxic for aquatic species (Randall and Tsui 2002), but not for humans at low concentrations (GESTIS Substance Database 2014). $NO_2^-$ is also extremely toxic to fish or other aquatic species (Metcalf & Eddy Inc., Inc. 2014). For humans, excessive nitrogen intake in the form of $NO_3^-$ or $NO_2^-$ through water can result in diarrhea or methaemoglobinaemia (blue-baby syndrome) in infants (Ward et al. 2005). When chlorination is used for the disinfection of drinking water, the presence of $NH_4^+$ in raw water causes the formation of chloramines even at low concentrations (Weil and Morris 1949). Carcinogenic products such as N-nitrosodimethylamine can be formed by reactions involving mono-chloramines (Choi and Valentine 2002). Furthermore,

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[1] Sections 1.3.1–1.3.5 were published in: Groeschke, M., Frommen, T., Grützmacher, G., Schneider, M., Sehgal, D. (2015) Application of Bank Filtration in Aquifers Affected by Ammonium – The Delhi Example. In: Wintgens, T., Anders, N., Elango, L., Asolekar, R. S. (Eds.) Natural Water Treatment Systems for Safe and Sustainable Water Supply in the Indian Context: Saph Pani. IWA Publishing, pp 57-77

higher chlorine doses are necessary to achieve required minimum residual chlorine concentration at the outlet of the WTPs and in the distribution system (Duong et al. 2003).

### 1.3.2 Nitrogen in Drinking Water - Guideline Values

Guideline values for nitrogen species given in the Indian standard for drinking water (IS 10500: 2012) and the WHO drinking water quality guidelines (WHO 2011) are compared in Table 1.3. The WHO did not establish a guideline value for total ammonia because it usually occurs in drinking water at concentrations well below those of health concern. Because the WHO includes the non-ionized form $NH_3$ and the ionized form $NH_4^+$ in their definition of ammonia, it is assumed that this is also the case in the Indian Standard BIS 10500, although it is not further defined.

**Table 1.3** Guideline values for nitrogen species in drinking water.

| Parameter | Unit | BIS 10500:2012 (India) | WHO (2011) |
|---|---|---|---|
| Nitrate (as $NO_3^-$) | mg/L | 45 | 50 |
| Nitrite (as $NO_2^-$) | mg/L | No guideline value | 3 |
| Ammonia (as $NH_3$-N and $NH_4^+$-N)* | mg/L | 0.05 | No guideline value |

* Definition of WHO, not specified in BIS 10500

### 1.3.3 Nitrogen in Surface Water Bodies

In surface water bodies, nitrogen concentrations depend on several factors, mainly land use, sewage disposal and the water balance of the water body, as dilution strongly affects the pollutant concentrations. In Europe, agricultural fertilizers are the primary source of nitrogen in surface waters and the prevailing nitrogen species is $NO_3^-$. In large rivers, for example, median $NO_3$-N concentrations are around 3 mg/L while $NH_4^+$-N concentrations range between 0.1 and 0.3 mg/L (EEA 2001a). In urban agglomerations in developing or newly industrialized countries nitrogen loads in surface water bodies are expected to be substantially higher: Nitrogen contamination of surface water through untreated or partially treated domestic sewage water is a concern in many of these countries. According to Corcoran et al. (2010), up to 90 % of sewage water in developing or newly industrialized countries is not collected or treated but discharged directly into rivers, lakes and coastal areas or leached into the subsoil. In the Asia-Pacific region alone, this amounts to approximately $150–250\times10^6$ $m^3/d$ of untreated (domestic) wastewater from urban areas released into the environment untreated (UN World Water Assessment Programme 2012). However, data on total inorganic nitrogen concentrations ($NH_4^+$, $NO_2^-$, $NO_3^-$) is scarce, as most studies on river water quality in Asian megacities only report concentrations of $NO_3^-$ and $NO_2^-$, e.g. Sikder et al. (2013) and Kido et al. (2009). But because of the high chemical oxygen demand (COD) in sewage contaminated rivers, the predominant form of inorganic nitrogen is expected to be $NH_4^+$.

### 1.3.4 Nitrogen in Sewage Water

In sewage water about 60–70 % of the nitrogen is present in the form of $NH_3/NH_4^+$, depending on the pH of the solution while the remaining 30–40 % are mostly found as biodegradable or non-biodegradable organic nitrogen (Metcalf & Eddy Inc., Inc. 2014, p.712). Fresh domestic wastewater usually contains no more than 1 % $NO_3^-$ and $NO_2^-$ (Eckenfelder and Argaman 1991, p.3) before it is aerated in the nitrification step at STPs. Total nitrogen concentrations in wastewater are highly variable depending on the diet of the population (Pescod 1992, Patterson 2003) and the per capita wastewater flow-rate (Eckenfelder and Argaman 1991, p.3). Concentrations between 20 and 85 mg/L are reported as an average for typical domestic wastewater in (Metcalf & Eddy Inc., Inc. 2014) and maximum concentrations can be much higher (sometimes above 150 mg/L − e.g. Ammary 2007). The main source of nitrogen in wastewater is urea, which is contained in urine and is degraded by biological hydrolysis (Mobley and Hausinger 1989), see Table 1.4.

**Table 1.4** Reactions of urea in the environment (Mobley and Hausinger 1989).

| **Reactant** | | **Product** | **Explanation** |
|---|---|---|---|
| *urea + water* | | *ammonia + carbamate* | Hydrolysis of urea |
| $(NH_2)_2CO + H_2O$ | $^*\rightarrow$ | $NH_3 + H_2NCOOH$ | * Naturally occurring enzyme urease catalyzes reaction |
| *carbamate + water* | | *ammonia + carbonic acid* | Hydrolysis of carbamate |
| $H_2NCOOH + H_2O$ | → | $NH_3 + H_2CO_3$ | |
| *carbonic acid* | | *hydrogen ion + bicarbonate* | Dissociation of carbonic acid |
| $H_2CO_3$ | → | $H^+ + HCO_3^-$ | Increase in pH |
| ammonia + water | | *ammonium + hydroxide* | Ammonia molecules equilibrate with water |
| $2NH_3 + 2H_2O$ | → | $2NH_4^+ + 2OH^-$ | |

Other sources of organic nitrogen are feces; grey water from laundry and personal washing is a source of $NH_3/NH_4^+$ (Patterson 2003). Products like toilet paper have the lowest nitrogen load contribution (Tjandraatmadja et al. 2010). In countries without a regular waste disposal system, garbage disposal in wastewater is another significant source of organic nitrogen.

### 1.3.5 Reactions of Nitrogen in Aquatic Systems

Different biochemical and physicochemical reactions (Fig. 1.5) affect the speciation of nitrogen in the aquifer (Böhlke et al. 2006). These reactions depend on the conditions in the aquifer, e.g. the availability of electron donors such as particulate or dissolved organic matter (for the reduction of nitrogen species) or the availability of electron acceptors such as oxygen (for the oxidation of nitrogen species). Because both aerobic and anaerobic oxidation and reduction of nitrogen are biologically mediated, the biological community in the aquifer plays an important role. Furthermore, sediment characteristics, e.g. clay mineral fraction and organic matter content, have an influence on the nitrogen balance of an aquifer.

The nitrogen cycle, or parts of it, is studied by different scientific disciplines, e.g. soil scientists, hydrologists, microbiologists. Sometimes differences in terminology exist regarding one and the same process, or one term is used to describe two different processes. The terminology used in this study is defined in Fig. 1.5 and Table 1.5.

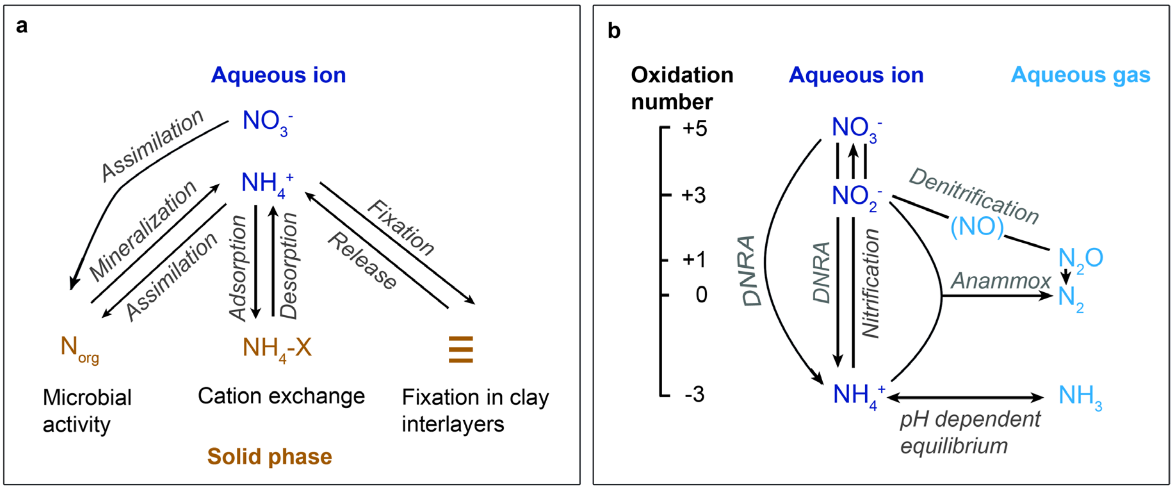

**Fig. 1.5** (a) Interactions of aqueous nitrogen ions with the sediment matrix and organic matter ($N_{org}$: organic nitrogen). (b) Biochemical and physicochemical reactions and processes that can occur in groundwater. Modified after Böhlke et al. (2006) and van de Leemput et al. (2011).

**Table 1.5** Overview of possible processes and reactions of nitrogen species in an aquifer.

| Process | Description | References |
|---|---|---|
| Assimilation | Incorporation of inorganic nitrogen into cell material. | Kanamori et al. (1989), Middelburg and Nieuwenhuize (2000), Glessner and Roy (2009), Moreno-Vivian et al. (2011) |
| Mineralization | Conversion of organic nitrogen to inorganic forms by soil microbes. Sometimes referred to as ammonification. | Crohn (2004), Glessner and Roy (2009), Szymczak et al. (2010) |
| Cation exchange | Adsorption and desorption of $NH_4^+$ onto negatively charged sites of clay minerals and organic matter. | Ceazan et al. (1989) |
| Fixation of ammonium | $NH_4^+$ may be bound in interlayers of clay minerals. This $NH_4^+$ cannot be recovered by methods of cation exchange but can be released again slowly under certain pH and redox conditions ("non-exchangeable ammonium"). | Osborne (1976), Schneiders and Scherer (1998), Nieder et al. (2011) |
| Nitrification | Aerobic ammonium oxidation to $NO_2^-$ and then to $NO_3^-$: Use of $O_2$ as the electron acceptor. | DeSimone and Howes (1996) |
| Anammox | Anaerobic ammonium oxidation: Use of $NO_3^-$ or $NO_2^-$ as an electron acceptor. | van de Graaf et al. (1995), Thamdrup and Dalsgaard (2002), Clark et al. (2008), Moore et al. (2011) |
| Denitrification | Reduction of nitrate to $N_2$ gas through a series of intermediate products. | Vidon and Hill (2004), Wunderlich et al. (2012) |
| DNRA | Dissimilatory $NO_3^-$ or $NO_2^-$ reduction to $NH_4^+$. Is thought to occur when $NO_3^-$ concentrations are high, and DOC concentrations are low. Sometimes also referred to as (nitrate) ammonification. | Brunet and Garcia-Gil (1996), van de Leemput et al. (2011), Rütting et al. (2011), Giblin et al. (2013), Algar and Vallino (2014) |

## 1.4 BACKGROUND, SCOPE AND PURPOSE OF THE DISSERTATION

The present work was conducted in the frame of the EU-funded project Saph Pani aiming at the enhancement of natural water treatment systems and treatment methods for a safe and sustainable water supply in urban areas in India. 20 project partners from India, Europe, Sri Lanka and Australia were involved in the project, working on nine study sites throughout the country. The three topics of study were bank filtration (BF), managed aquifer recharge (MAR), and constructed wetlands. The methods are not new and much research on them has been done in the past (e.g. Thomas et al. 1995, Bouwer 2002, Grünheid et al. 2005). However, the aim of the project was to study the use of the methods in the Indian context to evaluate their efficiency under local conditions and to optimize their use under the given circumstances. This thesis presents the results of the Delhi case study about the use of BF at a highly sewage contaminated river with a focus on nitrogen species.

At the studied well field sewage contamination leads to elevated concentrations of the reduced nitrogen species $NH_4^+$ in the river water (see section 1.3.4 – Nitrogen in Sewage Water). Due to losing stream conditions (see section 1.2 – Hydrogeology) this $NH_4^+$-rich river water infiltrates into the aquifer leading to elevated $NH_4^+$ concentrations in the groundwater, which is abstracted for drinking water purposes. In addition, agricultural return flow might be another source of $NH_4^+$ at the field site (Lorenzen et al. 2010). Complex biochemical and physicochemical processes determine the speciation of nitrogen in the aquifer (section 1.3.5) and can therefore strongly influence $NH_4^+$ concentrations. Furthermore, $NH_4^+$ does not move with groundwater flow velocity but is highly retarded in the aquifer due to cation exchange (e.g. Ceazan et al. 1989), which strongly depends on sediment characteristics. An assessment of the $NH_4^+$ contamination and predictions about its future development at the well field could therefore not be made in previous studies and were the goal of this work. The aim of the study was to:

- Assess the extent of the $NH_4^+$ contamination at the studied well field
- Understand the role of the unsaturated zone in the $NH_4^+$ contamination
- Explain the transport of $NH_4^+$ in the different sediments of the saturated zone
- Understand the transport of $NH_4^+$ at field scale
- Develop recommendations for an adapted treatment or remediation strategy to be able to further use the aquifer for the city's water supply.

## 1.5 ARRANGEMENT OF TOPICS

### Chapter 1: Introduction

This chapter gives an overview of Delhi, including the population development, water supply and sewage situation, geology and hydrogeology. The section 1.3 "Application of Bank Filtration in Aquifers Affected by Ammonium" contains section 4.2 (Nitrogen) of Chapter 4 in the Saph Pani Handbook[2]. The cited section about nitrogen was written entirely by me. However, I have profited from advice from and proofreading by my co-authors.

### Chapter 2: State of the Art

This work is not the first study about the hydrogeology of Delhi, the geology and hydrogeology of the central Delhi field site or about transport of $NH_4^+$. This chapter gives an overview of previous studies and the available information. It depicts the basis on which the new data, insights and conclusions described in the subsequent chapters were obtained.

### Chapter 3: Local Hydrogeology and Assessment of Ammonium Contamination at an RBF Site in Central Delhi

In this chapter, new insights about the geology and hydrogeology of the field site are described. A detailed conceptual model of the field site was set up, incorporating data obtained from six drillings conducted at distances between 35 m and 550 m to the current river bank, sediment analyses, water table measurements, and seven water sampling campaigns with focus on nitrogen species. The Yamuna River is identified as the primary source of the contamination. Existing ideas about the nitrogen distribution at the field site are revised.

Colleagues and students made the following contributions to this chapter: Vikas Gupta, Shams Ul Haq and Theresa Frommen conducted the field work together with me. The drillings were carried out by subcontractors under my supervision. The sediment analyses have been performed to a large part by Mario Eybing in the scope of his Bachelor thesis (see Appendix 1).

### Chapter 4: Characterization of the Unsaturated Zone and Influence of Agricultural Activity on the Ammonium Contamination[3]

In this chapter, the potential influence of irrigation return flow on the $NH_4^+$ contamination was studied. Data from seven shallow drillings at distances between 5 and 675 m to the riverbank was evaluated. Sediment analyses of 20 samples reveal that the floodplain is covered by alluvial loam of

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[2] Groeschke, M., Frommen, T., Grützmacher, G., Schneider, M., Sehgal, D. (2015) Application of Bank Filtration in Aquifers Affected by Ammonium – The Delhi Example. In: Wintgens, T., Anders, N., Elango, L., Asolekar, R. S. (Eds.) Natural Water Treatment Systems for Safe and Sustainable Water Supply in the Indian Context: Saph Pani. IWA Publishing, pp 57-77

[3] Groeschke M., Kumar P., Winkler A., Grützmacher G., Schneider M. (2016) The role of agricultural activity for ammonium contamination at a riverbank filtration site in central Delhi (India). Environmental Earth Sciences 75(2):1-14. doi:10.1007/s12665-015-4977-3

varying thickness underlain by fine sand. Low hydraulic conductivities therefore characterize the unsaturated zone. Laboratory column experiments with two sediment samples of the unsaturated zone showed that degradation or fixation of $NH_4^+$ occurs to an extent that can balance the nitrogen input from agricultural activity. Irrigation return flow, therefore, cannot be viewed as a significant additional source of the $NH_4^+$ contamination and does not have to be considered in a field scale model.

As the first author, I have written the entire manuscript. I am grateful for the discussions with and the proofreading by my co-authors. I carried out the field work (especially the shallow drillings) with Christoph Sprenger, Sajil Kumar and Vikas Gupta. Sajil Kumar furthermore conducted a large part of the sediment analyses at the Freie Universität Berlin. I have planned and designed the column experiments, but the laboratory work was carried out together with Theresa Frommen.

### Chapter 5: The Saturated Zone: Transport of Ammonium in Alluvial Sediments – Column Experiments and Reactive Transport Modeling

Laboratory column experiments were conducted with six sediment samples to understand the transport and fate of $NH_4^+$ in the different lithological units of the saturated zone (described in Chapter 3). The experimental data were reproduced with a reactive transport model incorporating cation exchange with adapted selectivity coefficients. This chapter describes the methodology and results of the experiments, the set-up and results of a non-reactive transport model used to determine transport parameters in the sediments and the reactive transport modeling. Results of detailed sediment analyses (organic matter, carbonate content, cation exchange capacity) of the six samples are also described along with the adapted selectivity coefficients.

This chapter was originally written as a section of Saph Pani Deliverable D5.3[4]. I am responsible for the content of the chapter and have written the entire section. I was also responsible for the design of the column experiments and the modeling. However, the following contributions were made by the co-authors: Theresa Frommen conducted about half of the laboratory column work. Furthermore, she carried out the detailed error analyses in the frame of her Master thesis (see Appendix 1). Enrico Hamann's contributions include numerous discussions with me about the modeling as well as critical reviews of the section. The chapter has profited from the advice from Gesche Grützmacher and Michael Schneider. I have revised and improved some sections of the original manuscript regarding language, structure and figures and a section about error analysis was added. However, the content of the chapter wasn't altered.

Furthermore, Laura Krömer helped with some of the column experiments in the frame of her Bachelor thesis (see Appendix 1) and Mario Eybing conducted some of the sediment analyses. Dietrich Lange constructed the laboratory columns.

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[4] Groeschke, M., Frommen, T., Hamann, E., Grützmacher, G., Schneider, M. (2014): Transport of Ammonium in Porous Media – Column Experiments with Alluvial Sediments and Reactive Transport Modeling (In: Synthesis of modeling, monitoring and optimising natural treatment systems in India. Saph Pani Deliverable D 5.3)

### Chapter 6: Field Site Modeling: How long will the Ammonium Contamination Prevail

Simple 2D flow models of the field site were set up to understand better the hydraulic conditions at the field site. To make estimations of the time an $NH_4^+$ contamination will prevail at the site, 1D flow paths in the sand and the kankar layers were modeled. Section 6.5 about the 1D modeling was presented in Chapter 4 of the Saph Pani Handbook[2]. I am responsible for setting up the models and for writing the text. I am grateful for the discussions with my co-authors and their critical reviews.

### Chapter 7: Remediation and Post-Treatment Strategies

In this chapter an overview of remediation and post-treatment strategies is given, the advantages and disadvantages of the use of the different methods in Delhi are discussed, and recommendations for remediation and treatment strategies are made. The chapter includes parts of the Saph Pani Deliverable D1.3[5] and parts of Chapter 4 of the Saph Pani Handbook[2].

Sections 7.2 and 7.4 were originally part of Saph Pani D1.3. As the person responsible for Deliverable D1.3 (authors are given in alphabetical order), I was in charge of all contents. Dhruv Sehgal and Theresa Frommen contributed to the literature research about remediation and post-treatment strategies and the writing of some parts of the Deliverable (the descriptions of the different methods). Gesche Grützmacher and Michael Schneider critically reviewed D1.3. For this thesis some changes to the original contents of D1.3 were made: The descriptions of the methods in section 7.2 and 7.4 are more concise, and the applicability of the methods in Delhi is discussed in more detail than in the original manuscript.

Section 7.5 contains parts of Chapter 4.4 of the Saph Pani Handbook[2], which were written entirely by me and proofread by my co-authors.

### Chapter 8: Concluding Remarks and Future Perspectives

A synopsis of the study is given in this chapter.

All of the chapters of this thesis support the overall argument. However, each chapter was written in a way that it can also be read on a stand-alone basis.

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[5] Frommen, T., Groeschke, M., Grützmacher, G., Schneider, M., Sehgal, D. (2014): Concept for application of BF in aquifers contaminated with nitrogen species – Delhi as an example for BF at sewage influenced surface waters. Saph Pani Deliverable 1.3.

# Chapter 2

# State of the Art

## 2.1 GROUNDWATER AND SURFACE WATER DATA FROM DELHI

Several hydrogeological and hydrological studies have been previously conducted in Delhi. The results of the studies were published in numerous journal articles (section 2.1.1). In addition, the data from several monitoring programs are regularly published in reports, which are also useful sources of information about the groundwater and surface water situation in Delhi (section 2.1.2).

### 2.1.1 Publications

This section gives an overview of the publications that are available about the groundwater of Delhi or which include scientific data about the Delhi stretch of the Yamuna River. Publications including information about the study site in central Delhi are presented in detail in section 2.2.

**General Hydrogeology and Groundwater Management**

The recharge areas in the city are identified by Kumar et al. (2011), who combined the analysis of isotopic tracers ($^{2}$H, $^{3}$H, $^{18}$O) and the evaluation of hydrological features. While the highlands of the Aravalli rocks are the main area for recharge through precipitation, the area around Najafgarh drain and the floodplain along Yamuna River are the main areas for recharge through infiltration of surface waters. Information given for the western bank of the Yamuna River are contradictory - on the one hand it is identified as a recharge structure, on the other hand, the groundwater flow direction is towards the river indicating gaining stream conditions in that area. Maps of the urban areas in NCT Delhi in 1958 and 2005 illustrate the importance of urbanization as a cause of the complex urban hydrogeology. Building on this, Kumar et al. (2013) further characterize four groundwater zones in Delhi (1) a land-use-change-impacted recharge zone, (2) an agriculturally impacted discharge zone, (3) the ridge recharge zone, and (4) the floodplain recharge zone.

The groundwater recharge in NCT Delhi was estimated by Chatterjee et al. (2009) considering rainfall as well as seepage from canals, ponds and through irrigation return flow. In seven out of nine districts, groundwater abstraction exceeds the recharge. They suggest restricting groundwater abstraction in most areas and recommend the further development of well fields in the Yamuna floodplain. Shekhar et al. (2009) recommend rainwater harvesting and other artificial recharge measures to increase groundwater recharge. Due to the aquifer recharge through river water (losing stream conditions), Shekhar and Prasad (2009) recommend setting up a numerical model to determine maximum abstraction, as the water rights of the lower riparian states also have to be considered. Furthermore, they highlight the need to study the effects of infiltrating highly polluted river water into the aquifer. Shekhar et al. (2015) give detailed suggestions for groundwater management in the North district of Delhi, and the use of the Yamuna floodplain aquifer upstream of Wazirabad barrage plays a significant role. Lorenzen et al. (2010) studied the potential for riverbank filtration at three different locations in Delhi and pointed out the problems that arise in the case of insufficient surface water quality.

The difference between monsoon time with heavy rainfall and the dry non-monsoon time might not only lead to differences in groundwater recharge but also influence groundwater chemistry. Kumar et al. (2006) give an overview of different hydrochemical processes leading to the different groundwater compositions in pre-monsoon and post-monsoon times. Combinations of various processes were found to explain the water compositions (silicate weathering, mineral dissolution, cation exchange, dissolution of kankar, groundwater-surface water interactions). Different processes prevail during pre-monsoon and post-monsoon season.

Most authors present groundwater contour maps (e.g. Kumar et al. 2006, 2011, 2013) or depth to water level maps (Chatterjee et al. 2009), which are all in agreement with each other as well as with the data from the Central Ground Water Board (e.g. CGWB 2012). Dash et al. (2010) undertook a geostatistical approach to produce spatial variability maps of depths to water, EC, $Cl^-$, F and $NO_3^-$ concentrations and came to results that contradict maps published by other authors (e.g. Chatterjee et al. 2009, CGWB 2012).

## Origin of Groundwater Salinity

Saline water can be found at deeper levels in all aquifers in Delhi. The source of the salinity is still not fully understood. Different theories have been presented and discussed: Eriksson (1976) analyzed chloride and bicarbonate data and concludes that the origin of the salinity is mostly airborne, originating from salt proportions in the dust. Das et al. (1988) find this theory insufficient to explain the salinity in different depths and aquifer layers. Instead, the authors present $^2H$ and $^{18}O$ data from which they conclude that the deep saline groundwater is of meteoric origin and has undergone evaporation. They point to problems with sampling because in Delhi deep wells often have additional filter screens at shallow depths to increase the discharge. Although Datta (1990) argued strongly against this conclusion in a comment, he did not offer an alternative explanation. Datta et al. (1996a) attribute high salinity values in the deeper aquifer to mixing with “high salinity groundwater”. It was understood that the authors suggest leaching of salts and transpiration during recharge as possible explanations for the development of those high salinity waters.

Kumar et al. (2009), Lorenzen et al. (2012) and Rao et al. (2013) conducted recent research on the origin of the groundwater salinity in Delhi. According to Kumar et al. (2009), who compared ionic ratios, the salinity is either due to mixing with old saline groundwater (not further defined) or due to the dissolution of surface salts in the soil, but does not originate from evaporative enrichment. Lorenzen et al. (2012) used a combination of methods (multi-level observations, water composition, $Br^-/Cl^-$ ratios). They came to the conclusion that anthropogenic activities disturb the natural hydraulic equilibrium and thus enhance the dissolution of salt stores in the unsaturated zone and in deeper sections of the aquifer, where they were formed during former arid periods. Rao et al. (2013)

conducted isotope studies ($^3H$, $^2H$, $^{18}O$) and conclude that the origins of salinity in the younger groundwater are anthropogenic activities and evaporative enrichment. For the older (and deeper) groundwater, they present a scenario of a salt playa or salt pan, which has developed during the time of deposition of the Older Alluvium and which influences the deeper groundwater.

### Studies Conducted at Palla Well Field

Palla well field is a large well field located in the very northern part of NCT Delhi, on the west bank of Yamuna River, upstream of Wazirabad barrage. Due to its significance for Delhi's water supply, the well field is thoroughly studied. Rao et al. (2007) set up a numerical model to optimize pumping schemes at the Palla well field in northern Delhi, without triggering salt water upconing. Mutiyar et al. (2011) studied the pesticide contents in raw water from bore wells and Ranney wells at the Palla well field. No significant differences between pre-monsoon and post-monsoon concentrations were found. The bore wells water was of better quality in this regard than the Ranney well water, which the authors attribute to the higher gradient induced by the Ranney wells, which prevents the adsorption of pesticides onto the soil matrix or forces the desorption. Furthermore, Mutiyar et al. (2013) compared the microbial quality of Ranney wells and bore wells from the same well field. Here the water quality was better in the pre-monsoon season compared to the post-monsoon season (probably due to land use – cattle manure polluting flood water) and better in bore wells compared to the Ranney wells. This could be because the Ranney wells are shallower than the bore wells and greater distance to the river bank of the bore wells. In their paper about the potential of riverbank filtration in Delhi, Lorenzen et al. (2010) also present data from Palla well field.

### Groundwater Contamination

Besides the issue of highly saline groundwater, nitrate, fluoride and arsenic contamination and antibiotic resistant bacteria in the groundwater are a concern in some parts of the city. Kumar et al. (2009) tried to identify the sources of nitrate pollution (along with the salinity) in Delhi by mapping and looking at ionic ratios. They conclude that elevated nitrate concentrations are solely due to anthropogenic activities. This is in accordance with Datta et al. (1997) who found a strong correlation of enriched $^{18}O$ with high nitrate concentrations concluding that agricultural return flow (evaporation) is one of the main sources of nitrate in the groundwater. Other sources are mostly point sources such as leaking sewers, septic tanks, and industrial waste. Datta et al. (1996b) take a more detailed look at the fluoride contamination. They found that about 50 % of the NCT area was affected by fluoride concentrations above 1.5 mg/L in the groundwater. The two most important sources are probably contamination from the brick industries and the leaching of fluoride from soils. Dubey et al. (2012) studied the arsenic contamination in the Yamuna floodplain aquifer (Newer Alluvium). The authors come to the conclusion that the high arsenic concentrations (up to 180 ppb) in the groundwater are purely due to anthropogenic influences. One of the main sources is coal based thermal power plants in the vicinity, which discharge their effluents into the Yamuna River, from which the contaminated water then infiltrates into the aquifer. Walsh et al. (2011) studied the presence of antibiotic resistant bacteria in tap water and groundwater samples and found contaminated groundwater samples (51 out of 171) throughout the city.

**Delhi Stretch of Yamuna River**

Two publications on Yamuna water quality are based on the CPCB report “Water Quality Status of Yamuna River 1999-2005” (CPCB 2006- see section 2.1.2). Upadhyay et al. (2011) summarize the data of the report and give additional information as to the source of the pollution (discharge of untreated sewage into the river) and list preventive and corrective measures to improve and maintain a good river water quality. The other paper about the 2000-2005 sampling period of the CPCB was written by Mandal et al. (2010). The authors discuss the correlation of parameters (DO, BOD, COD, TKN) in detail. In addition, $NH_4^+$ concentrations are published: maximum concentrations were measured in April-May (up to 23 mg/L), and minimum concentrations were found during monsoon season in August-September (about 5 mg/L).

Furthermore, the following studies were conducted: Sehgal et al. (2012) studied heavy metal concentrations in the Yamuna and identified the inflow of industrial wastewater as point sources. Riverbed sediments were analyzed for organochloride pesticide residues (Pandey et al. 2011) and heavy metals (Jain 2004). Jamwal et al. (2011) studied the influence of point sources and non-point sources of fecal coliforms and fecal streptococci (e.g. STP effluents, stormwater runoff). Although dilution results in BOD to be lower and DO to be higher during monsoon times, the microbial pollution is not affected by this as stormwater runoff in the city has a microbial load comparable to that of raw sewage.

### 2.1.2 Reports

**Central Ground Water Board (CGWB)**

The CGWB regularly publishes a “Groundwater Yearbook – National Capital Territory Delhi” in which data from depth to water measurements and selected parameters of the hydrochemical analyses (EC, nitrate, fluoride) from their monitoring network are published (e.g. CGWB 2006a, 2012). In 2011−12 this network consisted of 137 observation wells and 25 dug wells (CGWB 2012, p.3). The CGWB identified nitrate and fluoride as parameters of concern in Delhi. Elevated nitrate concentrations are found throughout the city, predominantly in shallow wells, as unlined sewers are the most common source of the pollutant. Elevated fluoride concentrations are mostly found in deep wells in the western part of the city and are of geogenic origin (CGWB 2012, p.58). In a separate report about the “Hydrogeological Framework and Groundwater Management Plan of NCT Delhi”, different geological cross sections are shown (CGWB 2006b, p.30-40). Vast areas of the floodplain along the Yamuna are classified as potential areas for further groundwater development owing to the aquifer’s high transmissivity and a deep saline-freshwater interface (CGWB 2006b, p.42-43, ii-iii).

**Central Pollution Control Board (CPCB)**

The CPCB is responsible for monitoring the water quality of Yamuna River since 1976 (CPCB 2006). Data about BOD, DO, nitrate, nitrite, total coliforms and fecal coliforms are regularly published in “Status of Water Quality in India” reports (e.g. CPCB 2010b, 2013a, b). More detailed information, including general physicochemical parameters and heavy metal and pesticide concentrations, can be found in the report “Water Quality Status of Yamuna River 1999−2005” (CPCB 2006). The river stretch between Wazirabad and Okhla is classified as a polluted river stretch, where BOD concentrations, fecal coliform, and total coliform counts are high and DO concentrations are often as low as 0 mg/L (CPCB 2013b, p.77-78).

**Geological Survey of India**

The Geological Survey of India carries out detailed geological and geomorphological investigations in NCT Delhi. A geological map depicting the surface geology is available (Geological Survey of India 2006). The most recent available report (Kazim et al. 2008) describes the geological set-up and formations in great detail and is the most thorough reference about the local geology.

## 2.2 PREVIOUS WORK DONE AT THE FIELD SITE

Previous research at the central Delhi field site was conducted in 2005−2006 in the frame of the feasibility study IDB India (International development of bank filtration: Case study India) and 2006−2010 in the frame of the EU-funded project TECHNEAU (Technology Enabled Universal Access to Safe Water).

During the IDB India study, the Delhi test sites for the subsequent TECHNEAU project were determined. In the TECHNEAU project, bank filtration was studied at three locations in Delhi, with the goal to evaluate the efficiency of this technology as a pre-treatment step to minimize the conventional water treatment. At the study site in central Delhi (Nizamuddin Bridge), a total of eight observation wells were built. Four of them were constructed end of 2006 (Lorenzen et al. 2007) at a distance of 50 m to the riverbank with filter screens in different depths (according to Pekdeger et al. 2008, p.10):

- 4–7 m
- 6–9 m
- 7–13 m
- 31–37 m

Another one was also constructed end of 2006 at a distance of 90 m to the riverbank with a filter screen at a depth of (Pekdeger et al. 2008, p.10):

- 6.5–9.5 m

In November/December 2007 three shallow observation wells were constructed very close to the river, at distances between 2, 3.5 and 5 m to the riverbank. According to Pekdeger et al. (2008, p.10) these observation wells had filter screens in the following depths:

- 2.6–3.4 m
- 2.0–2.8 m
- 3.1–3.9 m

From these observation wells, groundwater samples were taken regularly and analyzed for on-site parameters, main ions, trace elements and $^{2}$H and $^{18}$O isotopes (Pekdeger et al. 2008). In addition to the sampling of the observation wells, at least one sample was taken from a handpump at a distance of 500 m to the riverbank with a filter depth of about 5−15 m (Lorenzen et al. 2010), and two samples were taken from the Ranney well P3 (called RW1 in the publication - Sprenger and Lorenzen 2014).

Fecal coliforms and total coliforms were regularly tested in surface water samples and groundwater samples from the observation wells. In surface water and shallow observation wells somatic bacteriophages were tested several times, a non-target GCMS screening for trace organic substances was conducted in February 2007, and a one-time sampling for human-pathogen viruses was carried out in September 2007 (Sprenger et al. 2008). Temperature logs were measured in the observation wells (Lorenzen et al. 2010) and a modeling approach was used to determine travel times in the sandy aquifer material using temperature and chloride concentrations to calibrate the models (Sprenger 2011). Moreover, a 2D model of the field site was set up during the Saph Pani project to determine the shares of bank filtrate that the Ranney wells draw and the groundwater travel times to the wells (Sprenger 2013).

The results were published in the cited reports and journal articles and two doctoral theses (Sprenger 2011, Lorenzen 2011). The most important outcomes of the previous studies are:

- Three lithological units were found at the field site: Younger Alluvium (recent alluvium), Older Alluvium and hard rock. In the drillings at a distance of 50 m to the riverbank, the Younger Alluvium has a depth of 12 m (Sprenger and Lorenzen 2014) and consists of medium sand and fine sands (Lorenzen et al. 2007). The Young Alluvium is underlain by Older Alluvium consisting of clays and silts and a sand interlayer, and at a depth of 38 mbgl Precambrian hard rock was encountered. Sections were prolonged to the East with the help of information found in CGWB (2006b) (Sprenger and Lorenzen 2014).
- Temperature logs reveal that losing stream conditions prevail at the field site (Lorenzen et al. 2010).
- The average pore water velocity in the medium sand was found to be 0.9 m/d (Sprenger 2011, p.66). Sprenger and Lorenzen (2014, p.530) reported a range of pore water velocities between 0.8 and 2.2 m/d and Sprenger et al. (2014) published a range of pore water velocities between 0.4 and 1.4 m/d for the first 4 m from the river bank.
- In the observation wells, a high share of bank filtrate was only found in the shallow observation wells at distances of 5, 50 and 90 m from the riverbank. In the observation well with a filter screen between 7–13 mbgl at a distance of 50 m to the river, only a medium share of bank filtrate was estimated to be present. In the deep observation well with a filter screen between 31 and 37 mbgl the share of bank filtrate was estimated to be null (Pekdeger et al. 2008, p.10).
- According to numerical modeling by Sprenger (2013), the share of bank filtrate in the raw water of the Ranney wells in the floodplain varies from 20–98 % (in well P3), 0–80 % (in well P4) and 0–30 % (in well P5) − depending on the pumping scenarios, monsoon

inundation period and hydraulic head at the eastern boundary of the floodplain (set as a constant head boundary in the models).

- A redox sequence from sulfate-reducing conditions close to the river to oxidizing conditions farther away from the river is found in groundwater flow direction (Sprenger and Lorenzen 2014).
- The dominating nitrogen species in the floodplain is $NH_4^+$, which is transformed through anammox and nitrification (Sprenger and Lorenzen 2014).
- Concerning the inorganic components, not many positive effects of bank filtration were observed at the field site. Elevated concentrations of As, Fe, Mn, $F^-$ and $NH_4^+$ were measured in the bank filtrate, often in higher concentrations than in the surface water. A post treatment is, therefore, necessary (Pekdeger et al. 2008).
- Bank filtration proved to be highly efficient to remove viruses within the first 4 m of the soil passage at the field site (Sprenger et al. 2014).
- Bank filtration is an effective measure to remove or significantly reduce trace organic components found in the river water (Sprenger et al. 2008).

## 2.3 RESEARCH ON AMMONIUM CONTAMINATED GROUNDWATER

Previous studies about the transport of $NH_4^+$ were conducted at different scales (field and laboratory scale) and with different materials (aquifer materials, artificial sediments). The studies that are especially important in this field or which have significance for the present work are presented in some detail. The other publications are only summarized briefly. Studies on special aspects, such as detailed reactions of $NH_4^+$, e.g. the anammox process (e.g. Mulder et al. 1995, van de Graaf et al. 1995), $NH_4^+$ fixation in soils (e.g. Schneiders and Scherer 1998), or ammonification (e.g. Hanson et al. 2013) are not summarized in this section. Those references are given in the following chapters wherever necessary.

### Field Studies on Groundwater Contamination from Wastewater Discharge

Otis Air Force Base, Cape Cod, Massachusetts (USA)

A sewage plume in a sand and gravel aquifer was extensively studied in Cape Cod, Massachusetts. Between 1936 and 1995 secondary treated domestic sewage from an STP at Otis Air Force Base was discharged onto surface sand beds from where it infiltrated into the shallow unconfined aquifer. The aquifer has a thickness of 27−42 m and consists of well-sorted medium to coarse sand with some gravel with hydraulic conductivities of about $1\times10^{-3}$−$7\times10^{-4}$ m/s (60−90 m/d). It is underlain by finer grained sediments, which overlie crystalline bedrock. The plume spread in groundwater flow direction; the bottom of the plume is marked by the contact between the aquifer material and the fine-grained sediments, and the plume is covered by 6−15 m of fresh groundwater from recharge through precipitation.

Leblanc (1984) gave a detailed description of the field site and delineated the sewage water plume using different species, including $NH_4^+$ and $NO_3^-$. The composition of the infiltrating treated sewage water varied over time. At the time of the study, total nitrogen (N) concentrations between 19 and 24 mg/L were measured, whereby the $NH_4$-N concentrations varied between 0.72 and 6.4 mg/L and the $NO_3$-N concentrations were between 12 and 16 mg/L. Maximum $NH_4$-N concentrations measured in the center of the plume were 20 mg/L. Elevated $NO_3^-$ concentrations were found much farther downstream of the STP than elevated $NH_4^+$ concentrations and the author concluded that the oxidation of $NH_4^+$ to $NO_3^-$ is the main cause of the $NH_4^+$ attenuation.

Ceazan et al. (1989) used this study site to investigate the effect of cation exchange on the transport of $NH_4^+$ in the groundwater in an aquifer with a clay content of less than 0.1 %. Evidence for cation exchange being the reason for the retarded movement of $NH_4^+$ was presented on three scales. On a laboratory scale, batch experiments were conducted. Exchangeable $NH_4^+$ could be extracted from aquifer sediments taken from the contaminated zone. Furthermore, an average linear isotherm for $NH_4^+$ sorption was determined for a range of $NH_4^+$ concentrations with the help of batch sorption experiments with uncontaminated aquifer material, here 80 % of the sorbed $NH_4^+$ was later recoverable by KCl extraction. The resulting retardation factor ($R_f$), calculated using the $k_{d,iso}$ value was 2.5. Furthermore, small-scale field tracer experiments with $NH_4^+$, $NO_3^-$ and $K^+$ were conducted at an uncontaminated part of the aquifer. The distribution of cation concentrations strongly indicates cation exchange. The $R_f$ derived from the tracer tests was 3.5. On the field scale, the $NH_4^+$ plume extends only about half the length compared to the plume delineated by elevated specific conductance values. Assuming that only cation exchange is responsible for the retardation of $NH_4^+$ and not biological processes and source variations, the resulting retardation factor is 2.0.

Böhlke et al. (2006) conducted a long-term field study (1990−1998) on the movement of $NH_4^+$ in the plume. Besides groundwater sampling, the study included field-scale isotope tracer tests (with $^{15}N$ isotopes of $NH_4^+$, $NO_3^-$ and $N_2$) and desorption experiments with core material from contaminated areas. Extractable $NH_4^+$ was determined from the core material, and $NH_4^+$ concentrations in groundwater samples from corresponding observation wells were measured. An average linear partition coefficient ($k'_d$ value) was determined from the linear fit to the $NH_4^+$ concentrations of the core sediment/groundwater pairs. The $NH_4^+$ plume at the field site was found to be defined by a small cloud of high concentrations at the upper boundary of the wastewater plume. The travel distance of the $NH_4^+$ was only 0.28 times the hypothetical total length of the plume. In the observed period, the movement of the $NH_4^+$ cloud was at velocities between 0.17 and 0.36 times the average groundwater flow velocity of 0.33 m/d (120 m/yr). The retardation factor derived from the plume front migration (4.0) and the retardation factors from the field-scale isotope tracer tests (between 4.0 and 6.4) are larger than the retardation factors derived from the batch tests (2.8) and the values reported by Ceazan et al. (1989).

Using $^{15}N$ isotopes, Böhlke et al. (2006) were able to differentiate between different transport and biochemical processes. Sorption and desorption do not cause isotope fractionation while biochemical reactions do. Isotope fractionation was only found in the upper (suboxic) part of the plume while no evidence for $NO_3^-$ reduction or anaerobic ammonium oxidation (anammox) was found in the anoxic center of the plume. Because $NH_4^+$ transport is strongly retarded and the transport of other N species is not, $NH_4^+$ and other N species found in one sample do not have to come from the same source at the same time. The authors conclude that most of the $NO_3^-$ found in the plume was recharged with the wastewater and does not originate from nitrification. Although conditions would be favorable for anammox in some parts of the plume (presence of both $NH_4^+$ and $NO_3^-$), no conclusive evidence for this process was found.

Repert et al. (2006) conducted another long-term study (1995−2004) about the plume development after the discharge of the secondary treated wastewater was stopped. The authors described the development of the groundwater chemistry below the infiltration beds and along a plume transect of 600 m and included data about $NH_4^+$ and $NO_3^-$.

Other case studies

DeSimone and Howes (1996) evaluated field data (1990−1992) from another secondary treated wastewater effluent plume in a coastal aquifer in Cape Cod. Here, secondary treated septage effluents (which are more concentrated than treated sewage effluents) from a septage treatment plant are the source of the contamination since the plant started operating in 1990. In this publication, the authors focus on $NO_3^-$ and the process of denitrification. DeSimone and Howes (1998) calculated nitrogen mass balances of the field data and present the results of batch experiments conducted to quantify $NH_4^+$ sorption. They found that Langmuir isotherms derived from experiments conducted with artificial effluent (high ionic strength) best describe $NH_4^+$ sorption onto the sediment within the plume, while isotherms derived from experiments with low ionic strength solutions overestimate $NH_4^+$ adsorption as the competing ions are not considered. Although $NH_4^+$ was the dominating nitrogen species in the septage effluent, $NO_3^-$ was the dominating species after the passage through the 12 m thick unsaturated zone, where transformation processes (mostly nitrification, some mineralization of organic nitrogen) took place, but almost no net attenuation of nitrogen was observed. In the saturated zone, no nitrification occurred because of the prevailing anoxic conditions. However, $NH_4^+$ sorbed onto the aquifer matrix constituted a significant part of the total nitrogen in the system (16 %).

Hinkle et al. (2007) presented field data on aquifer scale (640 km$^2$) from Le Pine, Oregon (USA), where septic tank effluents were the source of $NH_4^+$ contamination in a shallow sandy aquifer. The goal of the study was to determine which process controls the distribution of $NO_3^-$ and $NH_4^+$ on aquifer scale. Elevated $NH_4^+$ concentrations were strongly linked to reducing conditions and were found in deep groundwater samples or in shallow samples taken near rivers where gaining stream conditions prevail. Maximum measured $NH_4$-N concentrations were 39 mg/L. The authors concluded that while septic tank effluents are the main source of $NO_3^-$ in the aquifer, the $NH_4^+$ is of natural origin (degradation of organic matter); this is supported by $^{15}N$ data and correlation with $Cl^-$ and dissolved carbon concentrations in the groundwater. Hinkle et al. (2008) studied the processes in packed sand filters of septic tank systems in detail and found that nitrification was efficient in the filters and 98 % of the nitrogen leaving the filter was in the form of $NO_3$-N.

Clark et al. (2008) studied a contaminant plume in Ontario (Canada) caused by drainage from a fertilizer company and infiltration from wastewater treatment ponds. $NH_4$-N and $NO_3$-N concentrations found in the source area of the fertilizer company were 840 ppm and 350 ppm. Downstream both $NH_4^+$ and $NO_3^-$ concentrations decreased more than could be explained by dilution through mixing with uncontaminated groundwater. The authors concluded that anaerobic ammonium oxidation occurred in the aquifer and supported this assumption by several lines of evidence, including $^{15}N$ isotope values. This was the first time anammox was detected in an aquifer.

### Studies on Riverbank Filtration at Sewage Influenced Rivers

Case studies about bank filtration at sewage influenced surface water bodies were conducted at an RBF site along the Seine (France) and the Aar River and Glatt River (Switzerland).

#### Seine River (France)

Doussan et al. (1997) and Doussan et al. (1998) studied the transport of N species at an experimental bank filtration site at a well field 40 km downstream Paris, where the discharge of a STP lead to high $NO_3^-$ concentrations (2.7 to 5.4 mg $NO_3$-N/L) and a high organic load in the Seine at the time of the study. The aquifer is a fissured chalk aquifer overlain by about 10 m alluvial sediments. Reducing conditions prevail in the aquifer owing to the decay of organic matter. Doussan et al. (1997) modeled the biogeochemical processes and subsequent changes in water chemistry during the first few decimeters of soil passage, focusing on nitrogen species. Pore water velocity and solubilization of particulate organic matter were found to be the two important factors controlling nitrogen reactions. High pore water velocities lead to a decreasing anaerobic zone, in which organic matter mineralization occurs, and the production of $NH_4^+$ is reduced. When no particulate organic matter is available bacteria have to feed only on dissolved organic carbon in the infiltrating water and $NH_4^+$ production is prevented. However, then denitrification, which also depends on organic matter as electron donor does not take place either. The authors conclude that it would be advantageous to have enough organic matter in a system to trigger nitrification but not too much to prevent the establishment of highly reducing conditions, which lead to $NH_4^+$ production. Doussan et al. (1998) describe the evolution of the water composition from river water to groundwater on field scale. Due to the high organic load of the infiltrating water, reducing conditions prevail in the aquifer and $NH_4^+$ is formed by the mineralization of organic matter in the riverbed sediments. Cation exchange retards the transport of the produced $NH_4^+$ in the aquifer, but a plume has probably started to spread towards the wells. Distribution coefficients ($K_d$ values) were determined for the chalk aquifer and the alluvial sediments with laboratory adsorption experiments.

#### Glattfelden (Switzerland)

The infiltration of sewage influenced river water was studied in Glattfelden (Switzerland) by Schwarzenbach et al. (1983) and Jacobs et al. (1988). Slightly elevated $NH_4^+$ concentrations (24–323 µmol/L) were only observed in the river, but no $NH_4^+$ was detected in the aquifer. Jacobs et al. (1988) concludes that organic matter degradation is the main process during early stages of groundwater recharge and that all $NH_4^+$ in the river water is consumed by nitrification.

## Reactive Transport Modeling Case Studies

### Contamination from a sewage farm in Berlin (Germany)

Hamann (2009) modeled the attenuation and fate of an $NH_4^+$ plume in southeastern Berlin (Germany) which originates from a sewage farm that operated from 1906 to 1976. Elevated $NH_4^+$ concentrations were measured at a well field 2–3 km downgradient of the sewage farm since the 1960s; the maximum $NH_4^+$ concentrations of 66 mg/L were found in the early 1990s. Since then concentrations decreased until the end of the 1990s and remained stable at 25–30 mg/L until 2005. The model has an extent of 8600 m (N−S) by 6700 m (E−W) and incorporates the entire sewage farm as well as the water works. Field investigations showed that the transport of $NH_4^+$ in the plume is dominated by cation exchange, which was implemented in the model with site-specific selectivity coefficients determined through laboratory analyses. The model demonstrates that the reason for the long tailing of the plume is desorption of previously sorbed $NH_4^+$ from the aquifer matrix. The modeled decontamination phase is longer in the reactive transport model than in simple sorption isotherm based models. Sewage borne organic matter deposited at the sewage farm (sewage sludge) is a further source of $NH_4^+$ (mineralization), but it was not incorporated in the model.

### Contamination from a coking plant in Mansfield (UK)

The development of an $NH_4^+$ and phenol plume originating from a former coking plant was modeled by Haerens (2004) and Haerens et al. (2006). The contaminated aquifer is made up of relatively uncemented Triassic sandstone. $NH_4^+$ is the dominant cation in the contaminated groundwater and cation exchange leads to a strong retardation of the $NH_4^+$ plume while $Ca^{2+}$ and $Mg^{2+}$ are found in front of the plume in higher concentrations than in the uninfluenced groundwater. After contamination has stopped, this process is reversed, and $NH_4^+$ is displaced instead. In contrast, phenol is not retarded but oxidized. The authors modeled a 45 year period using the MODFLOW and MT3DMS based multi-component transport model PHT3D and were able to reproduce and explain all effects measured in the field. Furthermore, Haerens et al. (2002) used a conceptual 1D model example of this case study to compare the two multi-component reactive transport models PHT3D and PHREEQC-2.

## Ammonium Laboratory Column Experiments

The behavior of landfill leachate containing high $NH_4^+$ concentrations was investigated in soils, disaggregated sandstone and clay liner materials typically used for the lining of landfills. Kjeldsen and Christensen (1984) conducted laboratory column experiments with four soils and diluted and undiluted acid landfill leachate with $NH_4$-N concentrations of 730 and 160 mg/L under anaerobic conditions. They found that $NH_4^+$ transport was governed solely by adsorption processes and that increasing clay content led to increasing adsorption. Thornton et al. (2000) studied the behavior of landfill leachate in disaggregated Triassic sandstone aquifer material. The different leachates used for the column experiments had $NH_4^+$ concentrations of 1977, 1398, 1029 mg/L. $NH_4^+$ retardation due to cation exchange was observed and could be described by simple retardation factors ($R_f$ between 1.28 and 2.52). Thornton et al. (2001) compared the attenuation of inorganic compounds (including $NH_4^+$ at a concentration of 1029 mg/L) in clay liner materials, which were mixed with quartz sand to make the columns permeable (5–15 % clay and 85–95 % quartz sand). The 50 % $NH_4^+$ breakthrough occurred after about 2 flushed pore volumes. Distribution coefficients ($K_d$) were determined by modeling the results of the column experiments; they range from 0.075 to 0.224 mL/g and increase with increasing clay content. Thornton et al. (2005) focused on whether chemical variations observed in the field could be reproduced in the laboratory and predicted using a transport model (PHREEQM code and experimental $K_d$ values).

Column experiments with lower concentrations of $NH_4^+$ have been conducted by Hinkle et al. (2008) and Jellali et al. (2010). Hinkle et al. (2008) conducted experiments with the filter sand from packed bed (sand) filters and synthetic septic tank effluent. Columns were operated under unsaturated conditions. During the sorption experiments, no breakthrough of $NH_4^+$ was observed. In the desorption experiments, 97 % of the sorbed $NH_4^+$ was retrieved again. To study the behavior of ammonium at an SAT pilot site in Tunisia, Jellali et al. (2010) conducted column experiments with sandy soil using different $NH_4Cl$ solutions ($NH_4^+$ concentrations between 5 and 36 mg/L) and wastewater. The authors applied different flow rates. $NH_4^+$ adsorption was 49 % higher when the contact time increased from 52 minutes to 159 minutes (Q of 45 and 15 mL/min). $NH_4^+$ adsorption decreased when the real wastewater was used because of the presence of competing ions.

## 2.4 SYNOPSIS

To date, $NH_4^+$ contaminations resulting from sewage contaminated surface waters have not been studied under similar conditions as those met in Delhi. High temporal fluctuations of $NH_4^+$ concentrations in the surface water (between 2.5 and 20 mg/L) and the groundwater (e.g. between 8 and 35 mg/L in one sampling point), as were found in Delhi, have not been reported elsewhere. Insights from previous studies can help to understand the $NH_4^+$ contamination at the Delhi field site, but results have to be adapted to local conditions or taken further. $NH_4^+$ field studies, especially those in Cape Cod, revealed that cation exchange is an important mechanism in sand and gravel aquifers with low clay contents (e.g. Ceazan et al. 1989). However, no research about contaminant transport in sediments containing kankar has been conducted so far, and it is necessary to close this knowledge gap. Column studies allow for a detailed study of transport behavior, and, therefore, are advantageous over batch experiments, especially when tracer experiments with $NH_4^+$ cannot be done on site to complement the batch studies. The results of previous column experiments (Jellali et al. 2010) stress the necessity of choosing conditions very close to those found in the aquifer regarding flow velocity and model water composition. Modeling studies (Hamann 2009, Haerens 2004) showed that reactive transport models with adapted selectivity coefficients give better results than $k_d$ approaches and have the advantage of being independent of solute concentrations. As previous studies of the field site (e.g. Lorenzen et al. 2010, Sprenger and Lorenzen 2014) focused on the first 100 m from the riverbank, detailed field studies further from the riverbank were necessary to understand the hydrogeological conditions at the site and the extent and dynamics of the $NH_4^+$ plume.

# Chapter 3

# Local Hydrogeology and Assessment of Ammonium Contamination

## Abstract

In the megacity Delhi, water resources are stressed, and an intensified use of the alluvial aquifer along the Yamuna River is proposed to increase the water supply. However, ammonium ($NH_4^+$) contamination was observed in the aquifer in central Delhi. Because the local hydrogeology strongly influences the transport and fate of $NH_4^+$, an extensive field study was conducted to determine the extent of the $NH_4^+$ plume and to develop a conceptual hydrogeological model of the field site. Six drillings with depths up to 27 m were conducted, and 85 river- and groundwater samples were collected in 2012–13. Results of the drillings and sediment analyses reveal that the saturated zone of the aquifer consists of two lithological units, medium sand with a hydraulic conductivity between $8.6\times10^{-5}$ and $3.2\times10^{-4}$ m/s and kankar, a sediment made up of calcareous nodules, with a hydraulic conductivity between $3.1\times10^{-3}$ and $4.2\times10^{-3}$ m/s. The riverbed sediments also consist of medium sand. Water level measurements conducted in November 2013 indicate that losing stream conditions prevail and that the groundwater consists to a large part of bank filtrate. $NH_4^+$ concentrations in the river show strong monsoon – non-monsoon variations between 2.5 and 20 mg/L and a strong variability in $NH_4^+$ concentrations also occurs in the groundwater. At a distance of 250 m to the river, concentrations between 4.5 and 35 mg/L were found. At a distance of 500 m, concentrations between 0.05 and 28 mg/L were measured in observation wells with filter screens in the sand, while a horizontal collector well with filter screens in the kankar layer only shows variations between 5.5 and 8 mg/L. Different transport characteristics in the sand and the kankar are assumed to have an effect on the plume migration and fingering patterns occur. This is supported by the results of column studies, in which the nitrogen released from the sediment samples were measured.

## 3.1 INTRODUCTION

Insufficient sewage treatment capacities are a common problem in rapidly growing urban agglomerations in developing and newly industrialized countries. This often leads to the discharge of untreated sewage water into rivers and lakes resulting in bacterial contamination, low oxygen concentrations and high nitrogen loads in surface water bodies. $NH_4^+$ is the dominant nitrogen species under such conditions. Its primary source in sewage water is the degradation of urea (Mobley and Hausinger 1989) and prevailing reducing conditions prevent nitrification ($NH_4^+$ oxidation to $NO_3^-$).

Depending on the local hydrogeology, sewage contaminated surface water bodies can constitute a serious threat to groundwater resources. At sites with naturally occurring or induced losing stream conditions, the sewage influenced water can infiltrate into the aquifer along the surface water body, leading to a contamination of the aquifer. In this case, $NH_4^+$ is a parameter of concern, especially when the aquifer is used for drinking water production. In the Indian Standard Drinking Water Specification, the guideline value for $NH_4^+$ is 0.5 mg/L as ammonia-N (IS 10500: 2012), and many countries have set the same limit in their national drinking water directives as higher $NH_4^+$ concentrations are usually an indication of a serious water quality problem. Although higher concentrations are generally not an acute threat to human health, the presence of $NH_4^+$ in raw water is a problem for the disinfection of water through chlorination. Chloramines form in the presence of $NH_4^+$ (Weil and Morris 1949), and higher amounts of chlorine are needed to achieve a sufficient free chlorine residual for a safe chlorination (Duong et al. 2003).

At a well field on the floodplain in central Delhi, where the Yamuna River is highly polluted by sewage water, unusually high $NH_4^+$ concentrations were measured in the groundwater (Pekdeger et al. 2008). Large horizontal collector wells are used for water production from the shallow alluvial aquifer. Losing stream conditions prevail (Lorenzen et al. 2010) and the wells are assumed to draw a high share of bank filtrate. $NH_4^+$ concentrations between 5.5 and 8 mg/L were measured in the raw water of the well located closest to the river (Groeschke 2013), which is often not used for water supply for this reason. Depending on the transport and fate of $NH_4^+$, the concentrations might also increase at other wells of the well field. To be able to plan appropriate treatment or remediation options, the extent of the contamination and the transport mechanisms of $NH_4^+$ at the field site have to be well understood. The aim of this study was to assess the extent of the $NH_4^+$ plume and to set up a conceptual model of the field site as a basis for a reactive transport model.

## 3.2 THE STUDY AREA

The study site is located on the Yamuna floodplain between 720800 and 722800 m E and 3165900 and 3168200 m N (UTM, WGS84 Zone 43) in the district East Delhi on the eastern Bank of the Yamuna River near Akshardham Temple. Here the undeveloped floodplain has a width of about 2400 m and is mostly used for irrigated agriculture. Several large horizontal collector wells (Ranney wells) are located in the area (Fig. 3.1), mostly used for drinking water production. In addition, groundwater is drawn through numerous handpumps and bore wells of the local population. Studies at this field site have been conducted previously (Lorenzen et al. 2010, Sprenger and Lorenzen 2014). The focus was set on understanding the groundwater flow in the first 100 m from the river bank and to evaluate the locations potential as a riverbank filtration site. Nitrogen data, therefore, remained insufficient to draw conclusions about the state of the contamination.

The Holocene floodplain aquifer (also called Newer Alluvium), which is the target of this study, stretches along the banks of the Yamuna River. It consists of mostly grey colored medium−coarse-grained sands with varying proportions of clay, silt and gravel (Shekhar and Prasad 2009) with hydraulic conductivities between $2\times10^{-4}$ and $7\times10^{-4}$ m/s (13−60 m/d) (Chatterjee et al. 2009). The thickness of the floodplain aquifer in Delhi varies between 70 m in the North and 30 m in the South of Delhi according to Shekhar and Prasad (2009), while Kazim et al. (2008) reported smaller thicknesses in central Delhi. It is underlain by Pleistocene sediments of the Older Alluvium, which consists of mainly cyclic silt-clay and sand deposits with lower hydraulic conductivities between $3\times10^{-5}$ and $5\times10^{-5}$ m/s (3−4 m/d) according to Chatterjee et al. (2009). The basement is formed by Precambrian bedrock. At the study site, the Older Alluvium was found at a depth of 14 mbgl by Kazim et al. (2008, p.13). Bedrock was encountered at a depth of 38 mbgl by Sprenger and Lorenzen (2014), whereas the Central Ground Water Board reported a depth of 88–120 mbgl for the floodplain area around Akshardham Temple (CGWB 2006b, p.31).

The Yamuna River is dammed by two barrages, Wazirabad Barrage and Okhla Barrage, which control the flow of the river (Fig. 3.1). The barrages are usually closed during non-monsoon times (October–June), and the river stretch in Delhi is mostly fed by the discharge of treated and untreated sewage water (CPCB 2006).

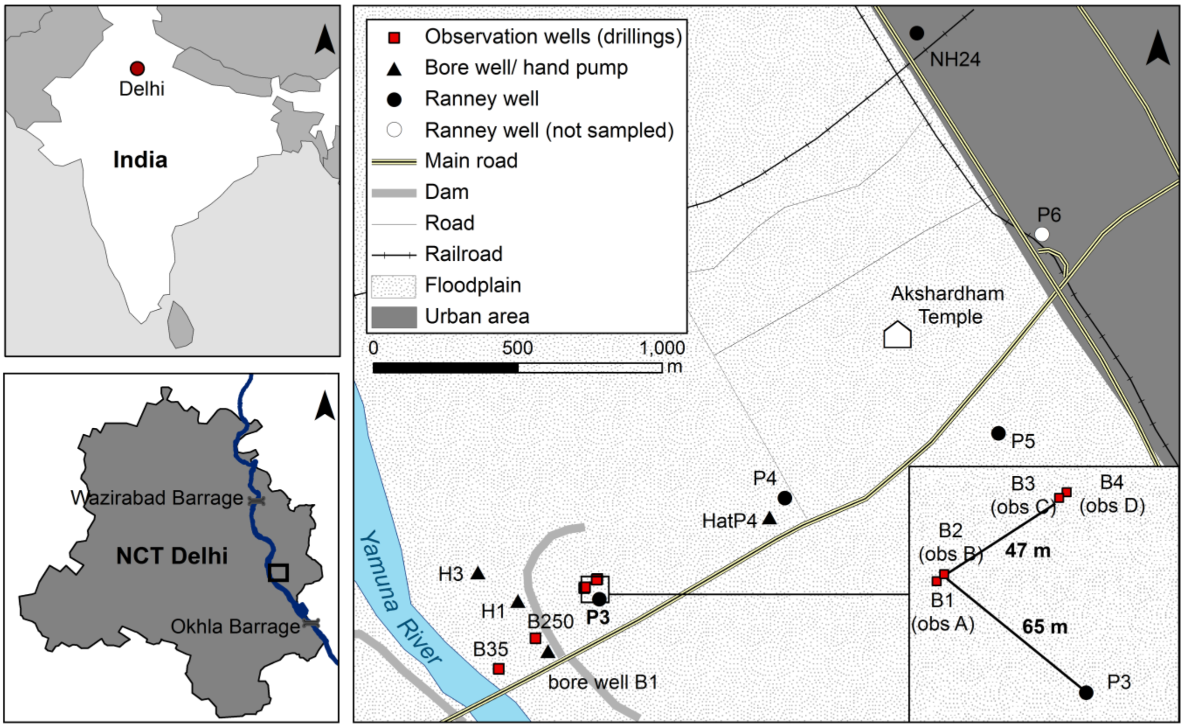

**Fig. 3.1** Location of the study area and the sediment and water sampling points.

## 3.3 MATERIALS AND METHODS

### Drilling and Collection of Aquifer Material

In 2012−2013 a total of six drillings were conducted by manual auger drilling with depths between 8 and 27 m at distances between 35 and 550 m from the current riverbank (Table 3.1). Sediment samples were taken from the saturated zone at regular intervals and according to changes in lithology. Samples were vacuum-packed and stored in the dark below 12°C until analysis at the Freie Universität Berlin.

### Construction of Observation Wells and Handpumps

The six drillings were used to install water sampling points. Observation wells were built at B1−B4 while handpumps were installed at B35 and B250. All sampling points were constructed using PVC pipes. The well screens – 2 to 6 m long – at the end of the tubing are made of the same PVC material, perforated with holes of about 2.5 cm in diameter and then wrapped with several layers of mesh fabric. The lengths and depths of the well screens are shown in Table 3.1. If the borehole was deeper than the planned depth of the sampling point, the bore was filled with sediment up to the anticipated depth of the water sampling point. No filter gravel was used; instead the annulus between bore and tubing was filled with the sandy material taken from the borehole. The observation wells were constructed with cemented protective iron casing. For the handpumps, the top few meters of the annulus were filled up with clay to prevent the direct infiltration of rain or flood water.

**Table 3.1** Depth and location of the drillings conducted in this study and characteristics of the newly constructed water sampling points (HP = handpump, Obs = observation well).

| **Drilling** | **B35** | **B250** | **B1** | **B2** | **B3** | **B4** |
|---|---|---|---|---|---|---|
| **Name of water sampling point** | **H35** | **H250** | **obs_A** | **obs_B** | **obs_C** | **obs_D** |
| Distance to river (m) | 35 | 250 | 500 | 500 | 550 | 550 |
| Depth of bore (mbgl) | 18 | 16 | 27 | 14 | 21 | 8 |
| Date of drilling (month/year) | 11/2013 | 11/2013 | 10/2012 | 10/2012 | 10/2012 | 10/2012 |
| Type of sampling point | HP | HP | Obs | Obs | Obs | Obs |
| Location of well screen* (mbgl) | 9-15 | 8.5-14.5 | 22-25 | 11-13 | 8.5-10.5 | 5.5-7.5 |
| Length of well screen (m) | 6 | 6 | 3 | 2 | 2 | 2 |

*Top of well screen – bottom of well screen

### River Profiles and Collection of Riverbed Sediment

To identify potential regions of river water infiltration, three W–E cross-sectional profiles of the river perpendicular to the flow direction were produced in November 2013 (Fig. 3.2). For each, a static line with clearly marked intervals was fixed across the river. Every 10 m the water depth was measured, and a sample of the riverbed sediment was collected with a Van-Veen grab sampler. The sediments were classified directly on site. One representative sand sample was furthermore vacuum packed for laboratory analyses.

**Fig. 3.2** Location of the riverbed sections taken in November 2013. Background image: Google Earth March 2014.

### Water Sampling and Analysis

A total of 72 groundwater, eleven regular river water samples and two samples of the flood event in June 2013 were taken during seven sampling campaigns between March 2012 and December 2013. Groundwater samples were taken from 14 locations, including handpumps, bore wells, four Ranney wells and the newly constructed observation wells (Fig. 3.1). Samples were collected after at least three times the well volume was exchanged by pumping. Surface water samples were taken at two places at the riverbank, 2 m from the shoreline and a depth of about 0.3 m below the water surface.

Electric conductivity (EC), pH, oxidation-reduction potential (ORP) and dissolved oxygen (DO) were measured on site with a Hach Lange multimeter. $HCO_3^-$, $NH_4^+$, $S^{2-}$, and $NO_2^-$ were also measured in the field using titrimetric ($HCO_3^-$) and colorimetric test kits. Cation and anion samples (50 mL each) were filtered through a 0.2 µm filter; cation samples were additionally acidified to a $pH < 2$ by adding 65 % $HNO_3$. Samples were stored in the dark below 12°C until analysis at the Freie Universität Berlin. Main cations ($Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$) as well as trace elements (Fe, Mn) were measured using an inductively coupled plasma-optical emission spectrometer Optima 5000 (ICP-OES). As was measured by flame spectrometry AAS. Anions ($Cl^-$, $NO_3^-$, $PO_4^{3-}$, $F^-$) were measured with a DIONEX 1100 Thermo ion chromatography system. Photometric measurement of DOC was conducted with a Technicon Autoanalyzer. Detection limits are summarized in (Table 3.2).

**Table 3.2** Limits of detection (LODs) of the analyses conducted on the water samples taken at the study site.

| Parameter | Unit | Method | LOD |
|---|---|---|---|
| $Na^+$, $K^+$ | mg/L | ICP-OES | 0.2 |
| $Mg^{2+}$, $Ca^{2+}$, Fe | mg/L | ICP-OES | 0.02 |
| $Cl^-$, $F^-$, $SO4^{2-}$, $NO^{3-}$ | mg/L | Ion chromatography | 0.1 |
| Mn | mg/L | ICP-OES | 0.002 |
| As | mg/L | FIAS AAS | 0.002 |
| DOC, Si | mg/L | Photometric | 0.5 |
| $NH_4^+$ | mg/L | Colorimetric determination | 0.05 |
| $NO_2^-$ | mg/L | Colorimetric determination | 0.005 |
| $S^{2-}$ | mg/L | Colorimetric determination | 0.02 |
| $HCO_3^-$ | mmol/L | Titrimetric determination | 0.2 |

The limit of quantification is three times the respective limit of detection

Total N is the sum of $NH_4$-N, $NO_2$-N, and $NO_3$-N, which were determined by dividing the measured concentrations of $NH_4^+$, $NO_2^-$ and $NO_3^-$ (in mg/L) by their respective molar masses (18, 46 and 62 mg/mmol). To be consistent with the units, the resulting total N (mmol/L) was multiplied by the molar mass of N (14 mg/mmol) so that total N concentrations in solution are also depicted in mg/L.

### Water Level Measurements

Water levels have to be measured against a reference datum (in this case mean sea level) to understand the hydraulic conditions at the field site. A leveling survey was conducted to determine the top casing elevation of one handpump (H3), four observation wells (obs_A, obs_B, obs_C, obs_D), and two Ranney wells (P3 and P4). Depth to water was measured in those sampling points on 16th November 2013. Both Ranney wells were not operating the entire day.

### Sediment Analyses

Grain size analyses and loss on ignition (LOI) were conducted on 14 aquifer material samples and one riverbed sediment sample. The origin of the samples is shown in Fig. 3.3. Grain size distribution was determined based on the DIN 18123 guidelines. 150–500 g of sample material were mixed with water and sodium pyrophosphate ($Na_4O_7P_2 \cdot 10H_2O$) and shaken for 24 hours. The fine-grained fraction (< 0.063 mm) was separated by wet sieving. If the sample contained a fine-grained fraction above 10 wt%, the fraction was further analyzed by gravitational sedimentation using the Casagrande hydrometer method. The sand and gravel fraction was dried and analyzed by dry sieving. In case the samples contained calcareous nodules, which were disaggregated in the process, the sieve test was repeated with undisaggregated sediment. To quantify the maximum share of organic material in the sediments, the LOI was determined at 550°C because most organic compounds transfer into $CO_2$ and $H_2O$ at temperatures over 500°C (Dean 1974). 10 g-portions of dry, homogenized sample material were heated to 550°C for 24 hours. The weight loss was measured after a cooling period in a desiccator.

Pyrite analysis[6] was conducted on one sample of the saturated zone (B3_35). In a first step, the complete sample was checked under a reflected light microscope. In a second step, heavy metal separation was conducted on the grain size fraction of 63–200 µm and the heavy metal fraction was examined under a stereomicroscope.

### Hydraulic Conductivities

Hydraulic conductivities were derived from the grain size analyses of the disaggregated sand samples and the undisaggregated kankar samples. Hydraulic conductivities for groundwater temperature of 10°C were calculated according to Eq. 3.1 (Beyer 1964) and temperature corrected to 25°C using Eq. 3.2 (Hazen 1893):

$$K_{10} = C \times d_{10}^2 \tag{3.1}$$

$$K_T = K_{10} \times (0.7+0.03T) \tag{3.2}$$

C is a factor dependent on the uniformity coefficient (U) of the sediment (Beyer 1964); $d_{10}$ is the "effective size" of the sediment (the grain diameter determined by the grain size distribution curve at 10 wt%) and T is the temperature on the centigrade scale.

### Laboratory Column Experiments

To determine the amount of $NH_4^+$ reversibly sorbed on the sediment matrix, laboratory column tests were conducted with five of the 14 analyzed sediment samples (origin shown in Fig. 3.3). The columns were flushed with $NH_4^+$-free water with a similar cation composition as the groundwater from the handpump H3. The effluent was collected under Ar-gas atmosphere to prevent the oxidation of $NH_4^+$ and the equilibration of the effluent with atmospheric nitrogen. The effluent was sampled twice per day. Flushing of the columns continued until the measured nitrogen concentrations in the effluent were sufficiently low. Nitrogen loading of the sediment was determined by setting up mass balances. It was assumed that all nitrogen desorbed was sorbed on the sediment matrix as $NH_4$-N.

$NH_4$-N, $NO_2$-N and $NO_3$-N concentrations in the effluent were measured photometrically with detection limits of 0.01 mg/L, 0.005 mg/L and 0.1 mg/L, respectively. While all solute concentrations (except for $HCO_3^-$) are given in mg/L, the results of the mass balance calculations are given in mmol N/100g sediment and millimole equivalents (meq) $NH_4^+$/100g sediment to comply with standard conventions.

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[6] The pyrite analysis was conducted in a commercial lab (LAOP- Consult).

# 3.4 RESULTS

## 3.4.1 Sediment Characterization

### Bore Logs

The shallow alluvial aquifer is covered by an about 4 m thick layer of clayey silt and fine–medium sand (chapter 4). The saturated zone consists of two lithological units, medium sand and kankar. The transition between the two units is gradual. The aquifer is underlain by brown silt-clay, which was found at depths between 14.5 and 16 m in all four deep drillings.

In the five drillings at distances between 250 and 550 m from the river the sand and kankar form two distinct layers: the medium sand reaches up to depths between 13.5 and 15 m and is underlain by a 1–2 m thick kankar layer. In drilling B35, the two layered build-up of the aquifer was not found: Instead, a thin kankar layer was encountered at a depth of 14 m, but unlike at the other locations, it was underlain by a 2 m thick sand layer (Fig. 3.3).

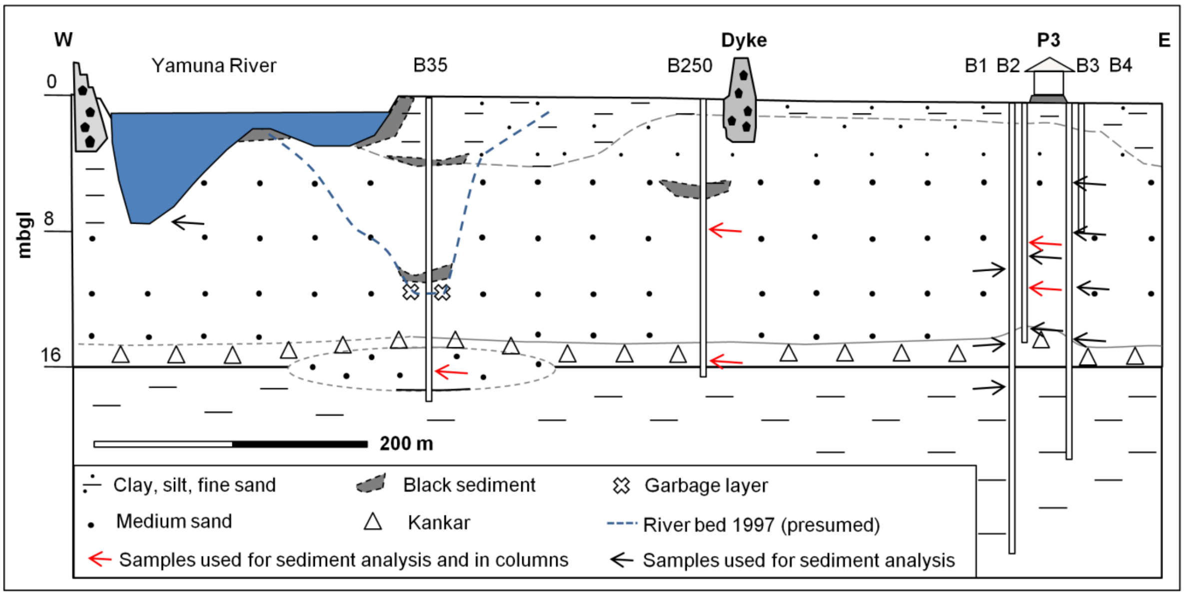


**Fig. 3.3** Cross section of the study area with the origin of the analyzed samples. The delineation of the fine grained unsaturated zone was done using additional shallow drillings.

### Grainsize Distribution and Hydraulic Conductivities

The medium sand is well sorted with a fine sand proportion between 15 and 30 % and less than 5 % coarse sand (Fig. 3.4). In this sediment, hydraulic conductivities determined from the grain size distribution ranged between $2.3\times10^{-4}$ and $3.2\times10^{-4}$ m/s (Table 3.3). The undisaggregated kankar (no addition of sodium pyrophosphate and no shaking of the sample before sieving) is poorly sorted with grain sizes from medium sand to gravel and hydraulic conductivities between $3.1\times10^{-3}$ and $4.2\times10^{-3}$ m/s. When the kankar samples were disaggregated (addition of sodium pyrophosphate and shaking), the sieve curves changed significantly: The proportion of the fine grain fraction increased from nil to 26–28 % while the gravel size fraction decreased by about 10 % and the sand sized fraction decreased by about 20 %. The transition zone between the sand and the kankar layers is characterized by an increasing proportion of coarse sand and gravel.

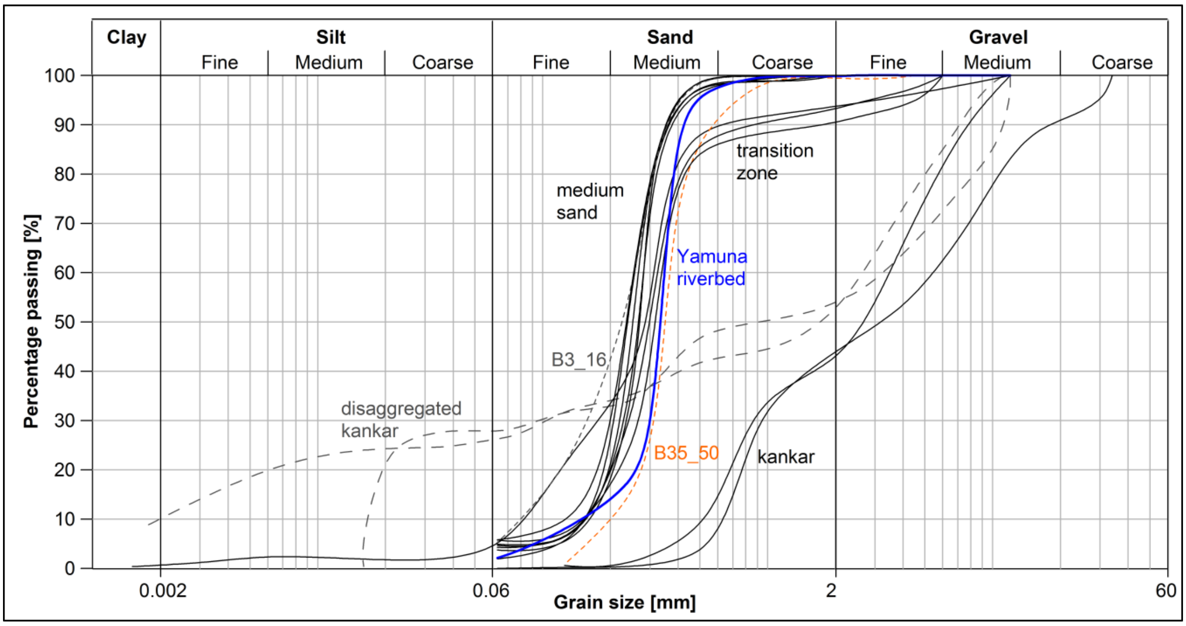


**Fig. 3.4** Grain size distribution of the sediment samples. The Yamuna riverbed sample is depicted in blue, the sample taken from the sand lense below the kankar layer in bore B35 is shown in orange.

**Table 3.3** Calculated hydraulic conductivities (K) and loss on ignition of the different sediment samples.

| Sediment sample[A] | Origin | Depth (mbgl) | Zone | K at 25°C (m/s)[B] | LOI (%) |
|---|---|---|---|---|---|
| B35_50 | B35 | 15 | sand lense | 6.4E-04 | 1.2 |
| B250_25 | B250 | 7.5 | transition zone | 8.6E-05 | 1.3 |
| B250_45 | B250 | 14 | kankar | 3.1E-03 | 1.3 |
| B1_32 | B1 | 10 | sand | 3.2E-04 | 0.5 |
| B1_45 | B1 | 14 | kankar | 4.2E-03 | 1.3 |
| B1_55-80 | B1 | 17-24 | Older Alluvium | * | 2.1 |
| B2_27 | B2 | 8 | sand | 2.9E-04 | 0.7 |
| B2_30 | B2 | 9 | sand | 3.1E-04 | 0.7 |
| B2_35 | B2 | 10.5 | sand | 2.8E-04 | 0.6 |
| B2_40 | B2 | 12 | kankar | NA | 1.2 |
| B3_16 | B3 | 5 | sand[C] | 1.1E-04 | 0.6 |
| B3_25 | B3 | 7.5 | sand | 2.3E-04 | 0.6 |
| B3_35 | B3 | 10.5 | transition zone | 3.1E-04 | 1.1 |
| B3_43 | B3 | 13 | transition zone | 3.2E-04 | 0.8 |
| Yamuna | Riverbed | -- | Yamuna sand | 2.4E-04 | NA |

[A] Sample IDs show the name of the bore (first part) and the depths in ft below ground level (second part)

[B] Calculated according to equations 3.1 and 3.2

[C] Shallow sample (transition from fine grained top layer)

*Beyer equation was not valid

NA: not analyzed

### Loss on Ignition and Pyrite Analysis

The loss on ignition was between 0.5 and 2.1 % in all samples (Table 3.3). The medium sand samples had lower LOI (average: 0.6 %) than the kankar samples, which had an LOI between 1.2 and 1.3 %. The sample from the underlying clay aquitard had the highest LOI of 2.1 %. No pyrite was found in sample B3_35.

### Riverbed Sediments

In drilling B35, a 0.5–1 m thick layer of sand mixed with plastic garbage was encountered at a depth of 11 m. The use-by and sell-by dates on the packaging revealed that it was deposited around the year 1997. As garbage disposal in the river is common practice in the study area, it can be assumed that the garbage layer indicates the riverbed of around 1997. This assumption is confirmed by satellite images showing the meanders of the river at that time. Furthermore, a few kankar nodules were found in this layer, indicating sediment reworking.

Today, the river in the study area has a depth of over 7 m. Two types of riverbed sediments were encountered: clayey-loamy sediments with assumed low hydraulic conductivities (not measured) and poorly graded medium sand, similar to the sandy aquifer material, with a saturated hydraulic conductivity of $2.4\times10^{-4}$ m/s. The clayey, loamy sediments were mostly found in the shore area and close to a small sandbank in the center of the river; the medium sand was found in the middle of the riverbed (Fig. 3.5). Sometimes the clayey sediments contained some sand.

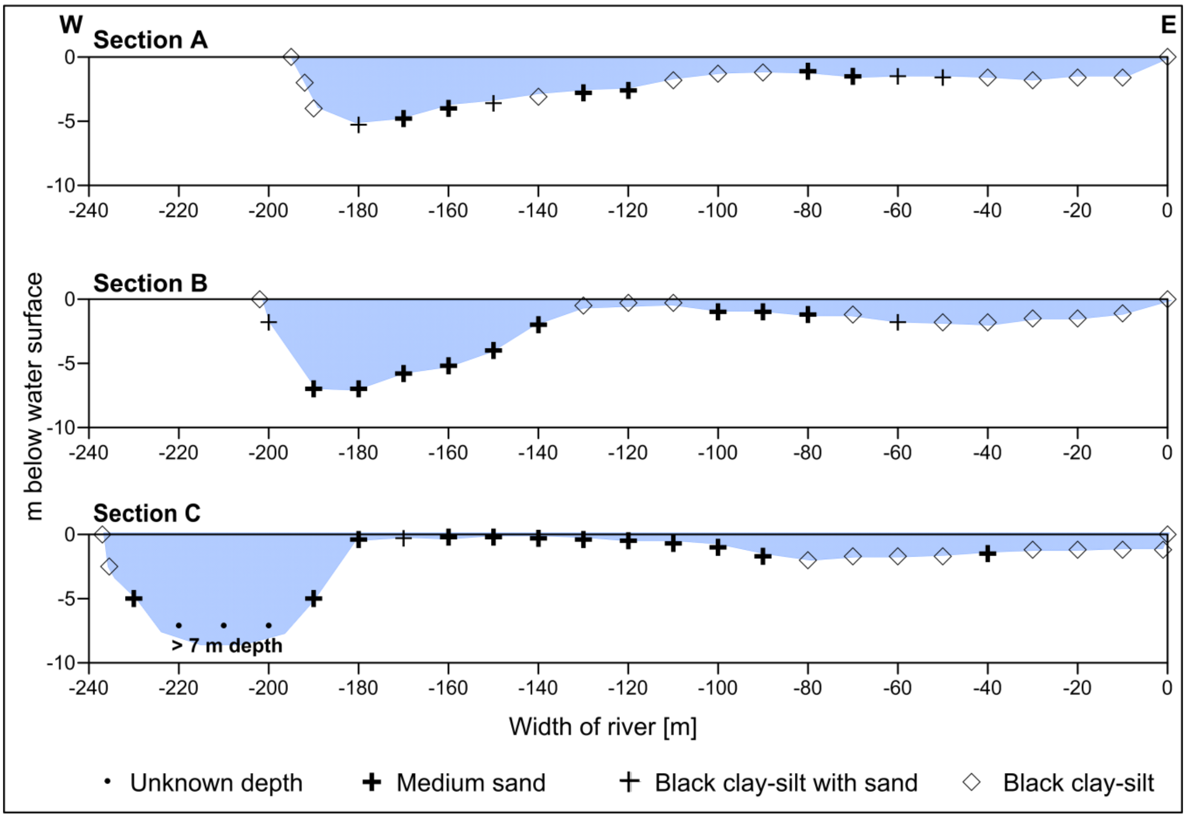


**Fig. 3.5** Depth of river and type of sediments encountered. The location of the three profiles is shown in Fig. 3.2.

### 3.4.2 Hydraulic Heads

The hydraulic heads determined at six sampling points revealed a west – east gradient in the potentiometric surface at the study area, indicating losing stream conditions (Fig. 3.6). The head difference of 2.27 m between P3 and P4 (distance: 710 m) results in a W−E gradient of 3 ‰, the head difference of 0.33 m between H3 and P3 (distance: 440 m) results in an NW–SE gradient of 0.7 ‰. It was not possible to determine the exact direction of the groundwater flow due to the distribution of the leveled sampling points.

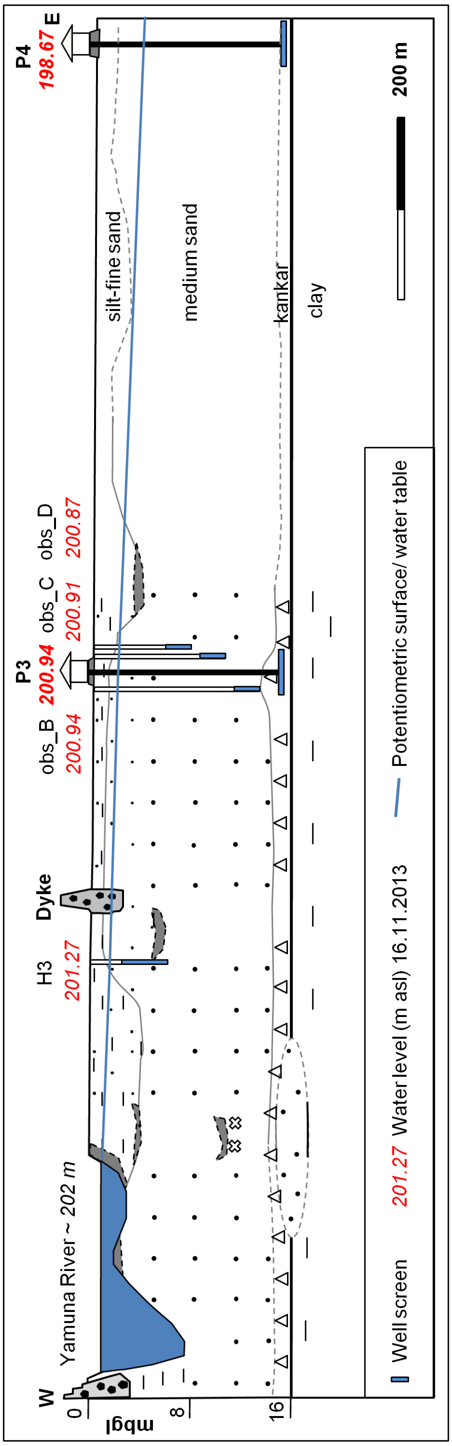


**Fig. 3.6** Hydraulic heads (in masl) measured in the leveled sampling points. Note that sampling point H3 does not lie in the transect path but was projected. The subsurface part of the dyke is made up of large boulders and is therefore not impermeable.

## 3.4.3 Hydrochemistry

### River Water Composition and Seasonal Changes in Nitrogen Concentrations in the Yamuna

River water compositions varied from monsoon to non-monsoon season (Fig. 3.7). This can be seen in almost all measured parameters, especially in the electric conductivity, which lies in the range of 1560–1760 µS/cm in non-monsoon times while only 400 µS/cm were measured during monsoon times. High $NH_4^+$ concentrations during non-monsoon times correlate with low oxygen, low $NO_2^-$ and low $NO_3^-$ concentrations (mostly below detection limit) as well as with high $HCO_3^-$, elevated $K^+$ and high $Na^+$, $Cl^-$ and DOC concentrations (Table 3.4). Maximum $NH_4^+$ concentrations of 20 mg/L were measured in October and December 2012. Minimum $NH_4^+$ concentrations of 2.5 mg/L were measured during the monsoon season in July 2013; at the same time, maximum $NO_3^-$ concentrations of 3.4 mg/L were found.

### General Groundwater Chemistry

The water samples taken from sampling points with well screens within the floodplain aquifer have a different water composition than the groundwater samples collected from obs_A with a well screen in the underlying brown sediments (Fig. 3.7).

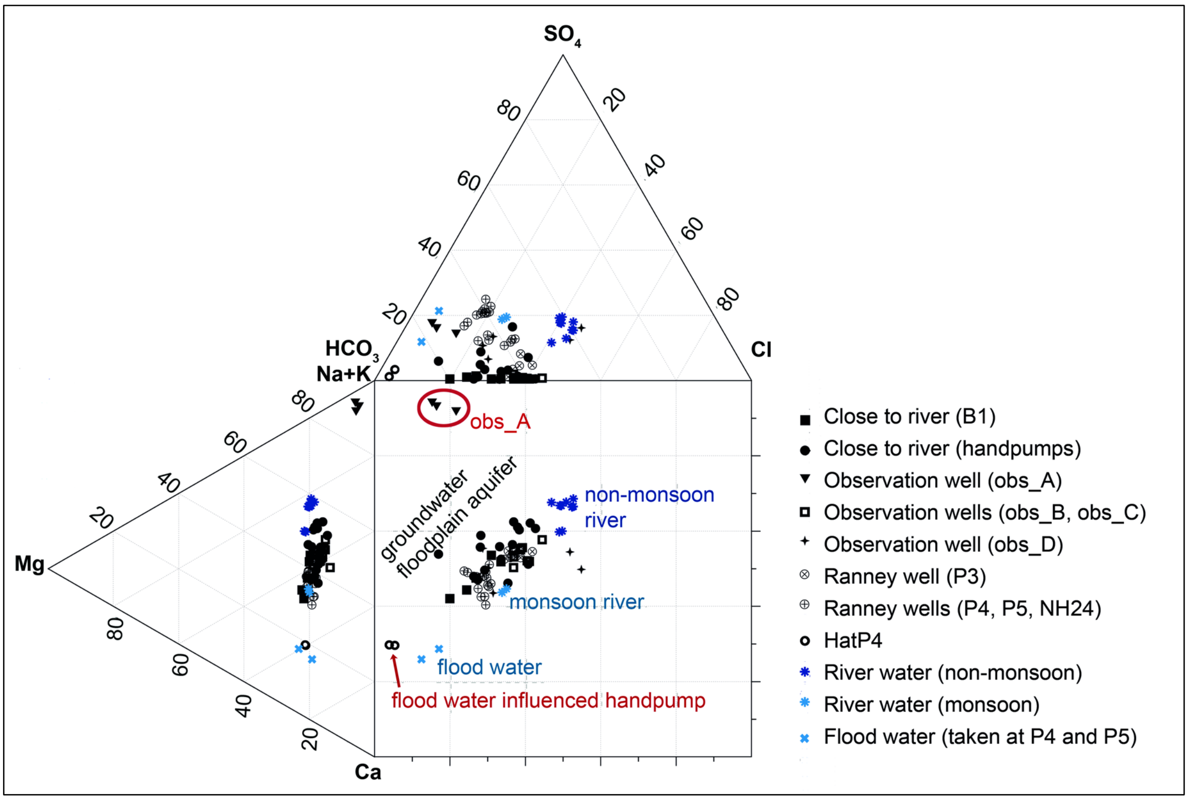


**Fig. 3.7** Durov plot of water samples taken at the field site.

High EC values (750−2000 µS/cm) and high bicarbonate contents (4.5−14.5 mmol/L) are characteristics of the groundwater samples from the floodplain aquifer. Both parameters are higher in the groundwater sampling points close to the river (≤500 m from the riverbank) than in the

Ranney wells farther away from the river. This spatial variation can also be discerned in the redox-sensitive parameters Fe, Mn, $SO_4^{2-}$ and $NH_4^+$ (Fig. 3.8). While Fe is absent in the river water, concentrations up to 22.3 mg/L were measured in the groundwater close to the river. In groundwater samples taken at a greater distance from the river (in Ranney wells P4, P5, NH24), Fe concentrations remained below 0.5 mg/L with a mean concentration of 0.16 mg/L. Mn concentrations show a similar trend, but concentrations are lower in sampling points close to the river (up to 3.4 mg/L). In the Ranney wells, Mn concentrations are slightly higher than Fe concentrations with a mean Mn concentration of 0.5 mg/L. $SO_4^{2-}$ shows an inverse development. $SO_4^{2-}$ concentrations up to 133 mg/L were measured in the river water, but handpumps and observations wells <500 m from the river only have low $SO_4^{2-}$ concentrations (bdl−47 mg/L with one outlier), with the exception of the shallow observation well obs_D. In the Ranney wells farther away from the river, $SO_4^{2-}$ concentrations increase with increasing distance from the river. The distribution of $NH_4^+$ is discussed in detail in the following section. As can be seen in all graphs of Fig. 3.8, the measured values have a greater variation in the sampling points close to the river, indicating that the seasonal effect is especially high in this zone.

### Nitrogen Species in the Groundwater

The groundwater samples show a high spatial and temporal variation of $NH_4^+$ concentrations (Fig. 3.9). In the sampling points close to the river (35 and 250 m from the riverbank), $NH_4^+$ was found to be the dominating nitrogen species. In all samples (22 out of 24) taken at sampling points near the river − except for samples from H3 in April 2012 and H1 in December 2012 – more than 99.5 % of the total nitrogen was found in the form of $NH_4$-N. Most of the missing 0.5 % of nitrogen was measured in the form of $NO_2$-N while $NO_3$-N was below detection limit in most samples. In the observation wells obs_B and obs_C at a distance of 500−550 m to the riverbank, the distribution of nitrogen species is similar.

Only in the shallow observation well obs_D with a depth of well screen of 5.5–7.5 m, the proportion of $NH_4^+$ varies between 0.2 and 86 %. $NO_3^-$ contributes between 13.9 and 99.3 % of the total nitrogen while the proportion of $NO_2^-$ remains below 0.5 %.

In the Ranney well P3, $NH_4^+$ concentrations between 5.5 and 8 mg/L and $NO_3^-$ concentrations between below detection limit (0.1 mg/L) and 4.2 mg/L were measured. The highest $NO_3^-$ proportion was measured in December 2013, where 17.6 % of the total nitrogen was found in form of $NO_3$-N. In March 2012 the highest $NO_2$ concentrations in Ranney well P3 (0.4 mg/L corresponding to 1.7 % of the total nitrogen) were measured.

In the Ranney wells P4 and P5, $NH_4^+$ concentrations remained below 1 mg/L, while $NO_3^-$ concentrations of up to 10 mg/L were found. The percentage of $NH_4^+$ with regard to total nitrogen varied between 7 and 62.5 % and was mostly clearly below 50 %. In Ranney well NH24, the $NH_4^+$ concentrations were slightly higher than in P4 and P5 – between 1 and 1.65 mg/L. In the two samples taken at a handpump near Ranney well P4 (HatP4), $NO_2^-$ concentrations of 0.005 mg/L were found. $NH_4^+$ and $NO_3^-$ remained below detection limit.

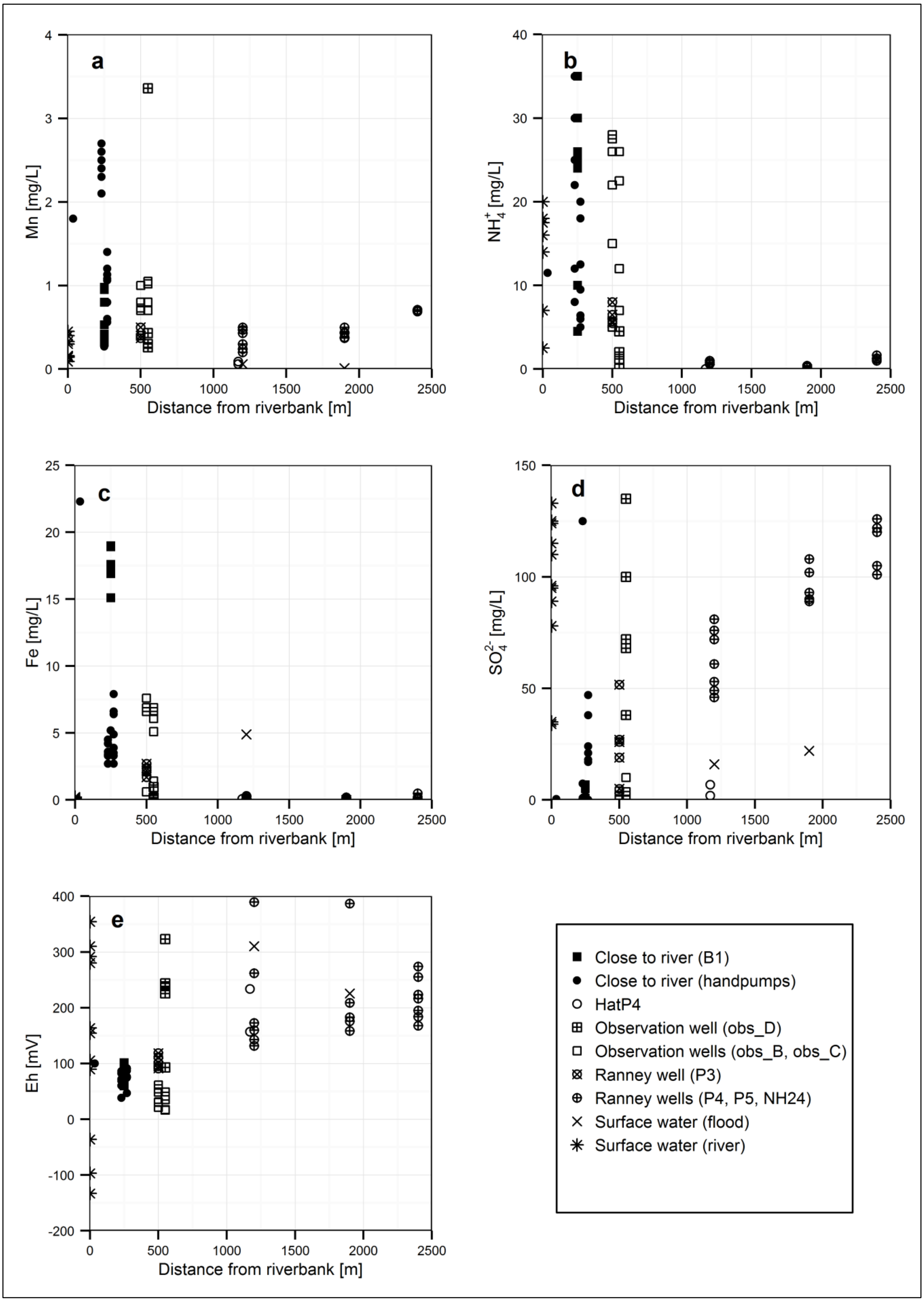


**Fig. 3.8** Relation of (a) Mn, (b) $NH_4^+$, (c) Fe and (d) $SO_4^{2-}$ concentrations and (e) E*h* to the distance of the sampling point from the river. Observation well obs_D is very shallow (7.5 m deep) and, therefore, shows particular high $SO_4^{2-}$ and low $NH_4^+$ concentrations.

**Table 3.4** Solute chemistry of Yamuna River water samples. Phosphate concentrations remained below 3.6 mg/L.

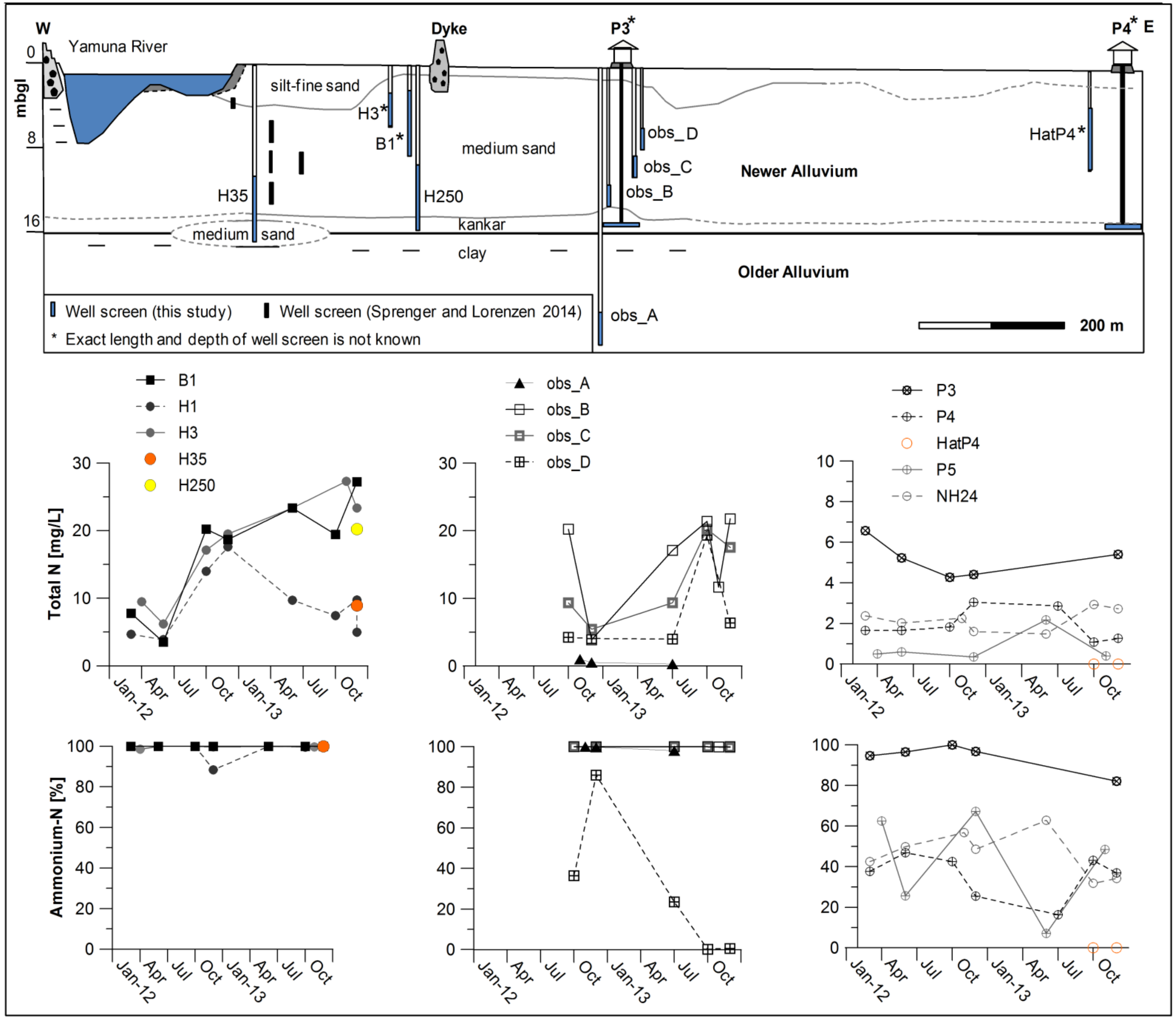
| Site | Date | T | EC | pH | ORP | $O_2$ | $HCO_3^-$ | $NO_2^-$ | $NH_4^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $Na^+$ | $K^+$ | $Cl^-$ | $SO_4^{2-}$ | $NO_3^-$ | $F^-$ | Fe | Mn | Si | DOC | As |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | °C | µS/cm | | mV | mg/L | mmol/L | mg/L | | | | | | | | | | | | | | |
| SW1 | Apr-12 | 28.8 | 1760 | 7.33 | -335 | 0.03 | 7.0 | 0.03 | 14 | 68.5 | 34 | 187 | 17 | 250 | 96 | bdl | 0.7 | 0.22 | 0.45 | 7.4 | 5.4 | 0.002 |
| SW2 | Oct-12 | 26.8 | 1624 | 7.62 | -299 | 0.04 | 7.0 | 0.012 | 18 | 66.2 | 35.9 | 183 | 16.1 | 210 | 78 | bdl | 0.8 | 0.07 | 0.4 | 7.1 | 15 | 0.002 |
| SW3 | Oct-12 | 26.9 | 1621 | 7.61 | -238 | 0.04 | 6.5 | 0.005 | 20 | 65.1 | 36.2 | 191 | 16.3 | 254 | 115 | bdl | 0.7 | 0.2 | 0.4 | 7.1 | 17 | 0.002 |
| SW4 | Dec-12 | 19.7 | 1566 | 7.47 | -97 | 0.53 | 6.4 | 0.005 | 17.5 | 64.5 | 33.9 | 170 | 15.1 | 211 | 124 | bdl | 0.7 | 0.05 | 0.3 | 7.5 | 12.1 | 0.002 |
| SW5 | Dec-12 | 20.5 | 1588 | 7.6 | -112 | 0.5 | 6.5 | 0.02 | 20 | 65.4 | 33.7 | 171 | 15.4 | 218 | 125 | bdl | 0.7 | 0.07 | 0.3 | 7.4 | 8 | bdl |
| SW6* | Jul-13 | 32.8 | 398 | 7.76 | 108 | 5.36 | 2.1 | 0.2 | 2.5 | 34.4 | 9.6 | 26.4 | 5.8 | 33 | 34 | 3.4 | 0.4 | 0 | 0.09 | 4.9 | 2.2 | 0.003 |
| SW7* | Jul-13 | 33.1 | 402 | 7.83 | 78 | 5.48 | 2.3 | 0.22 | 2.5 | 35 | 9.4 | 25.6 | 5.7 | 34 | 35 | 3.4 | 0.3 | 0 | 0.16 | 4.9 | 2.2 | 0.004 |
| SW8 | Oct-13 | 25.5 | 1069 | 7.54 | 152 | 2.23 | 4.2 | 0.5 | 7 | 60.7 | 26.8 | 109 | 9.3 | 137 | 89 | bdl | 0.5 | 0.02 | 0.15 | 6.3 | 15 | 0.003 |
| SW9 | Oct-13 | 24.9 | 1058 | 7.63 | 87 | 2.35 | 4.3 | 0.56 | 7 | 59.8 | 27.3 | 109 | 9.1 | 146 | 95 | 0.8 | 0.5 | 0.03 | 0.14 | 6.9 | 5.6 | 0.003 |
| SW10 | Dec-13 | 21.5 | 1557 | 7.5 | -48 | 1.59 | 6.2 | 0.025 | 14 | 70.7 | 38.5 | 186 | 14.5 | 243 | 133 | bdl | 0.7 | 0.15 | 0.3 | 6.7 | 14.4 | 0.002 |
| SW11 | Dec-13 | 18.5 | 1621 | 7.54 | -38 | 1.15 | 6.2 | 0.04 | 16 | 69.6 | 36.6 | 180 | 14.9 | 238 | 110 | 2 | 0.7 | 0.17 | 0.33 | 9.3 | 19 | 0.003 |

bdl: below detection limit

*samples taken during monsoon time

**Fig. 3.9** Depths of well screens of the sampling points (above) and total N concentrations and the proportion of $NH_4$-N (below). H1 does not lie on the transect but is projected. Locations of sampling points are given in Fig. 3.1.

(Approximate locations of the well screens of the study by Sprenger and Lorenzen (2014) are depicted. Their data was taken in 2006, when the shoreline of the river was approximately at the same position as it was in 2012-2013.)



**Arsenic**

All samples with high $NH_4^+$ concentrations also had high As concentrations, although there is no linear correlation between the two parameters (Fig. 3.10). As concentrations above 0.05 mg/L were only measured in samples in which no $NO_3^-$ was present and elevated Fe concentrations occurred. All sampling points with E*h* values >130 mV had As concentrations below 29 µg/L (Appendix 2).

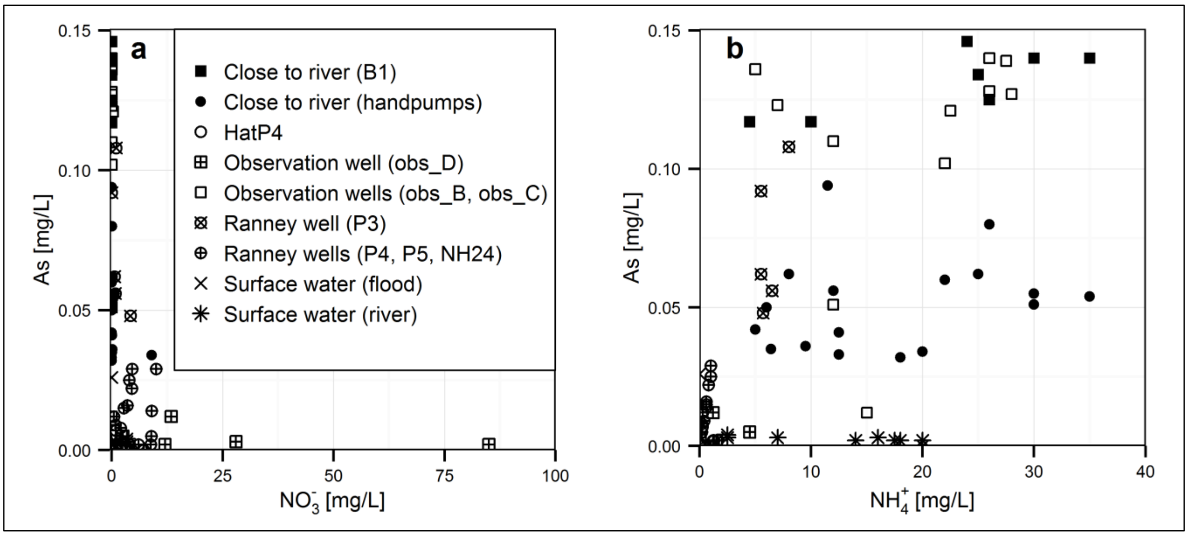


**Fig. 3.10** Relation of As to (a) $NO_3^-$ and (b) $NH_4^+$.

## 3.4.4 Ammonium Sorption on the Aquifer Matrix

The amount of $NH_4^+$ released from different sediment samples, determined by column experiments, is shown in Table 3.5. The comparatively high amount of nitrogen released from the sediments close to the river (35 m and 250 m) correspond to an $NH_4^+$ sorption of 0.13−0.15 meq $NH_4^+$/100g sediment, assuming that all nitrogen was originally present in the sediment as $NH_4$-N. This indicates that those drillings were conducted in the center of the $NH_4^+$ plume. In contrast, very little nitrogen was released from the two samples taken at a distance of 500 m.

**Table 3.5** Amount of nitrogen released from different sediment samples.

| **Sediment** | **Sample** | **Distance to river (m)** | **Depth (m)** | **N released from sediment (mmol/100g)** | |
|---|---|---|---|---|---|
| | | | | **Column 1** | **Column 2** |
| Sand | B2_27 | 500 | 8.2 | 0.03 | 0.02 |
| | B2_35 | 500 | 10.7 | 0.00 | 0.01 |
| | B35_50 | 35 | 15.2 | 0.13 | n/a |
| Sand mixed with kankar (transition zone) | B250_25 | 250 | 7.6 | 0.15 | n/a |
| Kankar | B250_45 | 250 | 13.7 | 0.13 | 0.13 |

n/a: not applicable because experiments were only conducted with one column

## 3.5 DISCUSSION

### 3.5.1 Aquifer Characteristics and River – Groundwater Interactions

The shallow aquifer (Newer Alluvium) consists of two permeable lithologies, medium sand and kankar, and is covered by finer grained sediments (mostly silt – Chapter 4). The aquifer is, therefore, semi-confined or unconfined depending on the depth of the water table or piezometric surface and the thickness of the top fine-grained zone. A clay-silt layer was found at depths between 14.5 and 16 mbgl in all four bores with more than 15 m depth. This layer can be assigned to the Older Alluvium as described by Kazim et al. (2008). The top of the Older Alluvium typically consists of brown silt-clay, whereas the sediments of the Newer Alluvium are grey in color and have a high proportion of mica (muscovite-biotite). Furthermore, the authors reported the occurrence of Older Alluvium at 14 mbgl at this field site. The older alluvial clay-silt layer is several meters thick. It has very low hydraulic conductivities and functions as an aquitard and, therefore, could be used as a lower boundary of the aquifer in a flow and transport model. Contrary to the descriptions of Sprenger and Lorenzen (2014), no dipping of the top of the Older Alluvium towards the east was observed.

The kankar layer is only 1–2 m thick and overlies the clay layer. It was found as a very distinct layer in the bores B250, B1, B2, and B3. In bore B35, the kankar layer was found not to be as distinct as in the other bores. Instead, two thin (only a few decimeters thick) kankar layers were divided by a sand layer. Given the fact that the riverbed sediments from 1997 were found at 12 mbgl in this borehole, it can be concluded that the irregular kankar layer found at 16 mbgl is also due to reworking of the sediments through the river. The kankar layer consists of some actual gravel particles and mostly gravel-sized calcareous nodules. Hydraulic conductivities in the kankar determined from grain size distribution (average: $3.7 \times 10^{-3}$ m/s) are one order of magnitude higher than the hydraulic conductivities of the sand (average: $2.9 \times 10^{-4}$ m/s), indicating that the kankar is the main pathway for groundwater despite the small thickness of the layer. However, because of the irregular shape of the kankar nodules and the large uniformity coefficient ($d_{60}/d_{10}$) of the sediment, the real hydraulic conductivity of the kankar layer might be lower as clogging of pore spaces is likely to occur. Although the Beyer equation (Eq. 3.1) takes into account both the grain size diameter $d_{10}$ and the uniformity coefficient, it was not developed for this kind of sediment.

According to most literature, kankar is typically found in the sediments of the Older Alluvium and is absent in the Newer Alluvium (CGWB 2006a, Shekhar and Prasad 2009). Only Kazim et al. (2008) report about kankar occurrences in the Newer Alluvium. This is confirmed by the bore log data of this study, as no clear boundary between the Newer Alluvium and the Older Alluvium could be discerned above the brown clay-silt layer, which was assigned to the Older Alluvium. Kankar is often found at parting zones between granular layers (i.e. above clay layers), which is the case at the field site.

The river and the aquifer have a good hydraulic connection. Medium sands with a hydraulic conductivity of $2.4 \times 10^{-4}$ m/s were found in the center of the Yamuna River while black silt-clays were found mostly at the borders of the river. This distribution of riverbed sediments is typical for a meandering river, where high flow velocities and high sediment loads, especially at flood events during the monsoon times, prevent the formation of colmatage layer at the center of the riverbed. The depths to water measurements in the groundwater sampling points indicate a clear hydraulic gradient from the western shoreline towards the East. Losing stream conditions, therefore, prevail at the field site, which is in accordance with the findings of Lorenzen et al. (2010). Due to a gradient of 3 ‰ between the wells P3 and P4 and the fact that further wells are located East of P4, it is unlikely that the wells P3 and P4 draw any share of ambient groundwater apart from the natural groundwater recharge on the floodplain. Although the depth to water measurement of all leveled sampling points in one day was carried out only once, measurements taken during water samplings indicate that the hydraulic conditions are similar throughout the year and are not a seasonal effect.

### 3.5.2 Hydrochemistry and Redox Zonation

Reducing conditions were found in the areas close to the Yamuna River. While $SO_4^{2-}$ concentrations between 34 and 133 mg/L were measured in the river water, concentrations were substantially lower in the groundwater sampling points within a distance of 550 m from the river (Fig. 3.8) indicating that a sulfate reducing zone is present along the flow path of the infiltrating water. High Fe concentrations of up to 22.3 mg/L are an indication for the reductive dissolution of iron oxyhydroxides in this zone. Arsenic concentrations above the permissible limit of 0.05 mg/L (IS 10500: 2012) were only found in the groundwater of this zone.

Farther away from the river, the groundwater becomes less reducing probably due to groundwater recharge from the floodplain. The presence of $NO_3^-$ and only slightly elevated Mn concentrations are indicators for suboxic conditions. Results of dissolved oxygen measurements during groundwater sampling are not reliable because only handpumps and Ranney wells - where the water is mixed with oxygen during pumping - were sampled in this zone. Sulfate concentrations gradually increase with distance to the river. This indicates that oxidation of sulfide minerals (other than pyrite, which was not found in the sediment) occurs in the aquifer. This is supported by results of column experiments conducted with aquifer material (from the saturated zone), which was flushed with sulfur-free water. Whenever experiments took place under anoxic conditions, $SO_4^{2-}$ concentrations <1 mg/L were measured in the column effluent. However, under oxic conditions $SO_4^{2-}$ concentrations of up to 25 mg/L were detected (data not shown). In column experiments conducted under oxic conditions with sediments from the unsaturated zone, no elevated $SO_4^{2-}$ concentrations were measured in the column effluent. This is in agreement with the low $SO_4^{2-}$ concentrations found in the shallow handpump HatP4, while $SO_4^{2-}$ concentrations between 46 and 81 mg/L were measured in P4.

### 3.5.3 Ammonium Contamination

Seasonal variations in river water composition lead to a fluctuating nitrogen load and nitrogen speciation in the river throughout the year. In non-monsoon times, when Wazirabad barrage is closed and little dilution with uninfluenced river water can occur, the discharge of sewage water leads to reducing conditions in the Yamuna River, with E*h* values as low as -133 mV. DO concentrations between 0.03 and 2.35 mg/L, DOC concentrations up to 19 mg/L and $NH_4^+$

concentrations of up to 20 mg/L were measured in the river water at the study site. $NO_3^-$ concentrations remained below the detection limit (0.1 mg/L) in most samples (7 out of 9). During monsoon time precipitation and – to a lesser extent – snow melt lead to high discharge in the river (Kumar et al. 2005, Babu et al. 2014). Wazirabad barrage is open, the sewage water discharged into the river is diluted and oxic conditions (E*h* of up to +310 mV and DO concentrations of 5.36–5.48 mg/L) prevail in the river: $NO_3^-$ concentrations of 3.4 mg/L were measured. This seasonal effect has been reported by several authors (e.g. Jha et al. 1988, CPCB 2006) and was confirmed in this study concerning the speciation and concentration of nitrogen.

The seasonal variability of river water composition leads to a strongly fluctuating $NH_4^+$ input into the aquifer through infiltrating river water and subsequently to varying $NH_4^+$ concentrations in the aquifer. In the sampling points close to the river as well as in the observation wells obs_B and obs_C located near Ranney well P3, $NH_4^+$ is the dominating nitrogen species with highly variable concentrations, e.g. between 5 and 28 mg/L in obs_B. These variations are likely to be due to a large part to the changing $NH_4^+$ input from the river, but the retardation of $NH_4^+$ in the aquifer due to cation exchange processes (Ceazan et al. 1989) makes it impossible to trace back maximum and minimum concentrations to corresponding river water concentrations.

Sometimes $NH_4^+$ concentrations in the plume (up to 35 mg/L) exceed the maximum measured $NH_4^+$ concentrations in the river water during this study (20 mg/L). This can be due to different processes. One possibility is the mineralization of organic nitrogen by heterotrophic bacteria. Doussan et al. (1998) described this process at a riverbank filtration site in France, and Lorenzen et al. (2010) supposed that this process, along with agricultural return flow, is a major additional source of $NH_4^+$ at the field site. However, the organic matter content in the aquifer material was found to be only between 0.5 and 1.3 %, and, therefore, it is unlikely that this process is a significant source of $NH_4^+$ in the groundwater. Another possibility is that maximum $NH_4^+$ concentrations in the river are higher than the concentrations measured in the five sampling campaigns during this study. $NH_4^+$ concentrations in the river depend on sewage input and dilution, which can frequently change. Pekdeger et al. (2008) reported $NH_4^+$ concentrations between 0.2 and 35 mg/L in the river water during the year 2007, and the Central Pollution Control Board measured concentrations between 0.3 mg/L and 33.3 mg/L in the years 1999–2005 (CPCB 2006).

Results of the column experiments indicate that a fingering effect of the $NH_4^+$ plume exists in the aquifer. This effect can occur, for example, when a preferential flow takes place in more hydraulic conductive layers of the aquifer, where the contaminant spreads faster than in the other layers (Patrick et al. 1987, p.56). This assumption can be drawn from the amounts of $NH_4^+$ desorbed from different sediment samples in comparison to the $NH_4^+$ concentrations measured in the groundwater. The amount of $NH_4^+$ sorbed on the sediment matrix through cation exchange depends on sediment characteristics, $NH_4^+$ concentrations and solute composition of the groundwater. The sediments samples taken from bores close to the river (35 m and 250 m) released 0.13–0.15 mmol N/100g sediment. Assuming that all nitrogen was originally present as $NH_4^+$, this corresponds to a sorption of 0.13−0.15 meq $NH_4^+$/100g sediment (2.3 and 2.7 mg $NH_4^+$/100g sediment). Shortly after the drilling, $NH_4^+$ concentrations of 11.5 (B35) and 26 mg/L (B250) were measured in the groundwater.

It can be assumed that the sediment and the groundwater were in equilibrium regarding $NH_4^+$ sorption and that the bores were located in the center of the plume. In contrast, little nitrogen was released from the two sediment samples taken at a distance of 500 m, but high $NH_4^+$ concentrations (e.g. 26 mg/L in obs_B) were measured in the groundwater shortly after the drilling and installation of the observation wells. Due to the 2 m long well screens in those observation wells, water from different micro-layers mixes in the wells and $NH_4^+$ concentrations measured in the groundwater do not have to be in equilibrium with the analyzed sediment samples.

The field data obtained in this study is not sufficient to draw definitive conclusions about the role of the kankar layer regarding the transport of $NH_4^+$. The well screens of the observation wells are located in the sand layer and the observations in support of fingering effects in the $NH_4^+$ plume are only valid for this lithology. However, $NH_4^+$ concentrations in well P3 are low (5.5–8 mg/L) compared to the concentrations measured in obs_B and obs_C, indicating a higher retardation of $NH_4^+$ in the kankar layer, where the horizontal filters of the Ranney well are assumed to be located. Because the kankar layer consists of silt and clay nodules bound by calcareous cement, it can be assumed that the cation exchange capacity (CEC) of this layer is higher than the CEC of the medium sand (see chapter 5) and that the retardation of $NH_4^+$ might be stronger than in the sand layer.

The conceptual model of a mostly sewage-borne $NH_4^+$ plume with highly fluctuating $NH_4^+$ concentrations – even in the center of the plume – and pronounced fingering phenomena contradicts previously published descriptions of the plume distribution. Sprenger and Lorenzen (2014) suggest that the center of the $NH_4^+$ plume is located at a distance of about 50 m to the river at a depth 8–13 m, while the concentrations closer to- and farther away from the river are low. However, the high standard deviations of $NH_4^+$ concentrations indicate that the fluctuations observed in the present study were already present in 2007. According to Pekdeger et al. (2008), $NH_4^+$ concentrations in the observation well at a distance of 50 m to the river with a well screen 7–13 mbgl varied between 0.05 and 32 mg/L. Furthermore, the authors described the belated construction of an observation well at 2 m distance from the river end of 2007, when the projects sampling campaigns were nearly completed. Subsequently, groundwater data from the later observation well is not available for the same period as data from the other observation wells. This data obtained at different times was used by Sprenger and Lorenzen (2014) to depict the $NH_4^+$ plume. In a system with high variations, low concentrations found at one point in time do not allow for the conclusion that concentrations are low at all times. Therefore, the comparatively low $NH_4^+$ concentrations of 5 mg/L next to the river that were used for the previous delineation of the plume are more likely an indication of the infiltration of monsoon-influenced river water. Overall, Sprenger and Lorenzen (2014) compared median $NH_4^+$ concentrations taken over different time spans or even at different times. The $NH_4^+$ concentrations measured in this study do not support their conceptual model of the plume, whereas the present conceptual model of the $NH_4^+$ plume can explain current data as well as previous findings.

Because the speciation of nitrogen is redox-dependent, it is possible that nitrification and anammox influence the transport and fate of $NH_4^+$ at the field site. Nitrification describes the oxidation of

$NH_4^+$ to $NO_2^-$ and then $NO_3^-$, whereby oxygen acts as an electron acceptor. Anammox is the anaerobic ammonium oxidation with $NO_2^-$ or $NO_3^-$ acting as electron acceptors. Reducing conditions prevail in the groundwater close to the river and in observation wells obs_B and obs_C. Nitrification can, therefore, not occur to a significant extent. This is supported by the observation that – with the exception of obs_D – $NO_3^-$ concentrations measured in sampling points down gradient (P4, HatP4, P5 and NH24) varied between below detection limit (0.1 mg/L) and 10 mg/L. $NO_3^-$ moves unretarded with the groundwater flow (Böhlke et al. 2006) and in the case of substantial nitrification higher $NO_3^-$ concentrations would be expected to be found in front of the $NH_4^+$ plume. Because almost all nitrogen is present as $NH_4^+$, electron acceptors necessary for the anammox process are not available. Therefore, anammox is also unlikely to occur at the field site to a significant degree.

## 3.6 CONCLUSIONS

This study confirms that an $NH_4^+$ contamination is present in the floodplain aquifer of the Yamuna River in central Delhi. Due to high $NH_4^+$ concentrations in the river, a good hydraulic connection of the river and the aquifer and prevailing losing stream conditions, the infiltrating river water seems to be the main source of the $NH_4^+$. The contamination already has effects on drinking water production, as elevated $NH_4^+$ concentrations were measured in well P3. They are expected to increase further when the center of the plume reaches the well. Furthermore, elevated $NH_4^+$ concentrations are expected to occur in the other wells in the future. Because of the hydraulic gradient from West to East, it is unlikely that the wells located on the floodplain draw ambient groundwater, apart from the recharge on the floodplain. Thus, dilution through unpolluted, ambient groundwater is limited.

The understanding of the plume distribution has greatly improved, and the new conceptual model can explain data from previous studies as well as the current findings. However, further investigations are necessary to be able to make predictions about the development of $NH_4^+$ concentrations. To be able to understand the transport of $NH_4^+$, the cation exchange capacity (CEC) for the two sediments (sand and kankar) have to be determined. Due to the high proportion of fine grain, it can be assumed that the kankar has a higher CEC and transport of $NH_4^+$ might be therefore slower in this sediment. Column experiments can help to determine whether other mechanisms such as degradation, fixation or mineralization play a role in the sediments besides cation exchange. Furthermore, the influence of agricultural return flow as a further source of $NH_4^+$ at the field site should be investigated.

# Chapter 4

# Characterization of the Unsaturated Zone and Influence of Agricultural Activity on the Ammonium Contamination[7]

## Abstract

At a riverbank filtration (RBF) site in central Delhi unusually high and strongly fluctuating ammonium ($NH_4^+$) concentrations were measured in the groundwater. Sewage contaminated river water has been identified as the main source of the $NH_4^+$ plume. The well field is located on an irrigated agricultural area, and irrigation return flow might have an additional impact on the groundwater contamination, especially as the contaminated river water is partly used for irrigation. To quantify the role of irrigation return flow, sediments of the unsaturated zone were characterized concerning their hydraulic and sorption characteristics; x-ray diffraction for clay mineral analyses and laboratory column studies were conducted with representative sediments. The sediments range between silt and fine–medium sand with calculated hydraulic conductivities between $1.0\times10^{-7}$ and $2.1\times10^{-4}$ m/s and a cation exchange capacity between 0.9 and 37.2 meq/100g sediment. The column experiments show that $NH_4^+$ retardation through cation exchange is the main process occurring in the sediments. Contrary to the results of similar experiments conducted with sediments from the saturated zone, mass balances reveal that $NH_4^+$ fixation or degradation also takes place in significant amounts and up to 0.09 meq $NH_4^+$/100g sediment were transformed this way. This indicates that irrigation return flow can be neglected as a major source of $NH_4^+$ at the field site. Instead, the $NH_4^+$ fixation or degradation in the unsaturated zone might be one reason for the observed variations of $NH_4^+$ concentrations in the groundwater.

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[7] Groeschke M., Kumar P., Winkler A., Grützmacher G., Schneider M. (2016) The role of agricultural activity for ammonium contamination at a riverbank filtration site in central Delhi (India). Environmental Earth Sciences 75(2):1-14. doi:10.1007/s12665-015-4977-3
Available at: http://dx.doi.org/10.1007%2Fs12665-015-4977-3

# Chapter 5

# The Saturated Zone: Transport of Ammonium in Alluvial Sediments – Laboratory Column Experiments and Reactive Transport Modeling[9]

## Abstract

In India‘s capital Delhi, the Yamuna River is highly influenced by sewage water. Ammonium ($NH_4^+$) concentrations up to 20 mg/L were measured in the river in 2012–2013. Large production wells located in the alluvial aquifer along the river draw high shares of bank filtrate and after nearly forty years of operation $NH_4^+$ concentrations reached 5.5–8 mg/L in the raw water of the production well closest to the river. To obtain input parameters for a field scale model, which is necessary for predicting the future development of $NH_4^+$ concentrations, the transport of $NH_4^+$ was studied in laboratory experiments. The aquifer consists of two lithological units, medium sand and gravel made up of calcareous nodules called kankar. Adsorption and desorption experiments were conducted with both materials in laboratory columns under suboxic and anoxic conditions with $NH_4^+$ concentrations of 10 and 20 mg/L and negligible nitrite ($NO_2^-$) and nitrate ($NO_3^-$) concentrations in the feed water. Nitrogen mass balances reveal that all $NH_4^+$ that is retained in the sediments during the adsorption experiments is desorbed again in the desorption experiments. Cation exchange is, therefore, the dominating transport mechanism. It took about 10−12 flushed pore volumes until the 100 % $NH_4^+$ breakthrough occurred in the sand columns and 30−35 flushed pore volumes in the kankar material. To simulate the $NH_4^+$ transport, 1D reactive transport models of the column experiments were developed with PHT3D. Transport parameters were obtained from pulse style tracer tests. Cation exchange was implemented in the model and the selectivity coefficients of the main cations and $NH_4^+$ were adjusted according to calculated values derived from water and sediment analyses. The modeled curves fit the measured data well for both, the $NH_4^+$ breakthrough and the other cation concentrations ($Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$).

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[9] Groeschke, M., Frommen, T., Hamann, E., Grützmacher, G., Schneider, M. (2014): Transport of Ammonium in Porous Media – Column Experiments with Alluvial Sediments and Reactive Transport Modeling (In: Synthesis of modeling, monitoring and optimising natural treatment systems in India. Saph Pani Deliverable D 5.3, unpublished project report). My part of the work and the changes made for this thesis are described in detail in section 1.5.

## 5.1 INTRODUCTION

Natural treatment systems such as managed aquifer recharge (MAR), constructed wetlands and bank filtration (BF) are increasingly used worldwide as the benefits become widely recognized. Especially bank filtration, sometimes also called riverbank filtration (RBF), is increasingly used for drinking water production (Doussan et al. 1997, Tufenkji et al. 2002, Grünheid et al. 2005) as it has two main advantages: (1) Sufficient quantity of water can be produced independently of the usable groundwater capacity as BF is a form of artificial groundwater recharge (Bouwer 2002, Dillon 2005). (2) Low-cost post treatment is often sufficient for the raw water as the process of bank filtration takes advantage of the natural filter capacity of the sediments during the soil passage (Kuehn and Mueller 2000). Usually, there is a significant increase in water quality for the bank filtrate compared to the surface water regarding organic substances, color, coliform bacteria and fecal contaminants (Weiss et al. 2005, Singh et al. 2010). However, when bank filtration is applied at sewage contaminated surface waters, which is often the case in developing or newly industrialized countries (Ray 2008) a range of problems can arise. When contaminated water infiltrates into the aquifer in large quantities, the capacity of the soil to filter the contaminants is often exceeded (Heberer 2002). One parameter of concern in this context is nitrogen, especially the reduced species $NH_4^+$ (Hiscock and Grischek 2002).

A bank filtration site in central Delhi was studied. Sewage-contaminated Yamuna River water infiltrates into the aquifer leading to a strong increase in groundwater $NH_4^+$ concentrations. Peak concentrations reached 35 mg/L $NH_4^+$ in the centre of the contaminant plume and concentrations between 5.5–8 mg/L were found in the raw water of the first production well (Fig. 5.1).

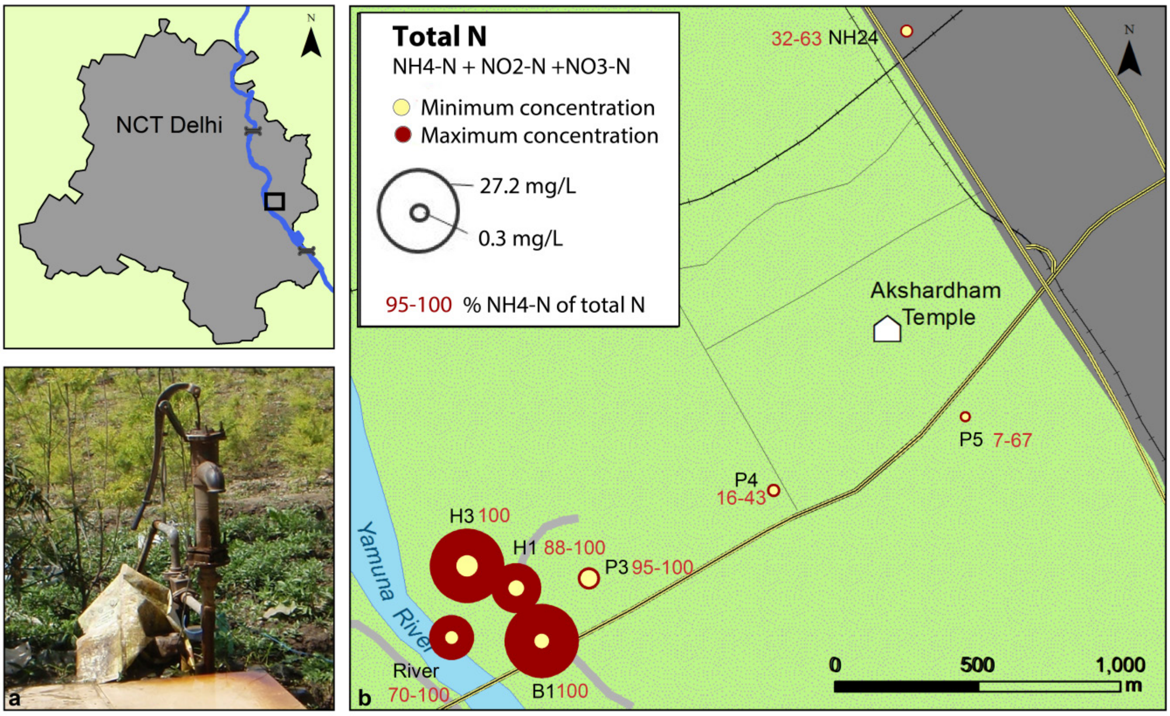

**Fig. 5.1** Location of the study area and nitrogen concentrations at the field site. Close to the river, almost all nitrogen is present in the form of $NH_4$-N. Note that concentrations are given as mg N/L.

Besides hydrogeological conditions like flow velocity and mixing, several factors may control or influence the transport and fate of $NH_4^+$. These factors include reversible interactions with the aquifer matrix (sorption and ion exchange) and irreversible processes such as fixation (absorption in the interlayers of clay minerals) or degradation, which often plays a major role in the transport of redox-sensitive contaminants. The transport of $NH_4^+$ is therefore strongly linked to site-specific conditions.

Numerous studies have investigated $NH_4^+$ contaminations in groundwater at different scales. Field investigations were focused on contaminations from point sources such as leachates from landfills (Young et al. 1994, Lewin et al. 1999), chemical companies and industrial sites (Haerens 2004, Haerens et al. 2006, Clark et al. 2008), septic tank effluents (Hinkle et al. 2007, Hinkle et al. 2008), and former sewage farms (Hamann 2009) and on contamination through artificial recharge of treated sewage water (Leblanc 1984, Ceazan et al. 1989, Böhlke et al. 2006, Repert et al. 2006) and treated septage water (DeSimone and Howes 1996, 1998). The infiltration of sewage influenced river water was studied in Glattfelden (Switzerland) by Schwarzenbach et al. (1983) and Jacobs et al. (1988), but elevated $NH_4^+$ concentrations were only observed in the river and not in the aquifer. The authors conclude that complete nitrification takes place during infiltration. Doussan et al. (1997) and Doussan et al. (1998) studied the transport of nitrogen species at a BF site at the Seine (France), where the river was, at the time of the study, heavily influenced by sewage treatment plant (STP) effluents and had high $NO_3^-$ concentrations. Reducing conditions prevailed in the aquifer owing to the decay of organic matter. The $NO_3^-$ was reduced to $N_2$ gas during the soil passage (denitrification) while the mineralization of organic matter was the main source of $NH_4^+$. On a laboratory scale, batch and desorption experiments have been conducted to determine Langmuir isotherms (DeSimone and Howes 1998) and distribution coefficients ($k_d$) (Ceazan et al. 1989, Böhlke et al. 2006) for $NH_4^+$ sorption on aquifer material. Column experiments to investigate transport of $NH_4^+$ were conducted with liner and filter materials (Thornton et al. 2001, Hinkle et al. 2008) and with aquifer materials. Thornton et al. (2000) and Thornton et al. (2005) studied the transport of landfill leachate with $NH_4^+$ concentrations of 1000 – 2000 mg/L in columns filled with disaggregated sandstone and Jellali et al. (2010) used synthetic wastewater with $NH_4^+$ concentrations of 5–36 mg/L and sandy soil from a soil aquifer treatment (SAT) pilot plant. Furthermore, von Gunten and Zobrist (1993) used column experiments to investigate microbially mediated redox processes during infiltration of polluted water; however, the behavior of $NH_4^+$ was not the main focus in this study.

In this study we investigate the transport of $NH_4^+$ at low concentrations (10–20 mg/L) and naturally occurring flow rates in porous alluvial aquifer material from Yamuna River under suboxic and anoxic conditions using laboratory column tests. The $NH_4^+$ degradation and attenuation were determined with adsorption and desorption experiments and reproduced in a 1D reactive transport model. The objectives of the study are: (1) To determine the dominant processes for $NH_4^+$ transport in an alluvial aquifer recharged by a sewage-contaminated river. (2) To quantify the retardation factor $R_f$ to give indications on how fast the $NH_4^+$ plume is spreading in the aquifer. (3) To determine optimum methodology for further research on RBF as natural treatment system. Results of this study provide input parameters for subsequent field-scale modeling investigations.

## 5.2 MATERIALS AND METHODS

### 5.2.1 Sediment Sampling and Analyses

The aquifer material investigated in this study was collected from the saturated zone of a shallow alluvial aquifer in central Delhi, which is contaminated by infiltrating sewage influenced water from the Yamuna River (Groeschke 2013). Samples were collected by manual auger drilling operations at three locations 35 m, 250 m, and 500 m from the riverbank (Fig. 5.2). They include medium-grained sand samples taken at depths between 7.6 and 15.2 mbgl and kankar samples (Fig. 5.3) taken at depths of 13.7 mbgl. The term kankar (sometimes spelled kanker) refers, specifically for India and North Africa, to calcareous nodules, which consist mostly of sandy loam or clay-loam (Singh and Singh 1972) and which are associated with cycles of evaporation and leaching (Salama 1987). After sampling, the material was packed airtight in plastic bags and stored in the dark at temperatures below 12 °C until it was filled into the columns.

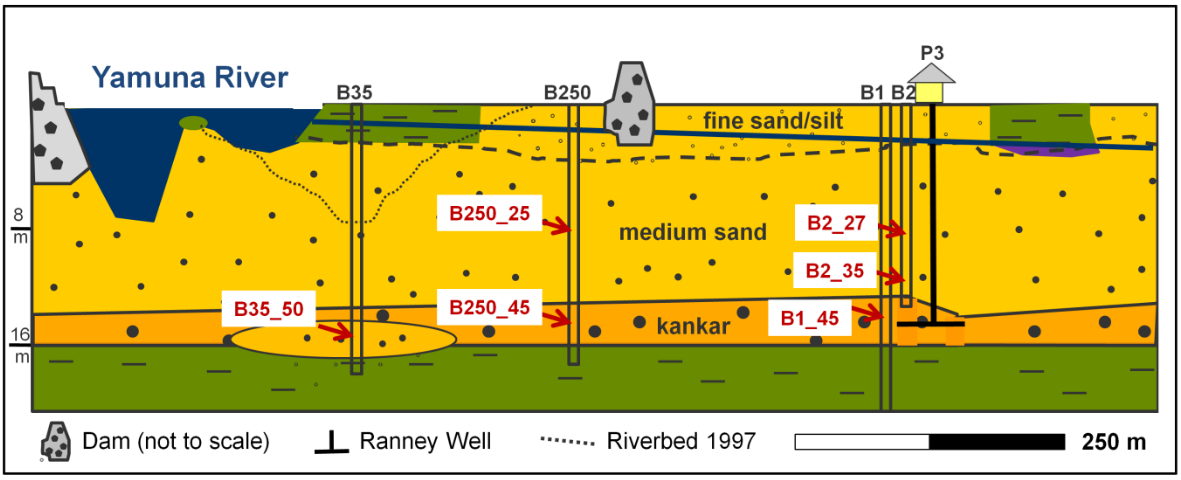

**Fig. 5.2** Origin of sediment samples used for sediment analyses and column experiments. The first number in the sample ID indicates the drilling location; the second number is the sampling depth in ft.

For all samples, grain size distribution was analyzed by sieve test and sedimentation (DIN 18123 2011-04), organic matter and carbonate content were measured by loss on ignition (DIN 18128 2002-12). $CEC_{sum}$ (Ross and Ketterings 2011) was analyzed by percolating 0.1 M $BaCl_2$ through 10 g of dried soil sample and measuring the extracted $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, and Fe by ICP-OES. $NH_4^+$ was determined photometrically. All kankar analyses were conducted with dried, unchanged material. Additionally, the kankar was disaggregated by mixing with natriumpyrophosphate ($Na_4P_2O_7$) and shaking for 24 hours. While all solute concentrations (except for $HCO_3^-$) are given in mg/L, $CEC_{sum}$ was calculated in meq/100g sediment.

Total porosities (n) were determined by measuring how much water could be added to small, tightly packed sediment columns until the sediment was water saturated. To confirm these results, total porosities were calculated according to equation 5.1 using the quartz density $\rho = 2.65$ g/cm$^3$, the volume of the columns (V) and the mass of the sediment in the column (m) (Vomocil 1965):

$$n = \frac{V - (\frac{m}{\rho})}{V} \tag{5.1}$$

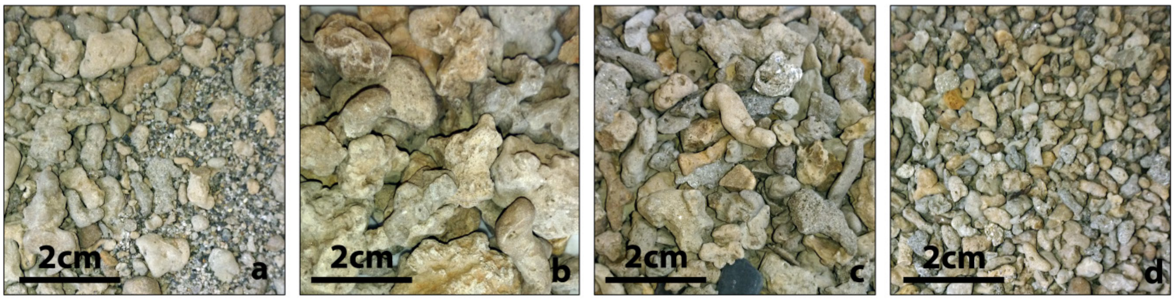

**Fig. 5.3** (a) Complete Kankar sample consisting of calcareous nodules of different sizes and sand. (b) Kankar fraction >8 mm, (c) Kankar fraction >4 mm and (d) Kankar fraction >2 mm.

### 5.2.2 Experiments

**Experimental Set-up**

Glass columns with an inner diameter of 45 mm and a sediment filled length of 145 mm were filled with aquifer material and flushed with artificial groundwater (model water) in upflow direction. The concentrations and ratios of the main inorganic cations in the model water correspond to the groundwater at the field site and are shown in Table 5.1. The flow was regulated using a peristaltic pump and was set to about 0.17 mL/min corresponding to an average linear flow velocity of 0.9 m/d in the aquifer. This is in the range of flow velocities ($9.3\times10^{-6}$– $2.5\times10^{-5}$ m/s; 0.8–2.2 m/d) reported for the field site by Sprenger and Lorenzen (2014). The column effluent was collected in glass vessels, which, like the model water reservoir, were kept under an Ar gas atmosphere to prevent interactions with atmospheric nitrogen and the oxidation of $NH_4^+$. Non-invasive oxygen sensors (Presens® Fibox mini) were attached to the artificial water reservoir, to the inlet of the columns, to two points inside the columns, to the outlet of the columns and in the sample collector vessels. ORP probes were installed at the outlet of the columns. The set-up of the column experiments is shown in Fig. 4.3.

**Ammonium Experiments**

With each sediment sample, experiments were conducted in two stages: adsorption experiments and desorption experiments. In the adsorption experiments, the columns were flushed with model water with $NH_4^+$ concentrations of either 20 or 10 mg/L (prepared by adding $NH_4Cl$ to the model water) until the $NH_4^+$ concentrations in the effluent were equal to the concentrations in the model water. During the following desorption experiments, the columns were again flushed with nitrogen-free model water until nitrogen concentrations in the column effluent were sufficiently low. Before the first adsorption experiment, columns were flushed with nitrogen free model water to remove any autochthonous nitrogen. To ensure reproducibility, the experiments were conducted with duplet or triplet columns and were repeated one or two times. All adsorption and most desorption experiments were conducted with hypoxic (DO < 3 mg/L), suboxic (DO < 0.4 mg/L) or even anoxic

(DO concentrations below detection limit) model water. In all cases, the oxygen was depleted within the first 5 cm of the column. Selected desorption experiments were conducted with oxygen saturated water. The number of columns and experiments conducted with each sediment sample and the redox conditions of the model water are shown in Table 5.2.

**Table 5.1** Model water composition during the adsorption and desorption experiments (average ± standard deviation).

| **Para-meter** | **Unit** | **Model water composition in the adsorption experiments** | | **Model water composition in the desorption experiments** | |
|---|---|---|---|---|---|
| | | **Start** | **End** | **Start** | **End** |
| $Na^+$ | mg/L | 165.4 ± 9.1 | | | |
| $K^+$ | mg/L | 16.5 ± 1.0 | | | |
| $Mg^{2+}$ | mg/L | 32.3 ± 1.6 | | | |
| $HCO_3^-$ | mmol/L | 3.8 ± 0.3 | | | |
| $NH_4^+$ | mg/L | 20.2 ± 0.4 | | 0.1 ± 0.1 | |
| $Cl^-$ | mg/L | 303.1 ± 12.5 | | 276.7 ± 9.1 | |
| EC | µS/cm | 1285 ± 33.8 | | 1191.8 ± 26.2 | |
| pH | | 8.47 ± 0.02 | | 8.52 ± 0.05 | |
| $Ca^{2+}$ | mg/L | 17.3 ± 4.2 | 15.5 ± 1.7 | 25.1 ± 8.4 | 17.9 ± 5.5 |

**Table 5.2** Number and kind of experiments conducted with the sediment samples and redox conditions in the model water.

| **Sed.** | **Sample ID** | **Depth [mbgl]** | **Dist. from river [m]** | **No. of columns** | **No. ads. exp.** | **$NH_4^+$ in model water [mg/L]** | **Redox cond. of feed water** | **No. des. exp.** | **Redox cond. of feed water** |
|---|---|---|---|---|---|---|---|---|---|
| Sand | B2_27 | 8.3 | 500 | 2 | 3 | 20 | Hypoxic/ suboxic | 3 | Hypoxic/ suboxic |
| | B2_35 | 10.7 | 500 | 2 | 3 | 20 | hypoxic/ suboxic | 3 | hypoxic/ suboxic |
| | B35_50 | 15.2 | 35 | 1 | 1 | 20 | Suboxic-anoxic | 1 | oxic |
| Mixed sand-kankar | B250_25 | 7.6 | 250 | 1 | 1 | 20 | Suboxic-anoxic | 1 | oxic |
| Kankar | B1_45 | 13.7 | 500 | 2 | 2 | 10/20 | Suboxic-anoxic | 2 | Suboxic-anoxic |
| | B250_45 | 13.7 | 250 | 2 | 1 | 20 | Suboxic-anoxic | 1 | oxic |

Sed.: sediment
Dist.: distance
No.: number
ads./des.: adsorption/desorption
exp.: experiments
cond.: conditions

## Sampling and Analyses

Effluent samples were collected according to a fixed sampling scheme. The complete column effluent was analyzed for $NH_4$-N, $NO_2$-N and $NO_3$-N. To obtain precise nitrogen breakthrough curves, small sample volumes < 20 mL were collected twice or thrice a day for the measurement of nitrogen species. In addition, samples for analyzing the main ions (and nitrogen species) were taken once a day (sampling volume 40–60 mL) in which the pH and EC were measured in the first few minutes after sampling. The methods of analysis and limits of detection are summarized in Table 5.3.

**Table 5.3** Methods of analysis, limits of detection (LOD), analytical errors and sampling scheme.

| Para-meter | Unit | Method * | LOD | Test number (Merck) | Measuring range | Error** | Volume [mL] | Sampling frequency |
|---|---|---|---|---|---|---|---|---|
| $NH_4^+$-N | mg/L | Photom. | 0.01 | 1.14752 | 0.010-0.500 | ±0.017 | <20 | Total effluent (2-3 samples per day and overnight sample) |
| | | | | 1.14752 | 0.05-3.00 | ±0.08 | | |
| | | | | 1.00683 | 3.0-30.0 | ±0.3 | | |
| $NO_2^-$-N | mg/L | Photom. | 0.001 | 1.14776 | 0.002-0.200 | ±0.005 | | |
| | | | | 1.14776 | 0.02-1.00 | ±0.03 | | |
| $NO_3^-$-N | mg/L | Photom. | 0.1 | 1.14773 | 0.2-10.0 | ±0.3 | | |
| | | | | 1.09713 | 0.5-12.5 | ±0.12 | | |
| | | | | 1.09713 | 1-25 | ±0.6 | | |
| $Na^+$, $K^+$ | mg/L | ICP-OES | 0.2 | n/a | <10 | ±20-50% | 40–60 | Once per day |
| $Mg^{2+}$, $Ca^{2+}$ | mg/L | ICP-OES | 0.02 | | 10-30 | ±10% | | |
| $Cl^-$, $SO_4^{2-}$, $NO_3^-$ | mg/L | IC | 0.1 | | 30-100 | ±5% | | |
| | | | | | 100-300 | ±2.5% | | |
| $HCO_3^-$ | mmol/L | Titrim. | 0.2 | 1.11109 | 0.2-10.0 | ±0.2 | | |

*Photom.: Photometric measurement IC: Ion chromatography Titrim.: Titrimetric determination
**Given in the respective unit (mg/L or mmol/L) unless it is stated that errors are given in %. n/a: not applicable

## Calculation of Nitrogen Mass Balances and Ammonium Sorption

Nitrogen mass balances were calculated subtracting the total measured nitrogen output from the total nitrogen input:

$$Total\ N_{sorbed/desorbed} = \sum(N_{NH4} + N_{NO2} + N_{NO3})_{inflow} - \sum(N_{NH4} + N_{NO2} + N_{NO3})_{outflow} \qquad (5.2)$$

The $NH_4^+$ sorption on the sediment was calculated using the total measured nitrogen. This assumption was made because over 95 % of the total measured nitrogen was in form of $NH_4$-N (see results). The low $NO_3^-$ and $NO_2^-$ concentrations that were measured could also have formed through oxidation during the sampling procedure; in the water samples taken at the field site from the center of the plume, 100 % of the nitrogen occurs as $NH_4$-N (Fig. 5.1). The potentially sorbed $NH_4^+$ was therefore calculated according to equation 5.3. Like the $\mathrm{CEC_{sum}}$, the $\mathrm{NH_4^+}$ sorption is given in meq/100g sediment. $M_N$ is the molar mass of N (14 mg/mmol):

$$\mathrm{NH_4^+}\left(\frac{\mathrm{meq}}{\mathrm{100g}}\right) = \frac{\mathit{total\ desorbed}\ \mathrm{N\ (mg)}}{\mathrm{mass\ of\ sediment\ in\ column\ (g)}} \times \frac{1}{\mathrm{M_N}(\frac{\mathrm{mg}}{\mathrm{mmol}})} \times 100\ \times 1 \tag{5.3}$$

### Mass Balances – Error Analysis[10]

Error analyses were applied based on the specified accuracy of a measurement value given in the data sheet of the reagents as well as the accuracy derived from a number of own standard measurements. The resulting uncertainties (errors) of the measurements are shown in Table 5.3. The *maximum possible uncertainties* of the mass balances were calculated by the linear addition of the uncertainties of every single measurement (Drosg 2009, p.155). Because the variables might show a correlation, the root mean square method of error propagation method was not used in this case, although the linear addition tends to give an overestimation of the overall error (Hughes and Hase 2010, p.37).

### Tracer Tests

Pulse style conservative tracer tests were performed on the columns to determine effective porosities. 1 mL NaCl solution with a concentration of 10 g/L was injected at the inlet of the column. Electric conductivity (EC) was measured in 5 minute intervals using an EC probe that was installed at the outlet of the column. Tracer concentrations were calculated according to:

$$_{tracer}(\frac{mg}{L}) = \mathrm{EC_{measured}}(\frac{\mathrm{\mu S}}{\mathrm{cm}}) - \mathrm{EC_{background}}(\frac{\mathrm{\mu S}}{\mathrm{cm}}) * 0.53 \tag{5.4}$$

Whereby the conversion factor 0.53 was determined through a laboratory test series, in which NaCl was added stepwise to the model water while measuring the changes in EC.

To ensure that no density stratification effects occur at those concentrations and injection volumes, an additional tracer test was conducted with 1 mL colored NaCl solution (addition of 0.1 g Rhodamin B to 20 mL tracer solution). Another test was conducted with 1 mL colored model water solution (addition of 0.1 g Rhodamin B to 20 mL model water).

### Determination of Hydraulic Conductivities

To determine the hydraulic conductivity (K) of the sediment using Darcy's law (equation 5.5), the hydraulic gradient was measured at the inlet and the outlet of the columns. Q is the flow rate, A is the area of the column, and *i* the hydraulic gradient.

$$K = \frac{Q}{A\ \times i} \tag{5.5}$$

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[10] This section was originally not part of D5.3

### 5.2.3 Modeling

Models were developed using the interface ipht3d (Atteia 2014), for the USGS flow simulator MODFLOW 2000 (Harbaugh et al. 2000), the transport simulator MT3DMS (Zheng 2010) and the reactive multicomponent transport model PHT3D (Prommer and Post 2010), which couples MODFLOW and MT3DMS with the geochemical modeling software PHREEQC-2 (Parkhurst and Appelo 1999). Tracer tests and adsorption experiments were modeled for all sediments; desorption experiments were only modeled in case they were not conducted under oxic conditions.

**Flow and Nonreactive Transport Model − Tracer Tests**

A 2D flow and nonreactive transport model was developed to determine the effective porosities and the dispersivities. The flow simulations were carried out with MODFLOW and the advective-dispersive transport of the NaCl tracer was simulated using MT3DMS and additionally with PHT3D. The horizontal extent of the model domain was 0.25 m and included the sediment filled column length (0.145 m) as well as the inlet and the outlet of the column. This takes into account the short lengths of the sediment filled columns and comparatively long flow paths in the inlet and the outlet, which might have an effect in pulse style experiments. The vertical extent of the model domain was 0.045 m; to reproduce the geometry of the columns (smaller diameter of the tubing compared to the column diameter) cells were set inactive at the inlet and the outlet. The resolution of the model grid was 0.002 m in the horizontal and 0.001 m in the vertical direction. The upstream boundary was defined by a constant flux, representing the actual inflow into the column, and the downstream boundary was defined by a constant head. The glass walls of the columns were represented by no-flow boundaries. Hydraulic conductivities obtained from laboratory measurements. The simulation time was one day. Tracer breakthrough curves were fitted by adjusting dispersivities and effective porosities, taking into account measured total porosities and literature values (e.g. Johnson 1967, Garling and Dittrich 1979). To ensure that no numerical dispersion or oscillations occurred, the simulations were run with TVD and MMOC solver and selected models were furthermore rerun with smaller grid spacing (0.001 m and 0.0005 m in horizontal and vertical directions).

**Flow and Reactive Transport Model – Ammonium Experiments**

Using the transport parameters determined with the tracer model, a 1D flow and reactive transport model was developed with MODFLOW and PHT3D to simulate the adsorption and desorption experiments. Because these experiments were conducted in step mode (with a constant input concentration) the effect of the column design on the breakthrough curves is negligible and 1D modeling is applicable. The horizontal extent of the model domain was 0.15 m, representing the sediment filled length of the column, and was divided into a grid of 0.001 m cell lengths. As in the 2D model, the inflow boundary was defined by a constant flow and the outlet boundary by a constant head. The adsorption and corresponding desorption experiments were modeled in one simulation. The sediment was equilibrated with the water composition of the first sample taken during the adsorption experiment. The model water composition of the adsorption experiment was used as the displacing solution for the duration of each adsorption experiment (3–8 days). The

$NH_4^+$-free model water composition was then used for the further 3 to 8 days simulation time as the displacing solution for the desorption experiment. The calcium concentrations decreased in the model water by 10 and 30 % during the adsorption and desorption experiments (Table 5.1). This is most likely due to the precipitation of $CaCO_3$ because the model water is oversaturated with respect to calcite as calculations with PHREEQC show. Therefore, the model water composition measured at the beginning of the adsorption or desorption experiment was used for the first half of the adsorption or desorption simulation and the composition measured at the end of the experiment was used for the second half of the simulation. For the sediments with which desorption experiments were conducted under oxic conditions, only the adsorption experiment was modeled. All water compositions were charge balanced using PHREEQC-3 (Parkhurst and Appelo 2013) before using them as input solutions.

**Implementation of Cation Exchange**

Many investigations show that at contaminant sites, where the infiltrating water is strongly influenced by one contaminant, simple sorption isotherm models are insufficient to describe the $NH_4^+$ behavior at field scale (Buss et al. 2004). Ion exchange models, which consider all species that compete for the exchange sites give better results (Hamann 2009). Therefore, reactive transport models were developed which consider ion exchange of all main cations present. The reactive transport was computed with PHT3D using a slightly modified database provided with the software PHREEQC-2 (Amm.dat). The Amm.dat database decouples $NH_4^+$ from the nitrogen system, which means that no oxidation of $NH_4^+$ can occur in the model. This is in accordance with the experimental results showing no oxidation of $NH_4^+$ to $NO_2^-$ and $NO_3^-$ at significant levels (section 5.3.3).

The cation exchange selectivity coefficient is the relative preference of an exchanger to adsorb different cations. It is not a thermodynamic constant, but varies with the exchanger composition (e.g. Tournassat et al. 2007). For the exchanger phases of the three sediment types (sand, mixed sand-kankar, kankar), equilibrium equations for $Na^+\backslash K^+$, $Na^+\backslash Mg^{2+}$, $Na^+\backslash Ca^{2+}$, $Na^+\backslash NH_4^+$ were set up using the Gaines-Thomas convention (Gaines and Thomas 1953) and measurements of the cation compositions on the exchanger as well as the corresponding activities in groundwater samples. Exchange selectivity coefficients with $Na^+$ as the reference ion ($K_{Na\backslash I}$) were then calculated using the Gaines-Thomas convention (Appelo and Postma 2007, p.155-162). $I$ represents the ion, $\beta_{Na}$ and $\beta_I$ are the equivalent fractions of $Na^+$ and the respective ion and $i$ is the charge of the ion.

$$K_{Na\backslash I} = \frac{\beta_{Na}[I^{i+}]^{1/i}}{\beta_I^{1/i}[Na^+]} \tag{5.6}$$

Log $K_{Na\backslash I}$ values were calculated according to:

$$\log K_{Na\backslash I} = \log(\frac{1}{K_{Na\backslash I}^{i}}) \tag{5.7}$$

PHREEQC splits ion exchange reactions into half reactions and the reference reaction, which is in this case

$$Na^{+} + X^{-} \leftrightarrow NaX \tag{5.8}$$

defined by log $K = 0$. Log $K_I$ for the half reaction of the ion $I$

$$I^{i+} + iX^{-} = IX_i \tag{5.9}$$

is therefore equal to log $K_{Na\backslash I}$. The log $K$ values were then used to replace the default values in the Amm.dat database. The number of exchange sites was used to fit modeled $NH_4^+$ breakthrough curves to measured data. The cation exchange capacity (CEC) is a measure for the number of exchange sites in sediments or soils and thus an important parameter for modeling cation exchange. Due to different factors (inhomogeneities in the sediment, pH dependency, uncertainties in the measurements) the exact determination of the number of exchange sites is difficult (Renault et al. 2009) and therefore it is the most uncertain factor in the system.

Modeled and measured cation concentrations in the column effluent ($NH_4^+$, $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$) are depicted in meq/L to better see the effects of cation exchange.

**Retardation Factors**

Retardation factors for $NH_4^+$ were determined by simulating a conservative tracer test by adding a non-reactive conservative tracer to the reactive transport model. The $NH_4^+$ retardation factors were then calculated using the modeled conservative tracer and the $NH_4^+$ breakthrough curves. The time required for the $NH_4^+$ to reach a relative concentration ($C/C_0$) of 0.5 at the outlet of the column was compared to the time that the tracer took to reach $C/C_0 = 0.5$ (Steefel et al. 2003). The conservative tracer represents the velocity of the water (Appelo and Postma 2007, p.79).

## 5.3 RESULTS

### 5.3.1 Sediment Analyses

The kankar and the sand have clearly distinct characteristics. The sand is a poorly graded medium sand with a low organic matter content between 0.6 and 1.2 %, carbonate contents up to 2.5 % and total porosities between 35 and 40 %. In comparison, the original (undisaggregated) kankar shows a better grading, has a high carbonate content of 14.4 % and a lower total porosity of 30 %. The $CEC_{sum}$ is slightly higher in the kankar (2.1 meq/100g sediment) than in the sand (1.6 meq/100g). The disaggregated kankar samples are characterized by a high fine grain content (< 0.063 mm) of almost 40 % compared to nil in the original kankar. Sieve curves are shown in Fig. 5.4 and sediments characteristics are given in Table 5.4.

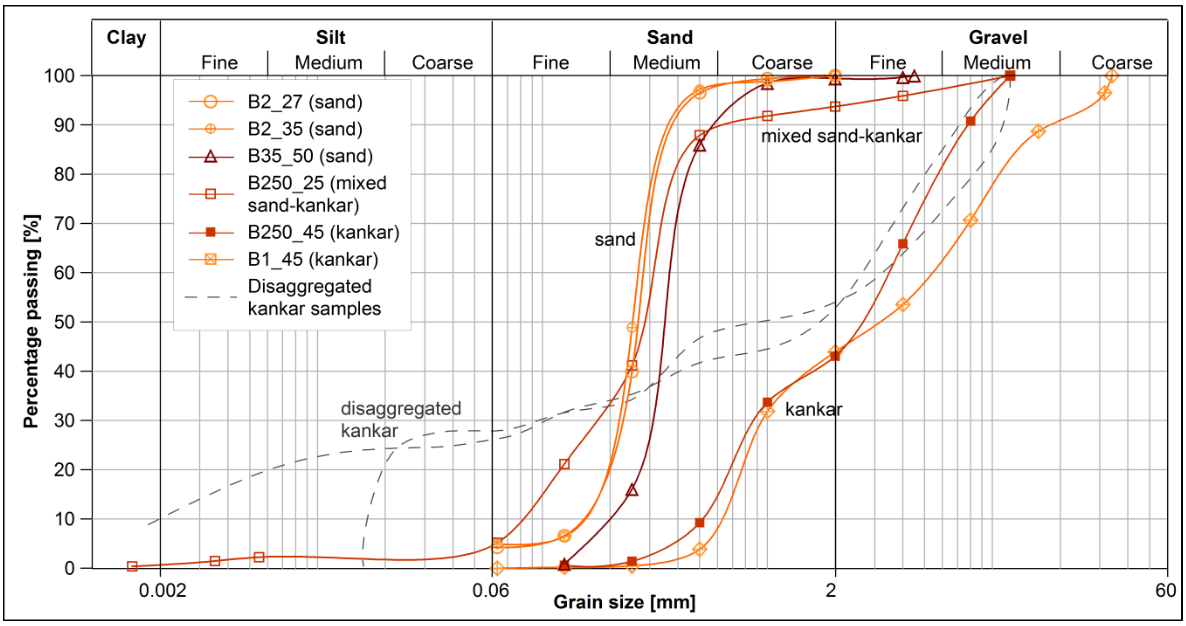

**Fig. 5.4** Grain size distribution curves of the different sediment samples.

**Table 5.4** Characteristics of the sediments used in the column experiments.

| **Sed.** | **Sample ID** | **Depth** [mbgl] | **Dist. from River** [m] | **Sed. type** | **CEC$_{sum}$** [meq/100g] | **Org. matter** [%] | **Carbo-nate** [%] | **n$_{meas}$** | **n$_{calc}$** | **Dry weight** [g] |
|---|---|---|---|---|---|---|---|---|---|---|
| Sand | B2_27 | 8.3 | 500 | poorly-graded medium SAND | 1.64 | 0.7 | 1.6 | 0.36 | 0.38 | 375 |
|  | B2_35 | 10.7 | 500 | poorly-graded medium SAND | 1.58 | 0.6 | 2.5 | 0.35 | 0.39 | 370 |
|  | B35_50 | 15.2 | 35 | poorly-graded medium SAND | 1.51 | 1.2 | * | 0.37 | 0.40 | 368 |
| Mixed sand-kankar | B250_25 | 7.6 | 250 | well-graded gravelly SAND | 1.29 | 1.3 | * | 0.35 | 0.33 | 407 |
| Kankar | B1_45 | 13.7 | 500 | coarse SAND-GRAVEL | 2.16 | 1.3 | 14.4 | 0.30 | 0.26 | 450 |
|  | B250_45 | 13.7 | 250 | coarse SAND-GRAVEL | 2.05 | 1.3 | * | NA | 0.29 | 430 |

$n_{meas}$: measured total porosity $n_{calc}$: total porosity calculated according to equation 5.1

*Addition of HCl showed that carbonate was present. NA: not analyzed

## 5.3.2 Tracer Tests and Transport Parameters

The hydraulic conductivities of the sand samples, determined by measuring the hydraulic head difference between the inlet and the outlet of the column, were in the range of $2.0\times10^{-5}$ to $6.7\times10^{-5}$ m/s in the sand samples and in the range from $1.2\times10^{-4}$ m/s to $1.6\times10^{-4}$ m/s in the two kankar samples. The mixed sand-kankar sample had a hydraulic conductivity of $2.1\times10^{-5} \pm 0.1\times10^{-5}$ m/s. Tracer breakthrough curves of the sand and the kankar differ substantially. While the peaks in sand columns are narrow and high ($C_{max}$ 285−370 mg/L) and occur after a flow of about 110 mL, the peaks in the kankar columns already occur after about 75 mL at a lower concentration (115−230 mg/L). 2D models of the tracer tests reveal that the sand samples have effective porosities between 23 and 25 %, resulting in an effective pore volume of 53–58 mL. The kankar samples have a slightly lower effective porosity between 16.5 and 19 %, resulting in effective pore volumes of 38–44 mL in the columns. Dispersivities of the sand were in the range of 1/100 while they were in the range of 1/10 for the kankar. The mixed sand-kankar shows an intermediate porosity and dispersivity. The measured and modeled tracer breakthrough curves for all the sediments of the saturated zone are shown in Fig. 5.5 and the transport parameters used in the $NH_4^+$ transport models are summarized in Table 5.5. The measured variations within each sediment group (sand, mixed sand-kankar and kankar) may be due to different packing of the columns or due to natural inhomogeneities in the sediments.

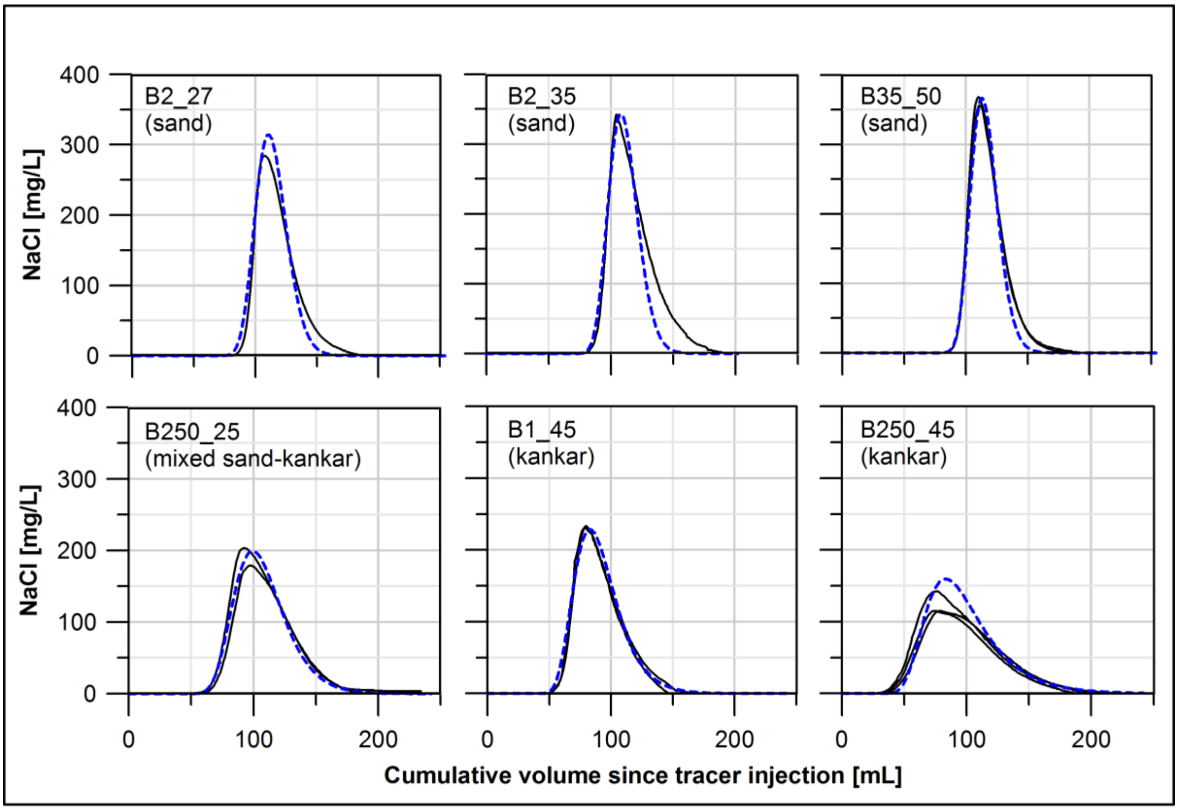

**Fig. 5.5** Measured (solid) and modeled (dashed) tracer breakthrough curves.

**Table 5.5** Transport parameters obtained from hydraulic head measurements (K), tracer tests and 2D solute transport models (effective porosity $n_e$ and dispersivity).

| Sediment type | Sediment ID | K [m/s] | K [m/d] | $n_e$ | Dispersivity [m] |
|---|---|---|---|---|---|
| Sand | B2_27 | $3.9\times10^{-5}$ | 3.4 | 0.24 | 0.0016 |
| | B2_35 | $2.0\times10^{-5}$ | 1.7 | 0.23 | 0.0012 |
| | B35_50 | $6.7\times10^{-5}$ | 5.8 | 0.25 | 0.0008 |
| Mixed sand-kankar | B250_25 | $2.1\times10^{-5}$ | 1.8 | 0.22 | 0.008 |
| Kankar | B1_45 | $1.2\times10^{-4}$ | 10 | 0.165 | 0.012 |
| | B250_45 | $1.6\times10^{-4}$ | 14 | 0.19 | 0.024 |

## 5.3.3 Behavior of Ammonium in the Sediments

### Nitrogen Species in the Column Effluents

In the experiments conducted with hypoxic model water >99.5 % of the nitrogen input was in form of $NH_4$-N and in the column effluent 90–95 % of the total N was present as $NH_4$-N. In the experiments conducted with suboxic or anoxic model water $NO_3$-N and $NO_2$-N were mostly below detection limit in the model water. In the column effluent 97–99 % of the total N was measured as $NH_4$-N (Fig. 5.6). This indicates that little or no oxidation of $NH_4^+$ occurred in the sediments.

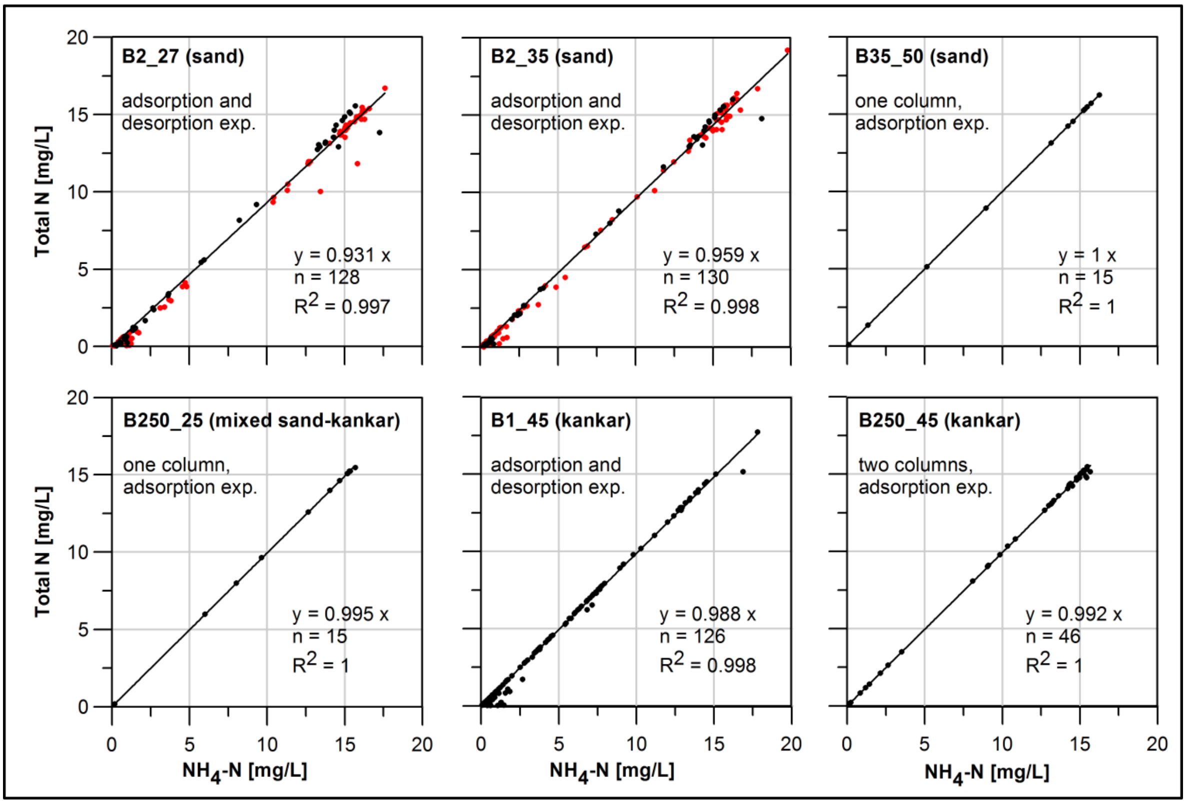

**Fig. 5.6** $NH_4$-N vs. total N in the column effluents. Experiments conducted under hypoxic conditions (*red points*) and under suboxic–anoxic conditions (*black points*).

### Mass Balances

The $NH_4^+$ that was sorbed on the sediment matrix during the adsorption experiments was completely desorbed again during the desorption experiments (Fig. 5.7). No nitrogen was lost as described in Chapter 4 (Characterization of the Unsaturated Zone). At an $NH_4^+$ concentration of 20 mg/L the sand samples had an average $NH_4^+$ exchange capacity of 0.11±0.01 meq $NH_4^+$/100g sediment (average±standard deviation), while the kankar samples were able to exchange 0.16±0.02 meq $NH_4^+$/100g sediment. The detailed results for all columns are shown in Fig. 5.7.

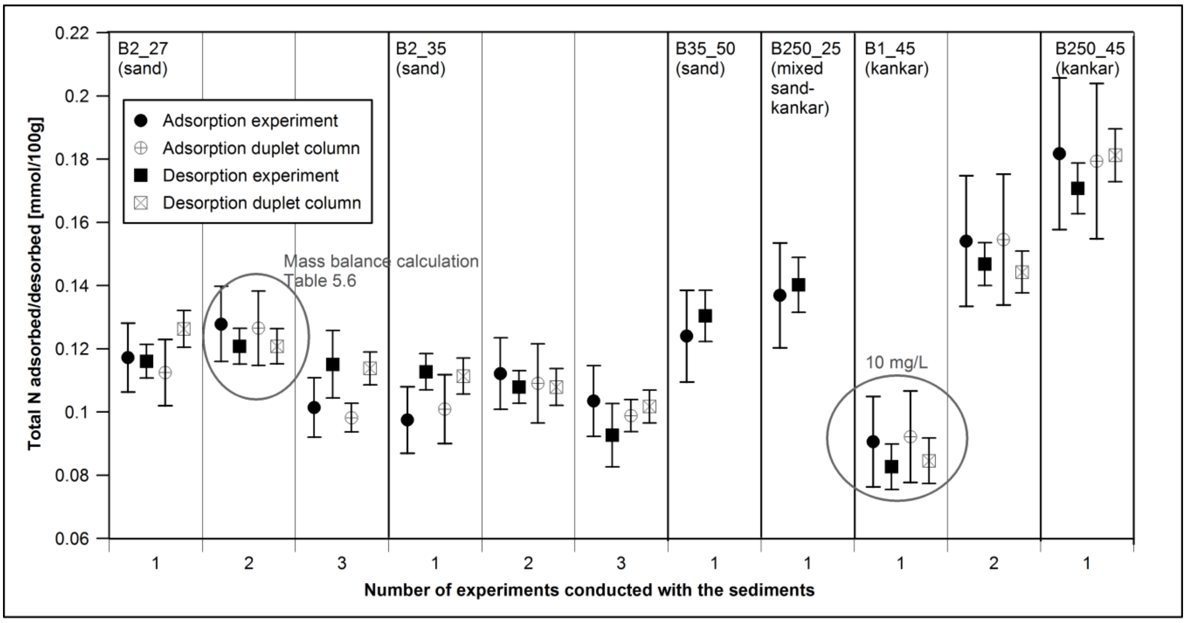

**Fig. 5.7** Total nitrogen adsorbed and desorbed during the experiments. All adsorption experiments with exception of the labeled set (10 mg/L) were conducted with 20 mg/L $NH_4^+$ in the feed water. Error bars represent *maximum* errors.

### Error Analyses of Mass Balances

The total *maximum* errors for the nitrogen mass balances of the adsorption experiment, were in the range of 9−15 % for the experiments conducted with 20 mg/L $NH_4^+$ in the model water. For the mass balances of the desorption experiments, the total errors were in the range of 5−8 %. Errors were larger for the adsorption experiments because of the higher error (±0.3 mg/L) for high $NH_4^+$ concentrations as opposed to an error of ±0.017 or ±detection limit (0.01) for low $NH_4^+$ concentrations (see Table 5.3). A summary of the errors of the second adsorption and desorption experiment of sediment B2_27 is given in Table 5.6.

**Table 5.6** Example of a mass balance calculation and error analysis (sediment B2_27, second experiment, column filling: 375 g). The total maximum error was calculated by adding the errors of every single measurement.

| **B2_27ft** | | **Adsorption experiment** | | | | **Desorption experiment** | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | **Column 1** | | **Column 2** | | **Column1** | | **Column 2** | |
| | **Unit** | **Value** | **Error** | **Value** | **Error** | **Value** | **Error** | **Value** | **Error** |
| **Input** | | | | | | | | | |
| $NO_3$-N | mg | 0.04 | 0.09 | 0.04 | 0.09 | 0.00 | 0.08 | bdl | 0.08 |
| $NO_2$-N | mg | 0.005 | 0.004 | 0.005 | 0.004 | bdl | 0.001 | bdl | 0.001 |
| $NH_4$-N | mg | 13.5 | 0.3 | 13.5 | 0.3 | 0.09 | 0.01 | 0.09 | 0.01 |
| Sum $N_{in}$ | mg | 13.5 | 0.4 | 13.5 | 0.4 | 0.1 | 0.1 | 0.1 | 0.1 |
| **Output** | | | | | | | | | |
| $NO_3$-N | mg | 0.21 | 0.10 | 0.27 | 0.10 | 0.32 | 0.10 | 0.29 | 0.10 |
| $NO_2$-N | mg | 0.434 | 0.023 | 0.457 | 0.034 | 0.273 | 0.018 | 0.307 | 0.018 |
| $NH_4$-N | mg | 6.2 | 0.2 | 6.2 | 0.2 | 5.8 | 0.2 | 5.8 | 0.2 |
| Sum $N_{out}$ | mg | 6.8 | 0.3 | 6.9 | 0.3 | 6.4 | 0.3 | 6.4 | 0.3 |
| $N_{in}$ - $N_{out}$ | mg | 6.7 | | 6.6 | | -6.3 | | -6.3 | |
| $N_{in}$ - $N_{out}$ | mmol | 0.48 | | 0.47 | | -0.45 | | -0.45 | |
| $N_{in}$ - $N_{out}$ | mmol/100g | 0.13 | | 0.13 | | -0.12 | | -0.12 | |
| $Error_{in}$ + $error_{out}$ | mg | | 0.7 | | 0.7 | | 0.4 | | 0.4 |
| $Error_{in}$ + $error_{out}$ | mmol | | 0.05 | | 0.05 | | 0.03 | | 0.03 |
| $Error_{in}$ + $error_{out}$ | mmoL/100g | | 0.01 | | 0.01 | | 0.01 | | 0.01 |
| Error* | % | | **10** | | **11** | | **6** | | **6** |

*calculated according to: ($Error_{in}$ [mg/L] + $error_{out}$ [mg/L] / $N_{in}$ [mg/L] - $N_{out}$ [mg/L]) × 100

### Ammonium Breakthrough

During the adsorption experiments, the $NH_4^+$ breakthrough in the sand columns commences after about five flushed pore volumes (Fig. 5.8). $NH_4^+$ concentrations in the column effluent then rapidly increase until the input concentration of 20 mg $NH_4^+$/L (15.55 mg $NH_4$-N/L) is reached after 10–12 flushed pore volumes. The sand samples taken at a distance of 500 m and 35 m from the river show the same behavior, while in the mixed sand-kankar sample B250_25, the input concentration is only reached after about 20 flushes. In the kankar, the $NH_4^+$ breakthrough is slower than in the sand columns and the input concentration is reached after 30–35 flushed pore volumes for both, $NH_4^+$ concentrations of 10 mg/L and 20 mg/L in the model water. In the desorption experiments it took about 15 and 40 pore volumes to flush the $NH_4^+$ out of the sand and kankar columns, respectively.

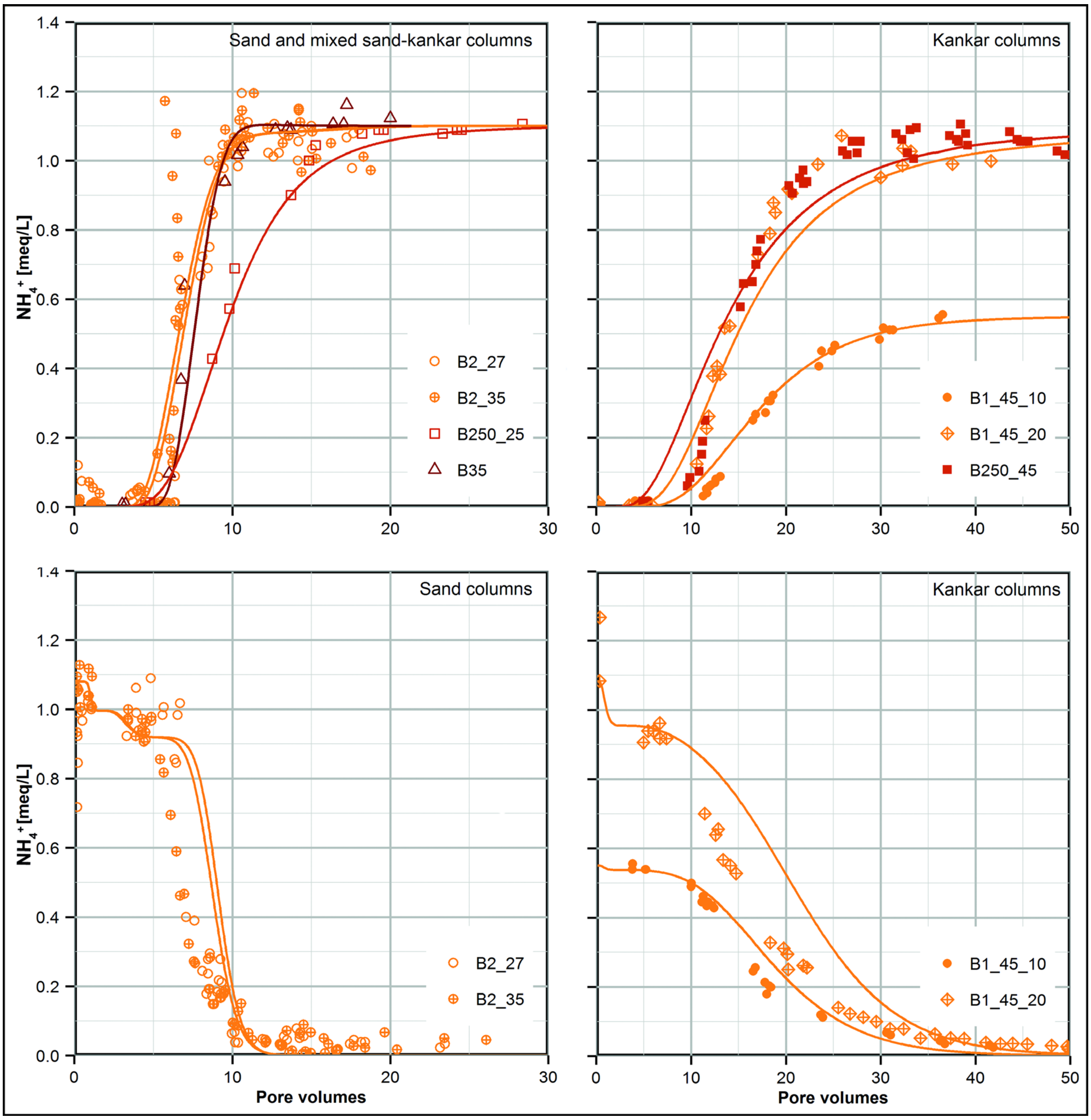

**Fig. 5.8** Measured data (points) and modeled breakthrough curves (lines) for the adsorption (above) and desorption experiments (below). Note the different scales on the x-axes. B1_45_10/20: Experiments conducted with 10 or 20 mg/L $NH_4^+$ in the model water.

## Reactive Transport Modeling and Sorption Coefficients

The $NH_4^+$ breakthrough was successfully modeled using adjusted selectivity coefficients for cation exchange (Fig. 5.8). It was furthermore possible to reproduce the concentrations of the main cations ($Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$) within a sufficient range (Fig. 5.9). Table 5.7 shows the PHREEQC-2 default selectivity coefficients, which are used in PHT3D if no changes in the PHREEQC database are made and the adjusted coefficients, which were employed in this study.

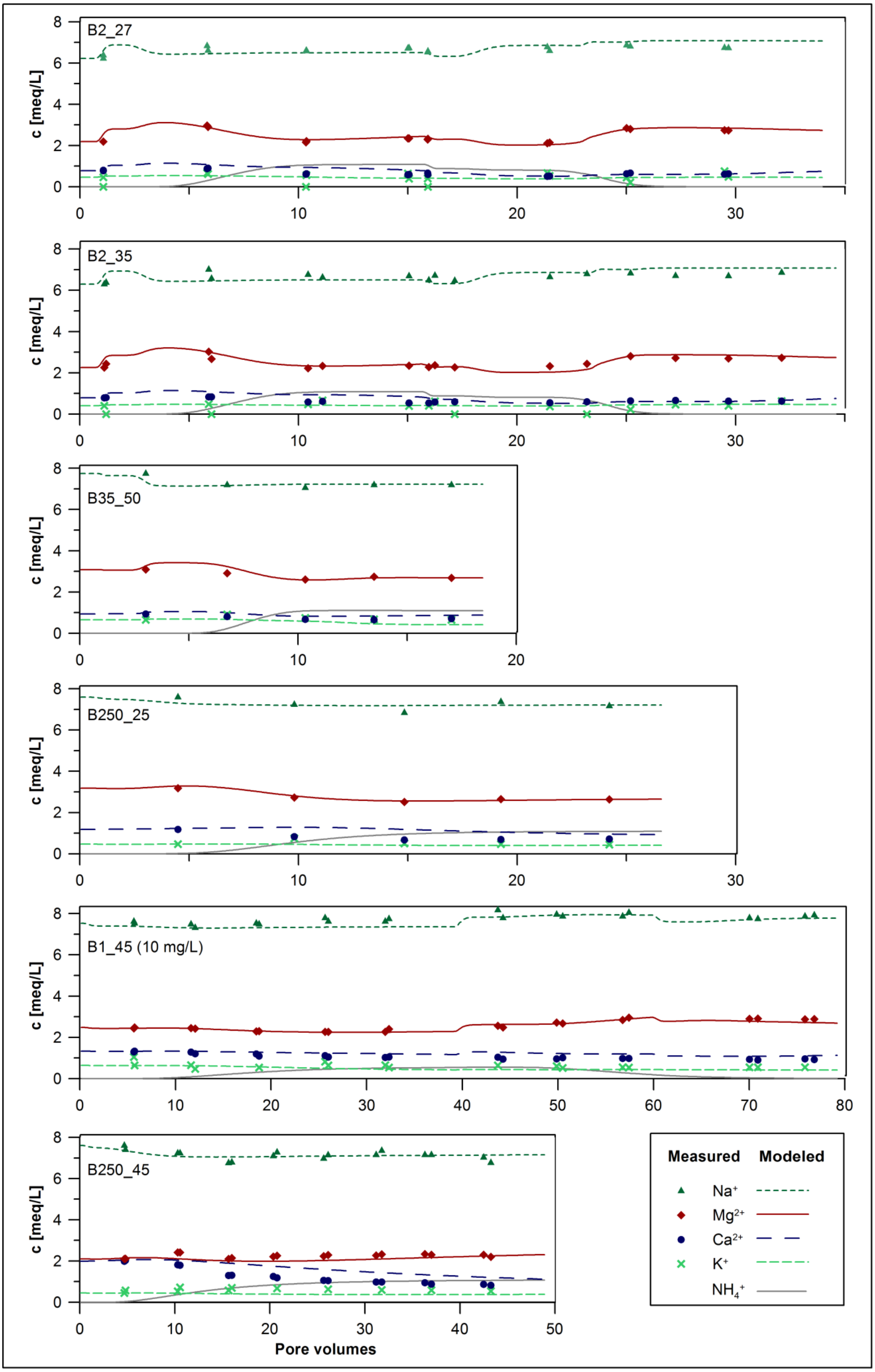

**Fig. 5.9** Measured and modeled cation concentrations. $NH_4^+$ data is shown in detail in Fig. 5.8.

**Table 5.7** Adjusted selectivity coefficients ($K_{Na\backslash I}$), which were used in the models, default selectivity coefficients of the PHREEQC standard database and literature values. The measured cation exchange capacities (CEC) were adjusted in the models.

| | $K_{Na\backslash K}$ | $K_{Na\backslash Mg}$ | $K_{Na\backslash Ca}$ | $K_{Na\backslash NH4}$ | **Sediment sample** | **CEC [mol/L sediment]** | |
|---|---|---|---|---|---|---|---|
| | | | | | | **Measured** | **Adjusted** |
| Sand | 0.1 | 1.1 | 0.82 | 0.16 | B2_27 | 0.026 | 0.013 |
| | | | | | B2_35 | 0.025 | 0.013 |
| | | | | | B35_50 | 0.024 | 0.016 |
| Mixed sand-kankar | 0.18 | 1.74 | 0.92 | 0.17 | B250_25 | 0.023 | 0.0155 |
| Kankar | 0.21 | 1.38 | 0.89 | 0.28 | B1_45 | 0.042 | 0.038 |
| | | | | | B250_45 | 0.038 | 0.038 |
| PHREEQC standard database | 0.2 | 0.5 | 0.4 | 0.25 | | | |
| Appelo and Postma (2007) | 0.15-0.25 | 0.4-0.6 | 0.3-0.6 | 0.2-0.3 | | | |
| Carlyle et al. (2004) | 0.2-0.67 | 1.48* | 0.26-3.16 | --- | | | |

*calculated using the geometric means of $K_{Ca/Mg}$ and $K_{Ca/Na}$

## Retardation Factors

Retardation factors ($R_f$) between 6.7 and 7.4 were determined for the sand; a factor of 10.0 was determined for the mixed sand-kankar. The retardation factor varied between 16.0 and 19.8 for the kankar. Conservative tracer breakthrough curves in comparison with nitrogen breakthrough curves are shown in Fig. 5.10.

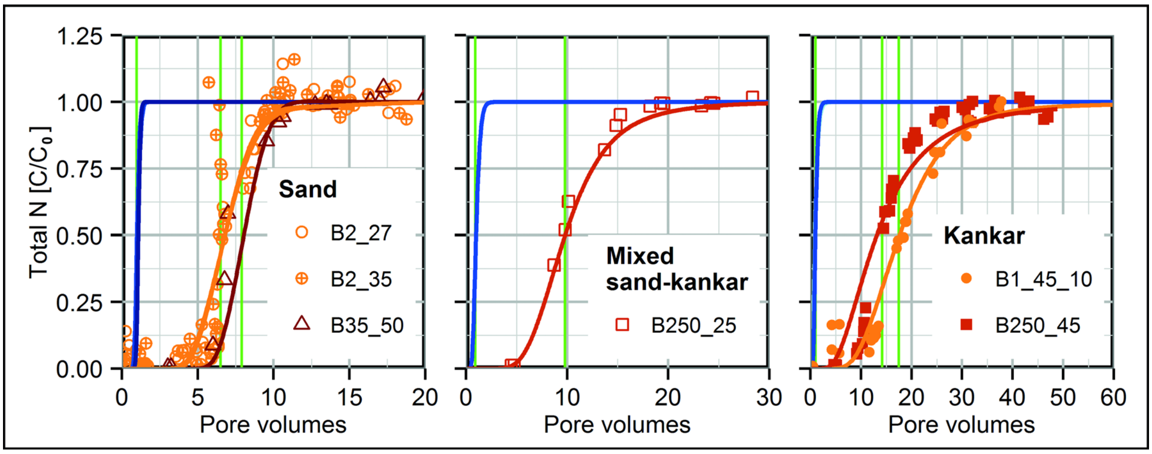

**Fig. 5.10** $NH_4^+$ retardation factors were determined by comparing the 50 % $NH_4^+$ breakthrough in the different sediments to the 50 % non-reactive tracer breakthrough. *Blue lines*: non-reactive tracer breakthrough curves, *green lines* mark the volumes at which 50 % of the initial concentration is reached.

# 5.4 DISCUSSION

## 5.4.1 Sediment Characteristics

In the saturated zone at the field site, three sediments were encountered: well sorted medium sand, mixed sand-kankar and kankar with high shares of sand and fine grain. The medium sand and the kankar can be viewed as endmembers. Transitions between the lithological units are gradual (see Chapter 3), and thus any mixture with different sand and kankar proportions can occur. The sand and the kankar have substantially different characteristics regarding grain size, $CEC_{sum}$ and LOI. Because of their different properties regarding flow and transport, the sand and kankar layers at the field site have to be considered conceptually as different hydraulic units.

**Hydraulic and Transport Properties**

The hydraulic conductivities determined in the kankar are clearly higher than the hydraulic conductivities of the sand (hydraulic conductivities in the range of $10^{-4}$ m/s in the kankar as opposed to $10^{-5}$ m/s in the sand). Conceptually, this implies that groundwater flow takes place preferentially in the kankar layer. This is generally in accordance with the findings obtained from the grain size distribution (Chapter 3). But the hydraulic conductivities obtained during the experiments are − in both cases – one order of magnitude lower than those derived from the grain size distribution curves ($K_{kankar}$: $3.7\times10^{-3}$ m/s, $K_{sand}$: $2.9\times10^{-4}$ m/s). The anisotropy of the sediments might be one reason for this discrepancy. In the columns, only the vertical hydraulic conductivity was measured. Because the sediment is horizontally layered, especially due to the mica minerals, the vertical hydraulic conductivity is expected to be lower than the horizontal hydraulic conductivity.

The dispersivities in the kankar samples are one order of magnitude higher than those of the sand samples (dispersivities in the range of 1/10 of the column lengths in the kankar and 1/100 of the column lengths in the sand). The comparably high dispersivities in the kankar can be explained by the poor sorting and more diverse flow paths. Due to the poor sorting, the effective porosities are slightly lower (0.165–0.19) than in the sand (0.23–0.25) and the linear flow velocity u is, therefore, higher in the kankar columns than in the sand columns (0.6 m/d as opposed to 0.9 m/d). Nevertheless, both are in the range of the values published for the field site (Sprenger 2011). The determined porosity values are in good agreement with literature values for sandy gravel and sand (e.g. Krapp 1983).

**Physicochemical Properties**

While the kankar hydraulically acts like gravel, it is similar to clay regarding the physicochemical properties. In the sand, clay contents were below 1 % and the organic matter content varied between 0.6 and 1.2 % leading to an average measured cation exchange capacity $CEC_{sum}$ of 1.6 meq/100g sediment. In original (undisaggregated) kankar samples, organic matter contents of 1.3 % were measured and no clay was found. In the disaggregated kankar clay contents increased up to 10 % of the total weight. A $CEC_{sum}$ of 2.1 meq/100g sediment was measured in the original kankar. A CEC difference of 0.5 meq/100g between the sand and the kankar does not seem large. But taking into account the total and effective porosities of the sediments leads to a 70 % higher number of exchange sites per kg water in the kankar than in the sand according to the measured CEC data and to a 200 % higher number of exchanges sites if the adjusted CEC values are evaluated instead. These adjustments of the CEC in the $NH_4^+$ transport models were made to fit the modeled to the measured data. The adjusted number of sites in the sand was only about half of the measured value (0.013 mol/L sediment as opposed to the measured value of 0.025 mol/L sediment) while only a minor adjustment had to me made for the kankar (Table 5.7). A reason for this gap might be the large errors of ICP-OES measurements at low concentrations (Table 5.3). In the CEC measurements of the kankar, the measured cation concentrations were significantly higher than the concentrations measured in the sand, making measurements more reliable. Because of the high number of exchange sites, the kankar is of great importance for the $NH_4^+$ transport at the field site.

## 5.4.2 Ammonium Transport

**Column Experiments**

According to mass balances derived from adsorption/desorption experiments, degradation or fixation of $NH_4^+$ does not occur in significant quantities. Fixation of $NH_4^+$ in the columns would have been unlikely as the sediments from the field site were in contact with groundwater containing $NH_4^+$, and any irreversible fixation would have most likely occurred there. Duplicate columns and the repetition of experiments show that results are reproducible; the total error in the mass balances fall in the range between 5 and 15 %. The differences between the sand and the kankar columns are above variations due to analytical errors. Because of the absence of electron acceptors – oxygen for the nitrification process or $NO_3^-$ and $NO_2^-$ for anaerobic $NH_4^+$ oxidation – no oxidation of $NH_4^+$ takes place in the columns.

**Ammonium Modeling**

Overall, modeled curves fit the measured data well (Fig. 5.8). All three sand samples were modeled using the same selectivity coefficients, and it was possible to reproduce the steep $NH_4^+$ breakthrough curves that were measured. Similar results were achieved for the mixed sand-kankar and the kankar. However, for the kankar, especially for sediment B250_45, the model overestimates $NH_4^+$ concentrations at the beginning of the breakthrough curve and does not reproduce the relatively steep slope of the curve at higher concentrations. This can also be seen in the modeled curve of the desorption experiments. The possible reasons for these deviations might be one of the following:

- Inaccurately determined selectivity coefficients due to the high analytical error in the $CEC_{sum}$ determination. More precise measurements or an automatic parameter optimization might increase the accuracy of the fit of the modeled to the measured data. Nevertheless, measured values cannot be reproduced using the default values of the Amm.dat database and $NH_4^+$ breakthrough in the kankar can also not be modeled with sufficient accuracy using the sand selectivity coefficients (data not shown).

- The presence of different clay minerals with different cation selectivity coefficients. Although this effect should also occur in the sand and the mixed sand-kankar, the effect must be most pronounced in the kankar as it has the most sorption sites. A multi-site approach as proposed by Vulava et al. (2000) might increase the model fit in all sediments, especially that of the kankar. The authors show that their data was reproduced reasonably by the Gaines-Thomas model, but that none of the one site models provided a perfect fit of the data. This can also be observed with our data.
- A dual porosity in the kankar sediment. The calcareous nodules themselves have a matrix porosity, which could be seen as an independent pore system with different water pressures and solute concentrations as described by Gerke and van Genuchten (1993).

Nevertheless, these deviations are not of great relevance concerning the questions posed, as the overall retardation is reproduced correctly. Although a simple $k_d$ model would be sufficient for this purpose, this approach would not take into account the influence of the cation composition of the displacing solution. If the decontamination of a sewage-contaminated aquifer should be predicted, the change in infiltrating water composition is a major factor and a modeling approach with cation exchange takes those changes into account.

**Selectivity Coefficients**

The determined selectivity coefficients for $Ca^{2+}$, $Mg^{2+}$ and $K^+$ fit in the range of selectivity coefficients published by Carlyle et al. (2004) and the $NH_4^+$ selectivity coefficients lie within the range or only slightly below the range given by Appelo and Postma (2007). The CEC was used to fit the modeled curves to the measured data. Before adjusting the CEC, the modeled $NH_4^+$ breakthrough curves were identical in the slope and form but showed a higher delay. This is a strong indication that the calculated selectivity coefficients were appropriate to describe the cation exchange, but the CEC was assumed to be too high (section Physicochemical Properties). Decreasing the CEC not only improved the $NH_4^+$ fits, but also improved the modeled concentrations of the other cations, especially $Mg^{2+}$.

Overall, the approach to model the transport of $NH_4^+$ using adapted selectivity coefficients gives reasonable good fits of the measured data. The crucial point with this method is the precise determination of CEC and selectivity coefficients. However, if this is done with the necessary accuracy, the models are a good tool to predict the transport behavior of $NH_4^+$ in natural sediments. Because of fingering effects in the $NH_4^+$ plume (Chapter 3) it is important to determine selectivity coefficients using sediment and water samples from the plume center.

**Retardation Factors**

To be able to compare the transport of $NH_4^+$ at the Delhi field site with data from other case studies, retardation factors were determined for the different sediments. The calculated retardation factors in this study (6.7–7.4 in the sand, 10.0 in the mixed sand-kankar and 16.0–19.8 in the kankar) are higher than the retardation factors reported by Ceazan et al. (1989) and Böhlke et al. (2006) with values of 3.5 and 4.0–6.4, respectively, for a shallow sand and gravel aquifer with a clay content less than 1 %. Erskine compared three case studies and concluded that $NH_4^+$ retardation factors are not higher than 3 (Erskine 2000). This shows the importance of evaluating each field site carefully concerning the transport of $NH_4^+$ as it strongly depends on the sediments, in particular the CEC-active matter, the solute composition and $NH_4^+$ concentrations. However, retardation factors are not best suited for making predictions for contaminant transport as they are only valid for certain solute compositions and pH values, and reactive transport models give better results.

## 5.5 CONCLUSIONS

The transport of $NH_4^+$ in aquifer material from an alluvial sand and kankar aquifer was studied in laboratory column experiments to gain a better understanding of the development of an $NH_4^+$ plume originating from infiltrating sewage water at an RBF site in central Delhi. The following conclusions can be drawn from the present study:

- Under flow and redox conditions similar to those found in the $NH_4^+$ plume at the field site, cation exchange was found to be the strongly dominating transport process in both lithological units.
- The transport of $NH_4^+$ is strongly dependent on the sediment characteristics. Retardation factors ($R_f$) vary between 6.7 and 7.4 in the sand and between 16.0 and 19.8 in the kankar. These values are much higher than previously published retardation factors for $NH_4^+$. Although reactive transport models, which consider cation exchange in a more sophisticated physical manner, give more precise results, the retardation factors display the fact that $NH_4^+$ transport in the kankar takes about three times longer than in the sand. However, for field application one has to consider that the linear groundwater flow velocity is likely to be much higher in the kankar layer due to higher hydraulic conductivities.
- The applied reactive transport model incorporating cation exchange with adjusted selectivity coefficients delivers reasonable results for each lithological unit. With this approach, both the measured $NH_4^+$ concentrations and the main cation concentrations could be reproduced. With a more precise measurement of the cation exchange capacity, it will most likely be possible to improve the modeled curves to measured data.
- Due to the completely different sediment properties, it is advised to at least differentiate between sand and kankar layers when developing a transport model on field-scale. Depending on the resolution of the model and the required degree of detail, a mixed sand-kankar transition layer might also be incorporated.

Transferring the results of our laboratory study to the field site, the desorption experiments reveal that all of the $NH_4^+$ that was sorbed onto the sediment particle surfaces can be desorbed again when infiltrating water is $NH_4^+$-free. The desorption approximately takes an equal time span as the $NH_4^+$ breakthrough and elevated $NH_4^+$ concentrations will prevail for a long time (in case of the field site several decades) in the groundwater at the studied well field.

# Chapter 6

# Field Site Modeling: How long will the Ammonium Contamination Prevail?[11]

## Abstract

Elevated ammonium ($NH_4^+$) concentrations were measured in a sand and kankar aquifer at a riverbank filtration site on the banks of the Yamuna River in central Delhi. To be able to predict the future development of $NH_4^+$ concentrations at the well field, it is necessary to understand the local flow regime as well as the contaminant's interactions with the sediment matrix. The first determines the flow paths of the contaminant and whether mixing with ambient groundwater occurs, lowering $NH_4^+$ concentrations in the raw water through dilution. The evaluation of the hydrogeological situation at the western and eastern borders of the study area led to different hypotheses, and simple 2D flow models were used to assess the influence of ambient groundwater at the well field. At the eastern model boundary, an inward flux of ambient groundwater can be induced by setting constant head boundaries, but an inwards flux seems highly unlikely due to the high population density and resulting groundwater abstraction in the area. In the western model area, an eastward flux below the river does not occur at either losing or gaining stream conditions at the western riverbank, thus no dilution of infiltrating river water takes place. Using the results of the 2D flow models, reactive transport was modeled with PHREEQC along two 500 m long flow paths (from the eastern riverbank to the first production well) to obtain a first estimation of the decontamination period in the two sediments of the aquifer. The reactive transport models revealed a decontamination time of 19 years in the sand and 61 years in the kankar.

## 6.1 INTRODUCTION

The urban agglomeration Delhi, which comprises the NCT Delhi as well as contagious cities, is the second largest urban agglomeration in the world after Tokyo (United Nations 2014). It is expected to further grow from 22 million inhabitants in 2011 to 31 million inhabitants in the year 2021 (National Capital Region Planning Board 2013, p.32). This leads to an increasing water demand and to big challenges for the city's water management. In this frame, new strategies to ensure a safe and sustainable water supply have to be developed and evaluated. Therefore, a well field on the floodplain in central Delhi was studied to optimize the use of riverbank filtration in the city. At the well field, elevated $NH_4^+$ concentrations were measured in several handpumps (up

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[11] Section 6.5 was published in: Groeschke, M., Frommen, T., Grützmacher, G., Schneider, M., Sehgal, D. (2015) Application of Bank Filtration in Aquifers Affected by Ammonium – The Delhi Example. In: Wintgens, T., Anders, N., Elango, L., Asolekar, R. S. (Eds.) Natural Water Treatment Systems for Safe and Sustainable Water Supply in the Indian Context: Saph Pani. IWA Publishing, pp 57-77.

to 35 mg/L) and in the production well located closest to the river (up to 8 mg/L). Field data strongly suggest that the main source of the $NH_4^+$ is infiltrating sewage-influenced water from the Yamuna River (Chapter 3), and laboratory column studies further revealed that agricultural activities on the floodplain do not contribute to the contamination (Chapter 4). Sediment characteristics and their distribution in the aquifer are well known (Chapters 3, 4, 5), yet crucial questions concerning the cause and development of $NH_4^+$ concentrations at the field site remain unanswered:

- Is there an inflow of groundwater from the western side beneath the river? This would lower $NH_4^+$ concentrations of the infiltrating river water by dilution. If this were the case, the high $NH_4^+$ concentrations observed in the groundwater could not be caused by the infiltrating water alone, meaning that another $NH_4^+$ source must be active.
- Do the production wells draw shares of ambient groundwater with low $NH_4^+$ concentrations from the eastern side? In this case it would be possible to minimize $NH_4^+$ concentrations in the abstracted water by well field management and optimization of pumping schemes.
- How long will it take to decontaminate the aquifer? An estimation of the decontamination time is vital to be able to set up a management concept for the well field and to choose appropriate remediation or post-treatment measures.

The available data about the central Delhi floodplain aquifer are not sufficient to set up a meaningful, well-calibrated and validated groundwater flow and transport model of the entire well field. Nevertheless, simple groundwater flow and reactive transport models of parts of the well field can help to answer the questions posed. As a first step, simple 2D flow models were set up with MODFLOW to understand the general flow conditions at the site. Subsequently, using the results of the flow models, the transport of $NH_4^+$ was simulated along two 1D flow paths using PHREEQC to estimate the contamination and decontamination periods in the two lithologies for the first 500 m zone near the river.

## 6.2 THE STUDY AREA

The study area is located on the east bank of the Yamuna River in central Delhi, in the district East Delhi near Nizamuddin Bridge and Akshardham Temple. In this area, the floodplain is asymmetrical (Fig. 6.1a). It is narrow on the western side of the river, where the incision of the river prevented the development of a floodplain as described by Sinha et al. (2005). On the eastern bank, the active (undeveloped) floodplain has a width of 2.4 km. The floodplain aquifer (Newer Alluvium) is not constricted to the area of the active floodplain but extends farther east, beyond the city's boundaries, where the contact between Younger Alluvium and Older Alluvium is hard to trace (Kazim et al. 2008, p.15). At the study site, the floodplain aquifer is 14.5−16 m deep and consists of a 1−2 m thick kankar layer, which is overlain by medium sand. The aquifer is underlain by a thick clay layer of the Older Alluvium.

Although drillings have only been conducted at distances of 35, 250, 500 and 550 m from the riverbank in this study, data from the Central Ground Water Board (CGWB) suggest that this geological set-up can be found across the entire field site. Figure 6.1b shows a SW−NE cross section (CGWB 2013) from the Yamuna River (Nagli Rajapur) to the eastern border of NCT Delhi (Gazipur). The western part of the section is located almost within the study area. The bore logs of drillings conducted during this study (Chapter 3) show good agreement with the CGWB cross section, assuming that the gravel layer in Figure 6.1b and the so called kankar layer in this study are the same units. This seems to be likely as the kankar layer also contains gravel.

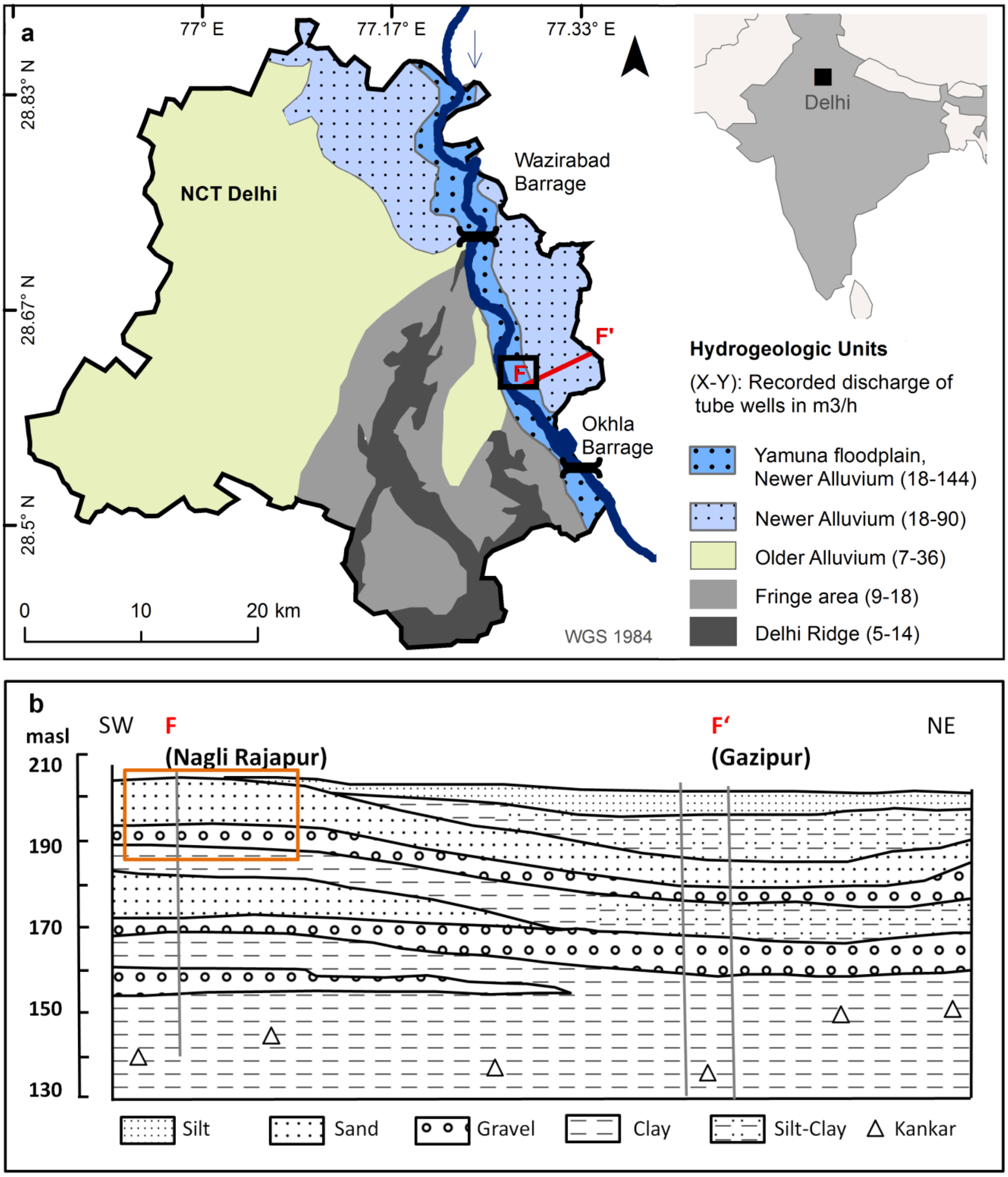

**Fig. 6.1** (a) Hydrogeologic units of NCT Delhi and location of the study area (black box). Map modified after CGWB (2012). Discharge of tube wells compiled from CGWB (2006b) and CGWB (2012) (b) SW-NE vertical cross section through East Delhi (location shown in a). The orange box represents the approximate position of the study area. Modified after CGWB (2013).

The study site is located in a part of a larger well field consisting of at least 10 Ranney wells (radial collector wells) and an unknown number of tube wells. Most of the Ranney wells are operated by the Delhi water supplier (Delhi Jal Board) and some belong to the Indian Railways. The Ranney wells sampled in this study (Fig. 3.1) have 10 radial well screens (information in pump houses), which are about 30 m long (personal communication well guard) and presumably located in the kankar layer. The abstraction rates of the Ranney wells strongly depend on the installed pumps (Kandra et al. 2004) and abstraction rates between 220 $m^3/h$ (Delhi Jal Board) and 580 $m^3/h$ (Indian Railways) were reported for the studied wells (personal communication well guards). Observations at the well field showed that the Ranney wells are not operated 24 h per day but according to demand.

## 6.3 SELECTION OF BOUNDARY CONDITIONS

Available data from the field site alone are not sufficient to determine the boundary conditions for a model of the study area and to make correct model assumptions. It is necessary to look at a larger zone around the study site and to consider several aspects in addition to the field and laboratory findings to be able to better identify all factors influencing the local groundwater flow regime:

- The geology and geomorphology on the western bank of the river
- Different groundwater abstraction scenarios on the western bank
- The geology and geomorphology on the eastern bank of the river
- The tremendous population growth in the eastern part of NCT Delhi and contagious cities

**The Western Riverbank**

On the western side of the Yamuna River (where Younger Alluvium is almost absent), the topography rises towards the west, where quartzitic bedrock forms the Delhi Ridge with an altitude above 240 masl (Das et al. 1988). In contrast, the elevation of the floodplain in the study area is at about 204 masl (result of leveling survey). The Delhi Ridge on one hand functions as a groundwater recharge structure (Chatterjee et al. 2009). On the contrary, the decline in groundwater levels is especially severe in the area of the Delhi Ridge, although more in the southern part (CGWB 2006a, Kumar et al. 2011). Therefore, two scenarios are possible at the western bank: losing stream conditions prevail as assumed by Sprenger (2013) or gaining stream conditions exist as reported by Kumar et al. (2011) who used data from 2003−2006 to create a groundwater table contour map. As a large part of the land between the Delhi Ridge and the Yamuna River is covered by a park and a bus depot, and interviews at both sites revealed that no large-scale groundwater abstraction takes place, flow conditions might be similar today to those in 2006.

Because the groundwater flow direction remains unclear, the effects of both, losing stream and gaining stream conditions have to be tested. This can be implemented by setting constant head boundaries with initial heads either above (in the case of gaining stream) or below (in the case of losing stream) river water level.

### The Eastern Riverbank

The ground surface of the active floodplain on the eastern bank of the river is extremely flat. In the 1980s, gaining stream conditions prevailed in this area with a groundwater flow direction towards the southwest (Das et al. 1988). However, the extremely high population growth in East Delhi and the contagious cities Ghaziabad and Noida led to changes in the groundwater flow regime. While only few people lived on the eastern bank in 1958 (Fig. 6.2), over 1.7 million people lived in the district East Delhi (CGWB 2013) in 2011. Additionally, 2.4 million people lived in Ghaziabad urban area (Census of India 2011b) and 640000 in Noida (Census of India 2011c). Because of the common use of private bore wells (Chapter 1), groundwater abstraction can be assumed to be very high. Furthermore, many large production wells are located at the border of the active floodplain (Fig. 6.3). This most likely results in losing stream conditions and groundwater flow towards the east or southeast as depicted by Kumar et al. (2011).

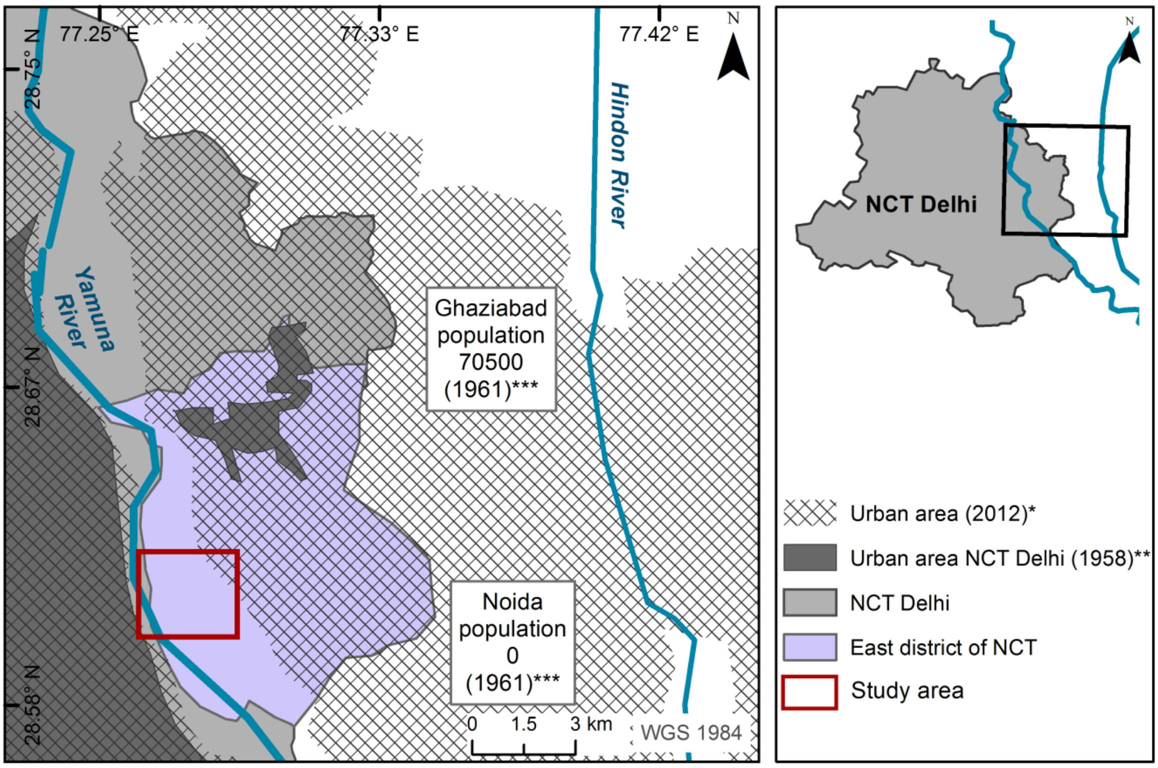

**Fig. 6.2** Population development in east Delhi, Ghaziabad and Noida. *Data from National Capital Region Planning Board (2013). **Modified after Kumar et al. (2011). ***Town and Country Planning Organisation (2007)

Taking into account the high groundwater abstraction in the populated areas east of the active floodplain, the most realistic boundary conditions for the eastern model border are constant flux conditions with a flux out of the model domain. Although it is challenging to determine a realistic flux, this option eliminates the problem of unintentionally creating a recharge zone at the eastern model boundary, when implementing too high pumping rates on the floodplain. In any case, the effects of a constant head boundary should be evaluated.

## 6.4 2D FLOW MODELING

Four steady state flow simulations were modeled in 2D to test the effects of different boundary conditions on the groundwater flow regime at the well field. The flow scenarios were simulated with MODFLOW 2000 (Harbaugh et al. 2000) using the 3D interface ipht3d version 2 (Atteia 2014). The steady state assumption implies that no change in storage occurs in the model and that the total inflow of water through recharge (infiltrating river water, precipitation, constant head model boundary) equals the total flow out of the model. Although this does not reflect the seasonal fluctuations in groundwater levels between monsoon and non-monsoon time, this simplification is reasonable because no significant long-term decline in groundwater levels has been observed in the floodplain aquifer (CGWB 2006a, plates 12 & 13).

### Model Domain and General Parameters

2D flow models were set up as E−W vertical cross sections (MODFLOW: XSECTION) with a total length of 3100 m (x-direction) and a depth of 19 m (z-direction). The model domain reaches from 400 m west of the Yamuna River to 100 m east of the undeveloped floodplain (Fig. 6.3). The width of the model (y-direction) was set to 2600 m. This is half the distance to a parallel transect of production wells in the northern part of the well field, multiplied by two because the radius of influence can also include the southern part of the well field.

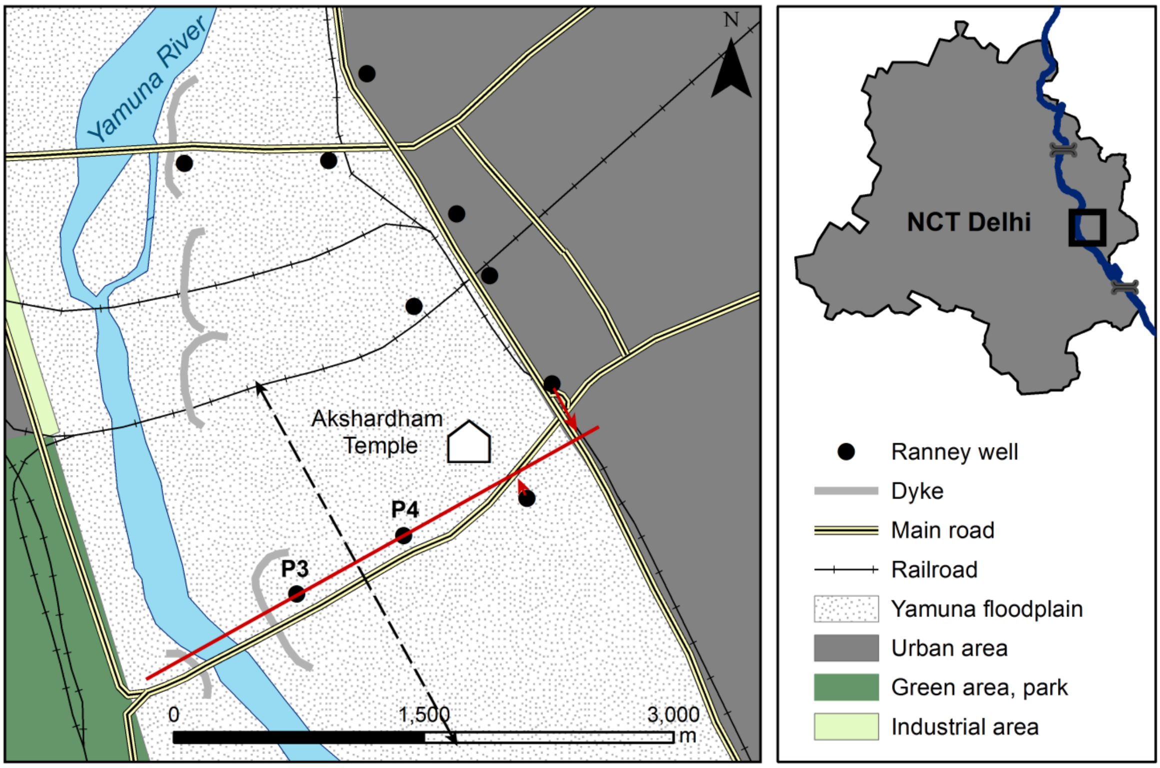

**Fig. 6.3** Overview of the study area, location of the modeled x-section (red line) and the model extent in y-direction (dashed arrows).

The different lithologies found at the field site were incorporated into the model by defining zones of different hydraulic conductivities, representing the sand, kankar and silt−clay. For the sand, the average hydraulic conductivity of 25 m/d ($2.9\times10^{-4}$ m/s) derived from the grain size distribution (Chapter 3) was taken as the horizontal hydraulic conductivity in the flow models. The average hydraulic conductivity of 3.6 m/d ($4.2\times10^{-5}$ m/s) determined during the column experiments (Chapter 5) was used as the vertical hydraulic conductivity. This results in an anisotropy ratio (horizontal to vertical hydraulic conductivity) of 6.9, which is realistic as the sand shows a clear anisotropy with respect to the orientation of the grains, especially the mica minerals. This ratio is only slightly higher than the anisotropy ratio of 5 determined by Su et al. (2004) for alluvial sediments. For the kankar, hydraulic conductivities were also derived from the grain size distribution (average 315 m/d, $3.7\times10^{-3}$ m/s) and determined in the laboratory (average 12 m/d, $1.4\times10^{-4}$ m/s). In this case, the large difference between both values results in an anisotropy ratio of 26.3. This is highly unrealistic. Therefore, models were set up using the laboratory value as the vertical hydraulic conductivity and assuming the same anisotropy ratio as in the sand. This results in a horizontal hydraulic conductivity of 83 m/d ($9.7\times10^{-4}$ m/s).

For the silt−clay, a horizontal hydraulic conductivity of 0.86 m/d ($1\times10^{-6}$ m/s) was chosen in accordance with hydraulic conductivities determined from grain size distribution (Chapter 4). To keep the models simple, only the silt−clay deposit along the west bank of the river was incorporated in the models, whereas the silt−clay layer at the top of the aquifer was left out. The top of the Older Alluvium, which acts as an aquitard, was incorporated in the model as a 2 m thick silt-clay layer at the lower model boundary, from 185 to 187 masl.

The river was defined as a zone of very high hydraulic conductivity (86400 m/d, 1 m/s). Kinzelbach and Rausch (1995) used this approach for modeling a groundwater fed lake and showed that the chosen value does not have a big influence on the model solution as long as it is significantly higher than hydraulic conductivities in the aquifer. This approach does not take into account a limitation of surface water-groundwater exchange caused by colmation layers with lower hydraulic conductivities. Because field investigations showed that no colmation layer was developed in most parts of the river, this simplification is valid for the field site. For the river, a constant head boundary was set with a head value of 202 masl.

Recharge was incorporated in the models. An average annual recharge of 74 mm on the Delhi floodplain (corresponding to 0.0002 m/d) was reported by Shekhar and Prasad (2009) who calculated the recharge using the average post-monsoon water level rise. This rate, therefore, includes recharge from precipitation, flooding and increased infiltration due to high river water levels. Nevertheless, it is a conservative estimation as it does not take into account the groundwater abstraction, which takes place throughout the year.

Four wells with horizontal well screens of 60 m length (two 30 m laterals) were placed in the kankar layer. The wells are located at distances of 500, 1200, 1900 and 2400 m from the eastern riverbank.

Since only steady state simulations were made, no specific temporal discretization or storage terms were necessary for solution (Holtschlag et al. 1996). Figure 6.4 depicts the river geometry and the spatial distribution of the different lithologies (zones). The values of the parameters are summarized in Table 6.1. The boundary conditions used at the model borders and the applied pumping rates are given in the following sections.

**Table 6.1** Parameters used to set up the initial 2D flow models (models 1 and 2).

| **Parameter** | **Value (general)** | **Values in different zones** | | | |
|---|---|---|---|---|---|
| | | **Sand** | **Kankar** | **Silt-clay** | **River** |
| Flow simulation | Steady state | --- | --- | --- | --- |
| Aquifer type | Free | --- | --- | --- | --- |
| Simulation time (days) | 1000 | --- | --- | --- | --- |
| Model extent column, x-direction (m) | 3100 | --- | --- | --- | --- |
| Model extent layer, z-direction (m) | 19 | --- | --- | --- | --- |
| $z_{min}$ (m) | 204 | --- | --- | --- | --- |
| $z_{max}$ (m) | 185 | --- | --- | --- | --- |
| Model thickness row, y-direction (m) | 2600 | --- | --- | --- | --- |
| Grid spacing Δx (m) | 5/2* | --- | --- | --- | --- |
| Grid spacing Δz (m) | 0.3 | --- | --- | --- | --- |
| Number of columns | 620/1550 | --- | --- | --- | --- |
| Number of layers | 63 | --- | --- | --- | --- |
| Number of rows | 1 | --- | --- | --- | --- |
| Horizontal hydraulic conductivity (m/d) | --- | 25 | 83 | 0.86 | 86400 |
| Vertical hydraulic conductivity (m/d) | --- | 3.6 | 12 | 0.43 | 86400 |
| Recharge (m/d) | 0.0002 | --- | --- | --- | --- |

*Because long linear cells can lead to numerical errors, the length-to-width ratio of cells should be as close to 1 as possible (Konikow 2000). To check for such numerical errors, models 1 and 2 were run with a grid length of 5 m as well as with a grid length of 2 m in x-direction.

## 6.4.1 Testing the Western Model Boundaries

Two models were set up to estimate the influence of different hydraulic head values at the western model boundary. The given hydraulic head values lead to (1) gaining stream conditions or (2) losing stream conditions on the western riverbank. This was done to determine whether a share of ambient groundwater from the west side can be expected to mix with the infiltrating river water along the flow path towards the Ranney well P3.

Model 1: A constant head boundary with a constant head value of 202.5 masl was defined as the western model boundary. This head level is 0.5 m above the constant head level of the river leading to gaining stream conditions on the western riverbank. The boundary flux at the eastern model boundary was set to a constant 1000 $m^3/d$. Pumping rates of 1000 $m^3/d$ were assigned to each of the four wells.

Model 2: A constant head boundary with a head value of 201 masl was defined as the western model boundary. Because this head level is 1 m below the head level of the river, losing stream conditions prevail. The boundary flux at the eastern model boundary was again set to 1000 $m^3/d$ and pumping rates of the wells remained at 1000 $m^3/d$.

### Results

Flow paths in models 1 and 2 indicate that the choice of constant head values at the western model boundary does not affect the groundwater flow in the floodplain aquifer east of the river. In case of a constant head value above the river water level (model 1), gaining stream conditions prevail at the western riverbank. All groundwater from the western side (including the water from the kankar layer) infiltrates into the river and thus no groundwater flow occurs beneath the river (Fig. 6.4). In case of losing stream conditions at the western side of the river, the infiltrating river water flows towards the west and does not mix with the infiltrating water from the eastern side of the river (Fig. 6.5). In both cases the groundwater flow on the eastern side of the river is the same.

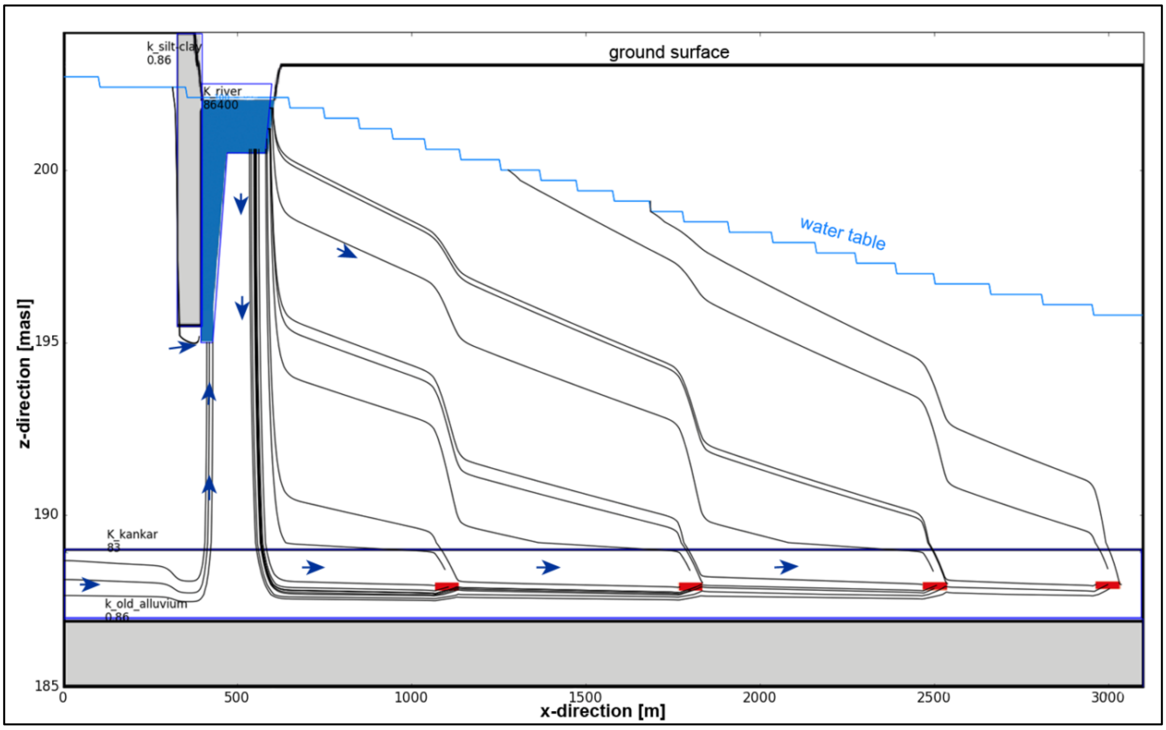

**Fig. 6.4** Model 1: Gaining stream conditions prevail in the west. Black lines: particle tracking (backwards), blue arrows: groundwater flow direction, red bars: well screens, grey areas: silt-clay zones. Numbers depict the horizontal hydraulic conductivities in m/d of the different zones. Note the different scales on the x- and z-axes. The original ipht3d output file was edited: Arrows and labels were added to enhance clarity.

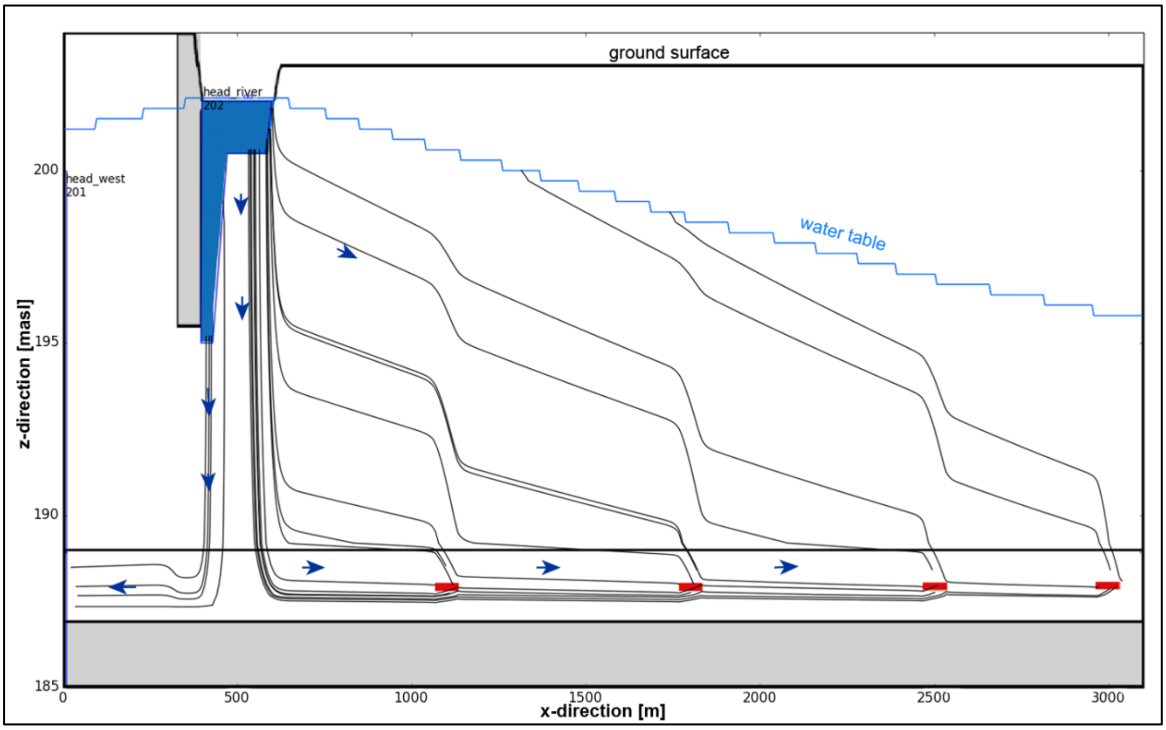

**Fig. 6.5** Model 2: Losing stream conditions prevail in the west. Black lines: particle tracking (backwards), blue arrows: groundwater flow direction, red bars: well screens, grey areas: silt-clay zones. The original ipht3d output file was edited: Arrows and labels were added to enhance clarity.

Numerical errors due to cell geometry most likely did not occur: The models with a cell length of 5 m and the models with a smaller grid discretization in x-direction have a very similar distribution of hydraulic heads and similar flow paths. Because model 2 did not converge with a cell size of 2 m in x-direction, a cell length of 1.8 m was chosen instead.

## 6.4.2 Testing the Eastern Model Boundaries

Two further models were used to demonstrate the effects of different boundary conditions (constant head and constant flux) at the eastern model boundary. The model set-up was modified to simplify the water balances of the models (shown in the MODFLOW lst output file). The westernmost 475 m of the original model domain in x-direction were excluded so that the models only comprise the eastern part of the river where losing stream conditions prevail (Table 6.2).

**Table 6.2** Model extent in x-direction for models 3 and 4. All other parameters are shown in Table 6.1.

| Parameter | Value |
|---|---|
| Model extent column, x-direction (m) | 2625 |
| $x_{min}$ (m) | 475 |
| $x_{max}$ (m) | 3100 |
| Number of columns | 525 |

Model 3: The western model boundary was defined by a constant head of 202 m in the river and a boundary flux of 1000 m$^3$/d was set at the eastern model boundary.

Model 4: The western model boundary was defined by a constant head of 202 m in the river. A constant head boundary with a head value of 196 masl was defined at the eastern model border.

Because the influence of the different boundary conditions on the model results can only be seen at different abstraction rates, different model runs were performed. First, both models were run with abstraction rates of 1000 m$^3$/d per well. In a second step, the pumping rates in all wells were increased to 1200 m$^3$/d and in a third step to 1400 m$^3$/d per well. Hydraulic heads and water balances were compared.

Additionally, the impact different wells have on the water level decline in the eastern floodplain was tested using model 3 (constant flux boundary condition at the eastern border). This was done by increasing the pumping rate first of well P3 to 1800 m$^3$/d and 2600 m$^3$/d while the pumping rates in all other wells remained at 1000 m$^3$/d. In a second step, P3 was set back to 1000 m$^3$/d and the pumping rates only in well P4 were increased to 1800 and 2600 m$^3$/d, respectively.

### Results

The results of models 3 and 4 showed that the choice of boundary conditions, as expected, has a big influence on the groundwater flow and the water budget. With the initial pumping rate of 1000 m$^3$/d per well, models 3 and 4 have the same hydraulic head distributions and similar water balances. Increasing the pumping rates to 1400 m$^3$/d in each well led to a declining groundwater table in model 3 (-3.3 m at the eastern border) and to a minimal outwards flux (29 m$^3$/d) at the eastern boundary in model 4 (Table 6.3). At the same time, the inwards flux from the river was much higher in model 3 (5310 m3/d) than in model 4 (4325 m/d). Increasing pumping rates further would induce an inwards flux at the eastern border in model 4 (constant head boundary).

**Table 6.3** Comparison of the water budget of models 3 and 4 with different pumping scenarios applied.

| **Model** | **Pumping rate** (m$^3$/d/well) | **Inflow (heads)** (m$^3$/d) | **Recharge** (m$^3$/d) | **Well (out)** (m$^3$/d) | **Flux (out)** (m$^3$/d)[A] | **Head$_{East}$** (masl)[B] |
|---|---|---|---|---|---|---|
| Model 3 | 1000 | 3692 | 1305 | 3998 | 1000 | 195.7 |
| Model 3 | 1200 | 4494 | 1305 | 4799 | 1000 | 194.2 |
| Model 3 | 1400 | 5310 | 1305 | 5616 | 1000 | 192.4 |
| Model 4 | 1000 | 3681 | 1305 | 4000 | 986 | 195.7 |
| Model 4 | 1200 | 4002 | 1305 | 4800 | 508 | 195.7 |
| Model 4 | 1400 | 4325 | 1305 | 5601 | 29 | 195.7 |
| Model 3 | P3: 1800[C] | 4487 | 1305 | 4793 | 1000 | 195.1 |
| Model 3 | P4: 1800[C] | 4487 | 1305 | 4793 | 1000 | 194.5 |
| Model 3 | P3: 2600[C] | 5293 | 1305 | 5599 | 1000 | 194.5 |
| Model 3 | P4: 2600[C] | 5293 | 1305 | 5599 | 1000 | 193.0 |

[A] In Model 3 the flux was defined by placing a well at the eastern model border, in Model 4, the flux is given in the water budget. [B] The vertical discretization is 0.3 m. [C] Pumping rate in all other wells is 1000 m$^3$/d.

Increasing the pumping rates of wells P3 and P4 individually showed that the water table decline is significantly smaller if the higher abstraction takes place near the river in well P3 (Table 6.3).

These results indicate that the hydrochemical evolution of the infiltrating river water along the flow paths (to a large part in the kankar, to some extent in the sand) is not influenced by mixing with ambient groundwater. 1D reactive transport modeling of flow paths is, therefore, a reasonable approach to get a first estimation of contamination and decontamination periods.

## 6.5 1D REACTIVE TRANSPORT MODELING

With the aim to predict the future concentrations of $NH_4^+$ at well P3, 1D reactive transport models (Haerens et al. 2002) were set up for the field site. Based on the results of the 1D reactive transport column models (Chapter 5), two flow paths in representative aquifer sediments were modeled with PHREEQC v3 (Parkhurst and Appelo 2013). One flow path comprises 500 m distance from the riverbank to Ranney well P3 (Fig. 6.6). These 500 m were set up as a column divided into 139 cells with a cell length of 3.6 m each. The time step was set to 4 d, resulting in the average linear velocity of 0.9 m/d as determined by (Sprenger 2011). Transport parameters (effective porosities, number of exchange sites and selectivity coefficients for the cation exchange) were taken from the 1D column modeling without any further adjustments (Table 6.4). Dispersivities were adjusted to the model length. Although dispersion is generally higher at the field scale than at the laboratory scale because of sediment inhomogeneities which are not present in laboratory columns (Gelhar et al. 1992), the dispersivities of the field model were adjusted to represent the magnitude measured in the column experiments. The longitudinal dispersivity was set to 5 m (1/100 of the flow path) in the sand and to 50 m (1/10 of the flow path) in the kankar. Because the sediment is carbonatic (Eybing 2014) and most water samples at the field site were slightly oversaturated with calcite, calcite was included as an equilibrium phase in the model. To check for numerical errors, the models were also run with 278 cells (1.8 m cell lengths) and 2 d time steps and with 556 cells (0.9 m cell lengths) and 1 d time steps.

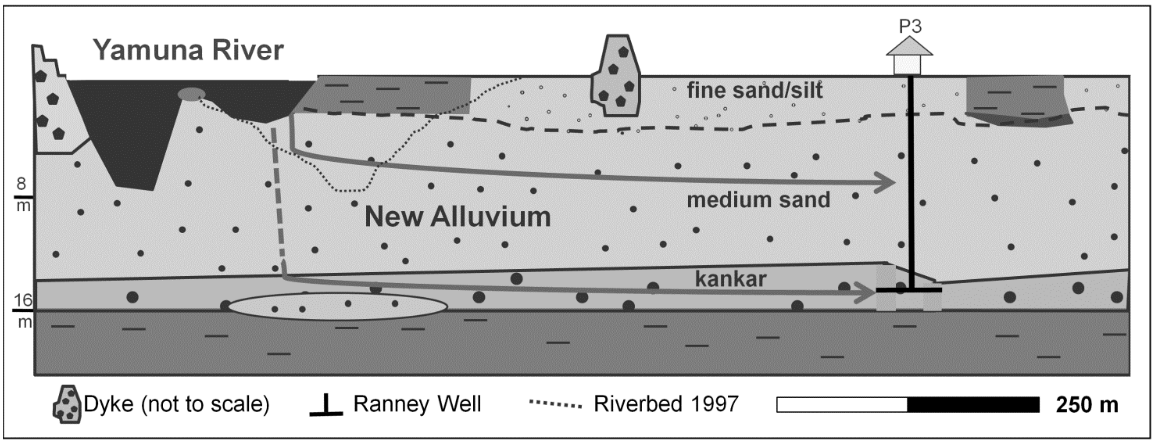

**Fig. 6.6** Flow paths from the river to well P3 in the 1D reactive transport models. The vertical flow from the river to the kankar layer was not considered and modeled.

**Table 6.4** Transport parameters used in the simplified 1D model.

| **Parameter** | **Unit** | **Sand** | **Kankar** |
|---|---|---|---|
| Effective Porosity ($n_e$)* | --- | 0.24 | 0.175 |
| Number of exchange sites | meq/1L water | 0.054 | 0.21 |
| log_$k_{Na\backslash K}$ | --- | 0.67 | 0.98 |
| log_$k_{Na\backslash Ca}$ | --- | 0.1 | 0.18 |
| log_$k_{Na\backslash Mg}$ | --- | -0.28 | -0.09 |
| log_$k_{Na\backslash NH4}$ | --- | 0.55 | 0.81 |

*Effective porosities are not explicitly included in PHREEQC models. They are incorporated through the number of exchange sites.

To keep the model minimal and straightforward, the following assumptions and simplifications were applied:

- Source water composition (displacing solution) was kept constant, although in reality there is a seasonal variability in the river water due to monsoon–non monsoon compositions.
- $NH_4^+$ was decoupled from the nitrogen cycle, meaning it cannot be oxidized to nitrate in the model. This would be representative of anoxic conditions in the aquifer, which by no means must prevail after an improvement of source water quality.
- An average linear flow velocity of 0.9 m/d (Sprenger 2011) was assumed for both flow paths. It is very likely that flow velocities are much higher in the kankar layer, but real data for this layer are not available.

### 6.5.1 Adsorption Modeling

The infiltration of sewage-influenced river water into the aquifer was modeled to estimate the increase of $NH_4^+$ concentrations at well P3. The cells were equilibrated with water samples taken at sampling points still uninfluenced by the $NH_4^+$ plume. A sample taken from HatP4 in December 2013 was used for equilibrating the sand layer and a sample taken at P4 in December 2013 was used to equilibrate the kankar layer. The cells were then flushed with a displacing solution with the composition of a sewage influenced river water sample taken at the field site in December 2012 with an $NH_4^+$ concentration of 20 mg/L. The compositions of the water samples are summarized in Table 6.5. In the models, it took about 15 years to reach the 100 % $NH_4^+$ breakthrough in the sand layer and 62 years to reach the 100 % $NH_4^+$ breakthrough in the kankar layer (Fig. 6.7).

**Table 6.5** Adsorption modeling: Composition of the equilibrating and displacing solutions. Water samples were charge-balanced with alkalinity as $HCO_3^-$. Groundwater samples were taken in December 2013. River water sample was taken in December 2012.

| Parameter | Unit | Equilibrating solution sand (HatP4) | Equilibrating solution kankar (P4) | Displacing solution (river water field site) |
|---|---|---|---|---|
| T | °C | 26.2 | 26.4 | 20.5 |
| pH | pH | 7.58 | 7.4 | 7.6 |
| $E_h$ | mV | 160 | 175 | 82 |
| EC | µS/cm | 495 | 893 | 1588 |
| Na | mg/L | 19.9 | 67.5 | 171 |
| K | mg/L | 5.4 | 6.8 | 15.4 |
| Mg | mg/L | 14 | 23 | 33.7 |
| Ca | mg/L | 63.7 | 80 | 65.4 |
| Fe | mg/L | 0.09 | 0.1 | 0.07 |
| Mn | mg/L | 0.09 | 0.3 | 0.3 |
| $HCO_3^-$ | mmol/L | 5.2 | 5.9 | 6.5 |
| Cl | mg/L | 6 | 78 | 218 |
| $SO_4$ | mg/L | 2 | 53 | 125 |
| $S^{2-}$ | mg/L | 0 | 0 | 0 |
| $NH_4^+$ | mg/L | 0 | 0.6 | 20 |
| $NO_2^-$ | mg/L | 0.005 | 0.03 | 0.02 |
| $NO_3^-$ | mg/L | 0 | 3.5 | 0 |

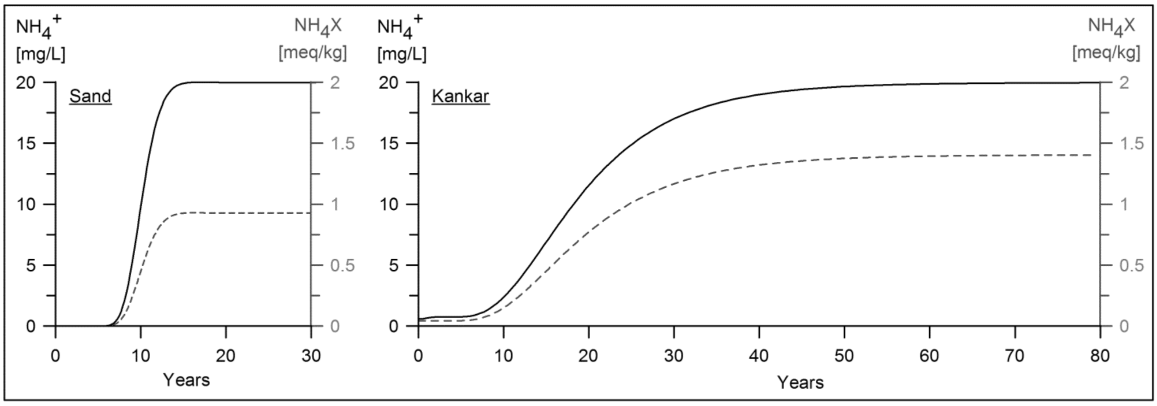

**Fig. 6.7** Results of adsorption modeling. Solid black line: $NH_4^+$ concentration in the water in mg/L (primary y-axis), dashed grey line: $NH_4^+$ concentrations on the exchanger in meq/kg sediment (secondary y-axis). The amount of $NH_4^+$ sorbed on the sediment depends on the number of exchange sites available, on the solute composition and on the selectivity coefficients, which are sediment-dependent. It can be clearly seen that more $NH_4^+$ can be adsorbed on the kankar material than on the sand.

## 6.5.2 Desorption Modeling

How long the $NH_4^+$ contamination will prevail in the aquifer after source water quality improves depends not only on the sediment properties, but also on the extent of the $NH_4^+$ plume. To model $NH_4^+$ desorption, it was assumed that:

- The $NH_4^+$ plume has completely reached the well P3.
- The $NH_4^+$ distribution within the plume is homogenous at 35 mg/L $NH_4^+$ in the groundwater in the sand layer and 26 mg/L in the kankar layer.

The cells of the sand flow path were equilibrated with a water sample from handpump B1 taken in December 2013 and the cells of the kankar flow path were equilibrated with water composition of sample H250 taken in December 2013 (Table 6.6). After equilibration, the column was flushed with a displacing solution with the composition of the river water upstream Delhi at Palla, where the Yamuna is still uninfluenced by sewage water.

**Table 6.6** Desorption modeling: Composition of the equilibrating and displacing solutions. Water samples were charge-balanced with alkalinity as $HCO_3^-$. Groundwater samples were taken in December 2013. River water sample was taken in March 2007 in the frame of the TECHNEAU project.

| Parameter | Unit | Equilibrating solution sand (B1) | Equilibrating solution kankar (H250) | Displacing solution (river water upstream) |
|---|---|---|---|---|
| T | °C | 25.2 | 24.3 | 22.3 |
| pH | | 6.93 | 7.23 | 8.56 |
| $E_h$ | mV | 105 | 84 | 268 |
| EC | µS/cm | 1615 | 1153 | 457 |
| Na | mg/L | 97 | 79.7 | 35 |
| K | mg/L | 17.3 | 13.2 | 9 |
| Mg | mg/L | 38.7 | 24.8 | 14 |
| Ca | mg/L | 126.5 | 89.1 | 44 |
| Fe | mg/L | 16.9 | 5.2 | 0.62 |
| Mn | mg/L | 0.42 | 0.27 | 0.05 |
| $HCO_3^-$ | mmol/L | 11.9 | 8.3 | 2.7 |
| Cl | mg/L | 141 | 115 | 38 |
| $SO_4$ | mg/L | 5 | 4 | 46 |
| $S^{2-}$ | mg/L | 0.04 | 0 | 0 |
| $NH_4^+$ | mg/L | 35 | 26 | 0.1 |
| $NO_2^-$ | mg/L | 0.005 | 0.005 | 0.2 |
| $NO_3^-$ | mg/L | 0 | 0.05 | 6 |

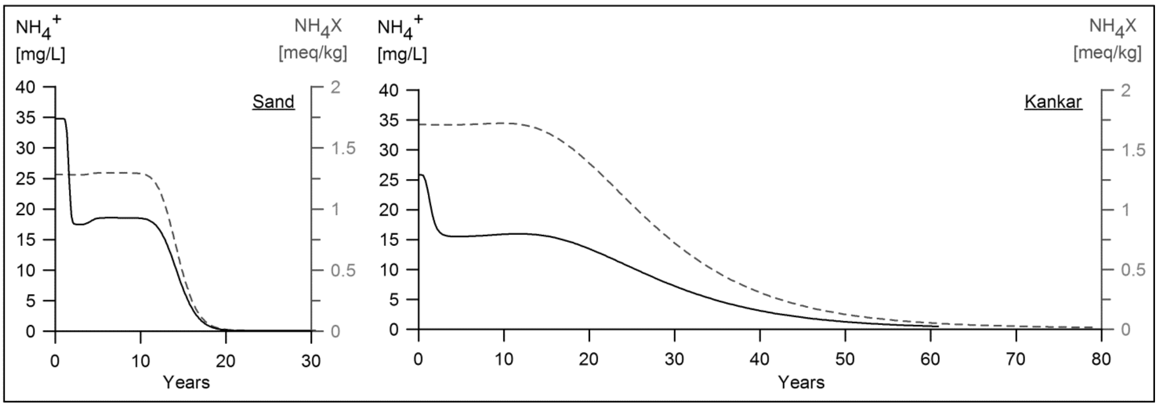

**Fig. 6.8** Results of the desorption modeling. Solid black line: $NH_4^+$ concentration in water in mg/L (primary y-axis), dashed grey line: $NH_4^+$ concentrations on the exchanger in meq/kg sediment (secondary y-axis). Like in the adsorption-model runs, more $NH_4^+$ is adsorbed on the kankar than on the sand. The actual amounts adsorbed in the beginning of the desorption-model run are higher than the amounts adsorbed in the adsorption-models (Fig. 6.7) because the desorption-model was equilibrated with higher concentrations of $NH_4^+$.

Assuming the same average linear velocity of 0.9 m/d in the sand and the kankar, $NH_4^+$ concentrations were below the drinking water limit value of 0.5 mg/L after about 19 years in the sand layer and after about 61 years in the kankar layer (Fig. 6.8). This is due to the higher number of exchange sites in the kankar and to different selectivity coefficients in both materials. Because degradation of $NH_4^+$ was not implemented in the models, the results can only be seen as conservative estimates. Furthermore, the average linear velocity in the kankar is probably higher than in the sand and flushing the $NH_4^+$ out of the kankar layer might, therefore, be faster than 61 years.

## 6.6 DISCUSSION AND CONCLUSIONS

The 2D modeling revealed that it is sufficient to set the Yamuna River as the western boundary. With the chosen hydraulic conductivities no groundwater flow occurs beneath the river in any case. This is probably due to the geometry of the aquifer (shallow) and the river (deep and wide). The choice of boundary conditions at the eastern model boundary has a big influence on model results. A constant flux boundary would ensure that no additional groundwater source at the eastern model border would be activated unintentionally when applying high abstraction rates at the wells. However, it is almost impossible to determine a realistic flux. A constant head boundary would therefore also be a reasonable option. However, it has to be ensured that a reasonable large outwards flux at the model border exists at any time. The simple models showed that the choice of boundary conditions have a big effect on the resulting infiltration rates of the river. A realistic estimation of infiltration rates, which determines the $NH_4^+$ input into the aquifer, can therefore only be made with an improved data basis.

The applied abstraction rates in the Ranney wells are very low. According to DWSSP (2004), 16 Ranney wells of the DJB located on the Yamuna floodplain produce $101\times10^3$ $m^3/d$ (22 MGD). This results in an average abstraction of 6300 $m^3/d$ per Ranney well. Using the current 2D models, it is not possible to apply such abstraction rates and remain in the frame of reasonable groundwater tables. This indicates that either abstraction rates are much lower than assumed or that the model parameters, especially hydraulic conductivities, need to be improved. Data about abstraction rates and pumping tests conducted in the different lithologies would greatly improve the understanding of the field site and the set-up of groundwater flow models.

The modeled decontamination time for the first 500 m of the aquifer varied between 19 years in the sand and 61 years in the kankar layer. This time period is similar to the time it took to achieve the 100 % $NH_4^+$ breakthrough in the respective sediments (15 and 62 years). The results of the 2D flow models showed that the Ranney well P3 draws almost the entire water from the kankar layer; the share of groundwater from the sand layer is low and there is no share of recharge-influenced groundwater. Therefore, the 1D flow path through the kankar layer is a realistic option and the decontamination time is more likely in the range of 61 years than of 19 years. The determination of groundwater travel times in the kankar layer would improve the prediction of the decontamination period.

# Chapter 7

# Remediation and Post-Treatment Strategies[12]

## Abstract

Ammonium ($NH_4^+$) concentrations of up to 35 mg/L were measured in the groundwater at a riverbank filtration site in central Delhi (India). To make $NH_4^+$ contaminated groundwater suitable for drinking purposes, either remediation measures have to be applied to lower $NH_4^+$ concentrations in the groundwater or the raw water has to be treated before distribution. Besides source control measures, a number of in-situ and ex-situ (mostly pump-and-treat) options are available for the remediation of $NH_4^+$ contaminated sites. Depending on the remediation method, the local hydrogeological situation and the (waste) water management, $NH_4^+$ concentrations within the permissible limit can be achieved in different time spans (between several months and several decades). Installing a suitable post-treatment would lead to fast improvements of water quality in the distribution network and could be used in concert with remediation measures or as a stand-alone option. Possible post-treatment methods include physicochemical treatment techniques and biological filters. The implementation of remediation measures would be difficult at the studied site: The Yamuna River is the main source of the $NH_4^+$, and thus the source area is several km long. The drinking water production wells are located on the floodplain, and groundwater flow paths towards the abstraction wells are relatively short. Furthermore, the area, where remediation measures would have to be applied, should be regarded as a drinking water protection zone. Therefore, it is strongly recommended to consider the option of a stand-alone post-treatment solution for the well field.

This chapter summarizes the remediation and post-treatment options available for $NH_4^+$ contaminated water and discusses the applicability of the methods under the conditions met in Delhi. Example case- and pilot studies are described.

## 7.1 INTRODUCTION

At the studied RBF site in central Delhi, almost all sampling points show $NH_4^+$ concentrations above the requirement of the Indian Standard Drinking Water-Specification of 0.5 mg/L (specified for total ammonia-N). $NH_4^+$ concentrations are especially high in the handpumps

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[12] This chapter is based on the Saph Pani Deliverable D1.3. Section 7.5 contains parts of Groeschke, M., Frommen, T., Grützmacher, G., Schneider, M., Sehgal, D. (2015) Application of Bank Filtration in Aquifers Affected by Ammonium – The Delhi Example. In: Wintgens, T., Anders, N., Elango, L., Asolekar, R. S. (Eds.) Natural Water Treatment Systems for Safe and Sustainable Water Supply in the Indian Context: Saph Pani. IWA Publishing, pp 57-77.

located close to the river (up to 35 mg/L). A large Ranney well at a distance of 500 m to the river has elevated concentrations between 5 and 8 mg/L. Although other studied Ranney wells currently have lower $NH_4^+$ concentrations of about 1 mg/L, the plume is expected to spread further, and increasing $NH_4^+$ concentrations can be expected in the wells further away from the river. Remediation or treatment is necessary to achieve drinking water quality.

Although a large variation of remediation and post-treatment techniques exists on the market, most of them are based on one or more of the following three principles: nitrification-denitrification, cation exchange or the pH dependent equilibrium of $NH_4^+$ and $NH_3$ (Fig. 7.1).

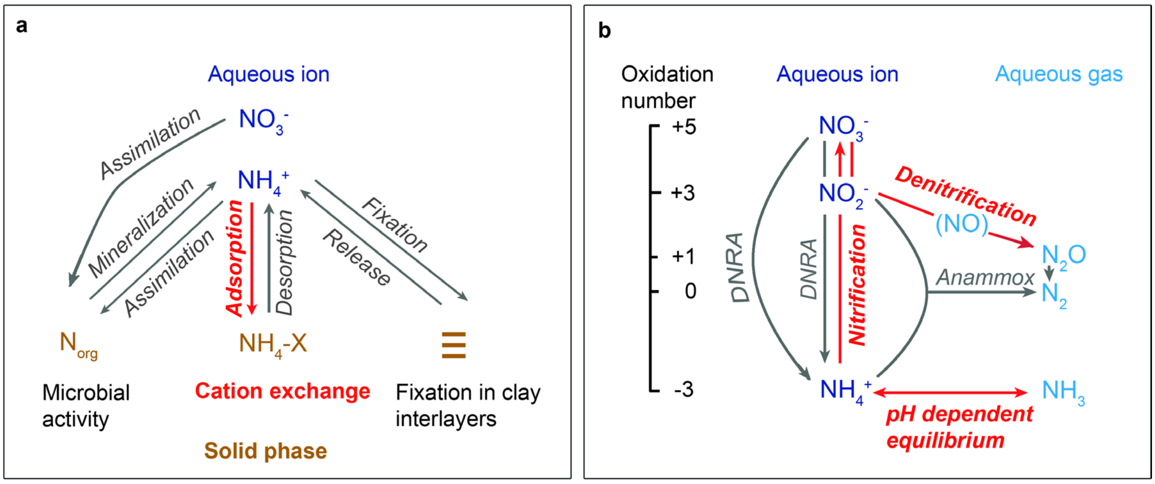

**Fig. 7.1** The most common approaches for $NH_4^+$ remediation and post-treatment options (marked in red and bold) (a) $NH_4^+$ adsorption and (b) nitrification followed by denitrification or the removal of $NH_3$ (gas) achieved by increasing the pH.

## 7.2 REMEDIATION OPTIONS

Remediation measures aim at removing the contaminants from the groundwater or converting them into harmless products. Remedial technologies can be based on physical principles and chemical reactions or on bioremediation (Reddy 2008). Bioremediation describes the use of organisms – mostly microorganisms – to degrade the contaminants. This can be achieved by providing favorable conditions for microbial growth, e.g. providing nutrients and adjusting the redox conditions or pH in the aquifer (Vidali 2001). The speciation of nitrogen is strongly dependent on the prevailing redox conditions, and microbial activity mediates oxidation or reduction of the different species. Most remediation measures for $NH_4^+$ contaminated aquifers therefore entirely or partly use bioremediation to lower $NH_4^+$ and total nitrogen concentrations in the aquifer.

Three approaches to restore $NH_4^+$ contaminated aquifers were identified: source control (removal or control of all known and suspected sources of contamination), in-situ treatment methods and pump-and-treat measures involving above-ground treatment of the water. The following techniques are discussed in the next sections:

(1) Source control measures
    - General improvement of river water quality
    - Aeration basins at the riverbank

(2) In-situ treatment methods
    - Injection of oxygen by sparging
    - Groundwater circulation wells
    - Permeable reactive barrier remediation

(3) Pump-and-treat measures
    - Surfactant enhanced ex-situ treatment
    - Nutrient enhanced ex-situ treatment

### 7.2.1 Source Control

Source control is an important aspect in remediation, especially in the case of a continuous source of contamination (in contrast to a one-time leak scenario). To achieve the restoration of the site, the source of contamination has to be removed or decoupled from the groundwater pathway (IAEA 1999). Decoupling can be achieved using physical barriers (e.g. soil-bentonite slurry walls) or hydraulic barriers (Houlihan and Botek 2007). These options are not discussed in this chapter: Measures would have to be implemented on an extremely large scale because the Yamuna River is the origin of the contamination. Furthermore, reducing groundwater recharge in the floodplain aquifer by reducing the infiltration of river water is not an appropriate management option in a water stressed city.

Removing the source term would usually include removing the infiltrating contaminant as well as the polluted soil by excavation. As was shown in chapters 5 and 6, the $NH_4^+$ contaminated sediment will be a source of $NH_4^+$ for several decades. Due to the large contaminant plume it is not possible to remove the contaminated soil and the only option is to change the infiltrating river water quality. This can be achieved by:

- Improving river water quality
- Constructing infiltration basins at the riverbank

Pump-and-treat methods are sometimes used as containment measures because they can help prevent the migration of the contaminant plume through hydrodynamic control (e.g. Cohen et al. 1997, Christ and Goltz 2004). In this study, the focus of the pump-and-treat methods is not hydrodynamic control but groundwater quality restoration. They are thus described in section 7.2.3 (Pump-and-Treat Methods).

**General Improvement of River Water Quality**

It is necessary to remove the source of the groundwater contamination, i.e. the discharge of untreated sewage into the river to obtain good quality bank filtrate in the long term. This can be achieved by:

- Increasing sewage treatment capacity so that the sewage generated will be treated before being discharged into the river
- Disposing untreated sewage elsewhere, e.g. on sewage farms

In the first scenario, the resulting river water quality will strongly depend on the guideline values for STP effluents. However, contaminants accumulated in the riverbed sediments during the years of heavy sewage contamination might have an influence on river water quality even after the discharge of untreated sewage is terminated. If the flow of the river is not restricted through barrages, upstream river water quality and dilution effects also play a role. The second option would inevitably lead to groundwater contamination at other locations and would cause long-lasting problems in other aquifers. Therefore, this option is not discussed further.

The improvement of river water quality is a long-term measure, and decreasing $NH_4^+$ concentrations cannot be expected to occur rapidly. Even after the $NH_4^+$ source is removed, a $NH_4^+$ contamination of an aquifer can prevail for decades as flushing the aquifer with $NH_4^+$ -free water will cause desorption of the sorbed $NH_4^+$ from the sediment matrix. A reactive transport modeling case study in Berlin (Germany) revealed that elevated $NH_4^+$ concentrations originating from a former sewage farm can prevail for over 200 years after the deposition of sewage water and sludge was terminated (Hamann 2009).

Aspects to consider in the evaluation of the applicability of this method in Delhi:

In general, aiming at this solution is inevitable in the long run. However, pronounced results are expected only in the medium−long term. Besides the fact that $NH_4^+$ desorption will lead to very long decontamination period, the following reasons make it especially hard to achieve the rehabilitation in Delhi: The current Indian guideline values for STP effluents will not solve the problem of high nitrogen loads in surface water and, therefore, nitrogen might remain a parameter of concern in the bank filtrate. Additionally, the implementation of this measure is difficult in a fast growing city with a constantly increasing sewage generation and numerous informal drains discharging into the river.

Results of simplified 1D reactive transport models at field scale show that it can take up to 61 years to decontaminate a 500 m wide zone along the river (see chapter 6). Even then, nitrogen concentrations in the groundwater might not meet the drinking water requirements. On one hand, the $NH_4^+$ plume will have moved further in groundwater flow direction causing elevated $NH_4^+$ concentrations in other wells of the well field. On the contrary, the models do not take into account elevated $NO_3^-$ concentrations in the source water, which have to be expected because of high STP effluent guideline values.

According to the guidelines for treated effluent quality of common effluent treatment plants (i.e. not for industrial waste water) the effluents need to meet guideline values of 50 mg/L ammonical-N ($NH_4$-N and $NH_3$-N) and 100 mg/L total Kjeldahl N (organic-N and ammonical-N) before it can be discharged into inland surface water bodies (CPCB 2010a, p.448). These limits are high compared to the guideline values in the European Union, where nitrogen pollution in rivers is low (see section 1.3.3). The guideline value for the annual means of total N concentrations (the sum of Kjeldahl N, $NO_3$-N and $NO_2$-N) is 15 mg/L for treatment plants of 10,000-100,000 population equivalent and 10 mg/L for plants above 100,000 population equivalent. Alternatively, a minimum reduction of 70−80 % of the total N has to be achieved (European Council 1991, European Commission 1998, Blöch 2005). The generous Indian guideline values are not a useful tool to solve the problem of high nitrogen loads in surface water bodies. However, in an oxic river, $NH_4^+$ would not be the predominant nitrogen species as it would be oxidized to $NO_3^-$. The transport of $NO_3^-$ is not retarded in the groundwater and contamination would, therefore, be easier to handle. Moreover, the permissible limit of $NO_3$-N (10.2 mg/L) in potable water is 20 times higher than the permissible limit for $NH_4$-N (IS 10500: 2012). Still it is advisable to set separate, stricter guideline values for new STPs.

Additional STPs need to be planned and built. Rapid population growth leads to a constant increase in sewage generation. According to the National Capital Region Planning Board (2013) the expected population growth rate is 19 % per decade (from 16.8 million in 2011 to 20 million people in 2021) in NCT Delhi and 41 % per decade for the total Delhi metropolitan area (from 22 million to 31 million people in 2021). Predictions about population development are highly uncertain, which makes it difficult to obtain a reliable prognosis, which is necessary for the planning of large scale infrastructure projects such as STPs. Moreover, the sewage network must be developed as well.

Despite all the difficulties, this measure is the only measure which would ultimately solve the problem of $NH_4^+$ contamination (if not the overall nitrogen problem) in the floodplain aquifer in the long term. Besides reducing $NH_4^+$ concentrations, it is expected that the redox zonation in the aquifer will change and that arsenic concentrations in the groundwater will decrease (see Chapter 7.3 – Effects of Remediation on the Aquifer). Many STPs and sewerage facilities are currently under construction, and more STPs are proposed. Therefore, an improvement of river water quality can be expected in the future.

### Aeration Basins at the Riverbank

Large aeration basins could be constructed parallel to the river along the riverbank to induce a similar effect as the general improvement of river water quality on a short term basis. River water could be then pumped or diverted into the basins where aeration would be achieved by pressing oxygen gas or air into the water, whereby the first is to prefer due to its higher efficiency. From these basins, the aerated water could then either be infiltrated directly into the aquifer, or it could be distributed back into the main stream to dilute the river water and increase water quality.

Aspects to consider in the evaluation of the applicability of this method in Delhi:

This method would allow for a short-term improvement of surface water quality. It is a low-tech and cost-efficient method, as it allows the possibility to treat only a fraction of the river water. Besides the problem of long decontamination periods due to $NH_4^+$ desorption from the aquifer matrix (discussed above), the following difficulties with this method might occur in Delhi:

Elevated costs and difficult operation, infiltration of $NO_3^-$-rich water from the aeration basins, and a strong necessity of health and safety measures.

Elevated costs and difficult operation are expected with this measure in Delhi because the chemical and biological oxygen demand (COD and BOD) of sewage-influenced water bodies is high, leading to a high oxygen consumption. Therefore, a large oxygen input is necessary to significantly increase dissolved oxygen concentrations in the water. It could be difficult to achieve sufficient distribution of the injected oxygen in the water body and clogging of the oxygen diffusers could occur due to the high loads of suspended solids in the river. This leads to higher operational costs. Furthermore, the Yamuna River is a meandering river with a frequently shifting riverbed and high sediment loads during monsoon times. Thus, the aeration basins would have to be constantly adjusted according to the changing course of the river. The high sediment loads might also lead to clogging of the oxygen diffusers and the filling up of the aeration basins due to sedimentation.

The problem of high total nitrogen concentrations in the river water is not solved by this method. Constructing aeration basins at the riverbank would help decrease $NH_4^+$ concentrations through the process of nitrification. Nitrification is a biologically mediated process and depends on the occurrence of microorganism communities. Therefore, the system is complex and limiting factors are not only oxygen but also pH, temperature and nutrient concentrations (Pollice et al. 2002). Incomplete nitrification can occur for several reasons. For example, Hellinga et al. (1998) showed that at temperatures above 30°C and a pH above 7, $NH_4^+$ oxidizers grow faster than $NO_2^-$ oxidizers. In the Yamuna River in central Delhi, a pH between 7 and 8 is common, and river water temperatures up to 33°C were measured in the summer months. Therefore, the danger of elevated $NO_2^-$ concentrations persists, which can be toxic for aquatic species (Jensen 2003). In STPs, a nitrification step is usually followed by a denitrification step to eliminate the nitrogen from the water. This cannot be achieved in aeration basins at the riverbank. However, as is mentioned in the previous section (General Improvement of River Water Quality), the $NO_3$-N limit is 20 times higher than the $NH_4$-N limit in the Indian Standard Drinking Water-Specification (IS 10500: 2012).

Strict health and safety measures would have to be implemented because the river stretch between Wazirabad and Okhla barrage is highly polluted. Fecal coliform counts of up to $6\times10^{10}$ MPN/100mL and total coliform counts up to $12\times10^{10}$ MPN/100mL were measured (CPCB 2013b, p.77–78). This constitutes a serious threat to the health of personnel in charge of the maintenance of the facilities, and occupational health and safety measures would have to be applied.

### 7.2.2 In-Situ Remediation

In-situ remediation measures aim at treating contaminated groundwater directly in the aquifer without extracting groundwater for treatment in above-ground systems (U.S. Environmental Protection Agency 2013). In-situ remediation involves the injection of reagents into the aquifer to trigger biological or chemical reactions to promote the degradation or immobilization of the contaminants. The following in-situ remediation concepts were applied for the restoration of $NH_4^+$ contaminated aquifers:

- Bioremediation through oxygen gas injection
- Groundwater circulation wells
- Sequential reactive barrier remediation

**Bioremediation through Oxygen Gas Injection**

The injection of oxygen into the aquifer is one example of enhanced aerobic bioremediation. Oxygen gas is directly injected into the aquifer where it partitions into the groundwater and spreads with the groundwater flow. Nitrification (oxidation of $NH_4^+$) takes place in the induced oxic zone. This zone is limited because microbial degradation processes in the aquifer consume the injected oxygen. Denitrification reactions then take place in the naturally occurring anoxic zone downstream of the oxic zone.

One application of the method is the BIOXWAND (Bio-Oxidation Wall) technique (patented by Berliner Wasserbetriebe, BWB). The method is a variation of in-situ air sparging (IAS) methods described by Johnson et al. (1993), where the oxygen is provided by the injection of air.

**Example**: A BIOXWAND was installed to treat an $NH_4^+$ contamination in Berlin, Germany. Groundwater within the subsurface catchment area of a waterworks in the southeastern part of the city is in part highly contaminated with $NH_4^+$. The source of the $NH_4^+$ is a former sewage farm located upgradient of the groundwater flow, where domestic and industrial sewage water was disposed until 1976. Currently, the $NH_4^+$ plume in the unconfined coarse to medium grained sand aquifer is about 1.5 km long, 3 km wide and 45 m deep. $NH_4^+$ concentrations in the groundwater are in the range of 10-90 mg/L $NH_4^+$-N. The plume is described in detail by Hamann (2009).

To protect drinking water production wells at the waterworks, a remediation concept was developed on the basis of oxygen injection into the aquifer. In 2007, a pilot site of 100 m length was installed perpendicular to the groundwater flow (BWB 2008). It was upgraded in 2010−2012 and currently has a length of 800 m (BWB 2012). At 15 m intervals, technical oxygen and air are injected into the normally oxygen-free aquifer through gas lances with 1 m long filter screens at depths between 13 and 36 mbgl (Engelmann and Schmolke 2014). This leads to the development of a trapped oxygen gas phase in the groundwater, the so called bubble wall zone (Giese et al. 2003). This zone supplies oxygen to the passing groundwater flow for microbial oxidative degradation of $NH_4^+$ (nitrification). The artificially induced aerobic zone is naturally followed by an anaerobic zone further downstream. In this zone denitrification occurs (Engelmann et al. 2004, Horner et al. 2009).

Besides the desired nitrification and denitrification processes, secondary processes were observed, including sulfate release and acidification through pyrite oxidation and hardening owing to pH buffering by calcite dissolution. Modeling results showed that the elevated sulfate generation is limited to an initial phase until all pyrite is consumed in the oxic zone (Horner et al. 2009). Mass and volume balances indicate that the risk of long-term pore clogging due to the precipitation of ferric iron in the oxic zone is very low. Nitrification was observed to be inhibited when oxygen concentrations exceeded 50 mg/L (Giese et al. 2015); otherwise stable nitrification was achieved (Giese et al. 2003).

The BIOXWAND remediation measure is expected to be necessary for the duration of 80 years, until the $NH_4^+$ contamination is flushed out of the aquifer (Horner et al. 2009).

<u>Aspects to consider in the evaluation of the applicability of this method in Delhi:</u>

In general, an implementation of this measure seems possible regarding the aquifer characteristics and groundwater chemistry, which were thoroughly studied at the Delhi study site (Lorenzen et al. 2010, Lorenzen 2011, Sprenger 2011, Groeschke 2013, Sprenger and Lorenzen 2014). Pyrite has not been detected in the sediments (Chapter 3) and acidification due to pyrite oxidation is not expected. However, in case of the presence of other sulfide minerals, a calcite-buffering system is expected to develop in the aquifer because of the carbonate contents of the sediments. Therefore, a significant decrease in the pH is not to be expected at the field site.

Both, pH and temperature affect nitrification rates which are dependent on the growth of nitrifying bacteria. Nitrification rates are strongly inhibited at temperatures below 10°C and increase with rising temperatures (Wild et al. 1971). An optimum temperature of 25−33 °C was reported by Shammas (1986). At very high temperatures enzymatic proteins denature, leading to a decrease in nitrification (Zhu and Chen 2002). High groundwater temperatures around 25 °C at the field site would, therefore, be an advantage for the application of this method as it would result in a faster nitrification process. Wild et al. (1971) found that the optimum pH for nitrification at a constant temperature was 8.4 and that the nitrification rate at pH 7 was only 50 % of the optimum rate. At the field site, the pH in the groundwater varied between 6.9 and 7.5. Although optimum nitrification rates might not be achieved, the rates would probably still be higher than at the BIOXWAND in Berlin, where a pH of 6.5−7.5 (Hamann 2009) and a temperature of 12 °C is found in the groundwater (Rössner et al. 2000).

High Fe concentrations in the groundwater at the field site might lead to the clogging of pores and filter screens of the lances. Although Giese et al. (2015) did not observe this effect in Berlin and mass and volume balances clearly showed no danger of the occurrence of clogging, this might be different in Delhi. Fe concentrations of up to 22.3 mg/L were measured at the field site and the wells in the Yamuna floodplain are rehabilitated regularly because of clogging problems. In contrast, a background concentration of only 1.7 mg/L was reported by Hamann (2009) for the groundwater in the southeast of Berlin.

The installation costs of this measure are expected to be high and operation and maintenance challenging. While the origin of the $NH_4^+$ contamination is a point source in Berlin, in Delhi the source of the contamination is the Yamuna River. A several hundred m long BIOXWAND would therefore not be sufficient to solve the $NH_4^+$ problem in the well fields on the floodplain. Even if it would be decided to protect a specific well with such a measure, it would be difficult or even impossible to ensure a constant flow field for the next decades with Delhi's rapid population development and a constantly changing riverbed. Furthermore, during monsoon times, the area is sometimes flooded – in 2013 water levels were reported to reach up to 3 m on the floodplain. A special flood-proof design of the gas lances might be necessary. Appropriate maintenance of the oxygen injection wells is of great importance to preserve the efficiency of this long-term measure.

Nevertheless, the measure would be suitable for application at a well field used for drinking water production as it only involves the injection of oxygen gas into the aquifer. To calculate the size of a potential BIOXWAND implementation, it would be essential to fill the knowledge gaps about the groundwater flow regime and to set up a groundwater flow model.

### Groundwater Circulation Wells

Another method of adding oxygen to the aquifer is the installation of groundwater circulation wells (GCW). GCWs usually have two well screens (a lower and an upper screen) and are used to induce a circulating flow field in an aquifer. The injection of compressed air or oxygen gas into the bottom of the well creates a gas-water mixture with a reduced density and a reduced fluid pressure. This draws the surrounding groundwater into the well through the lower well screen and induces an upward flow inside the well. Along the flow path within the well, oxygen is introduced into the groundwater and volatile contaminants are removed from the water. At the upper filter, the oxic groundwater is discharged into the aquifer while the gaseous phase is removed. Thus, a circulating flow cell is created around the well (Borden and Cherry 2000). Besides air, other additives (e.g. nutrients) can be injected into the aquifer for bioremediation and the treatment step of the water (removal of the contaminant) can be modified. GCWs can be furthermore combined with other technologies such as vapor stripping (OST 2002).

IEG Technologies has adapted this technology to make it suitable for treating $NH_4^+$ contaminated groundwater (IEG GCW technology patented by IEG). In information material from the company an overview of the technique (IEG Technologie GmbH 2008) and a very brief description of an application are given (IEG Technologies UK Ltd year unknown):

**Example:** In a chalk aquifer of the London Basin, UK, $NH_4^+$ concentrations of up to 160 mg/L were observed in an about 105 m wide plume. The installation of three parallel lines of IEG GCWs perpendicular to the groundwater flow path was proposed for a two-step treatment to reach the target $NH_4^+$ concentration of 0.5 mg/L in the groundwater:

- 1. Removal of the bulk $NH_4^+$ by GCW combined with air stripping of $NH_3$
- 2. Further lowering $NH_4^+$ concentrations by means of a nitrification–denitrification sequence (bioremediation)

For the first step, a GWC equipped with a negative pressure air stripper was recommended for $NH_4^+$ removal. To increase the efficiency of the $NH_4^+$ removal, the pH of the inflowing water has to be increased to a pH of 9−10, so that the predominant species in the water would be unionized ammonia ($NH_3$). The stripped $NH_3$ can be recovered ex-situ using a wet scrubbing system. With this method, $NH_4^+$ concentrations of 20 mg/L can be achieved. The second step involves two parallel lines of GCWs. Through the first line oxygen and nutrients are added to the groundwater to induce nitrification of the residual $NH_4^+$. At the second line of GCWs an anaerobic zone is created by addition of carbon and nutrients to trigger denitrification. The bioremediation step can be further enhanced by addition of zero-valent iron to the groundwater (IEG Technologies UK Ltd year unknown).

Aspects to consider in the evaluation of the applicability of this method in Delhi:

Because $NH_4^+$ concentrations at the Delhi field site range between 20 and 35 mg/L in the centre of the plume, the air stripping of $NH_3$ through negative pressure would probably not be effective as target concentrations here seem to lie at 20 mg/L. Therefore, it would probably be sufficient to install two rows of GCWs, which induce the aerobic and anaerobic zones for nitrification-denitrification to take place. However, this method is complex.

Anisotropy of the target aquifer must be within a range that allows the circulation cell to develop and GCWs might have a limited effectiveness in shallow aquifers because of the limited space for circulation (OST 2002). In central Delhi, the floodplain aquifer is only 14.5−16 m deep. Therefore, this remediation measure might not be suitable for the location, especially because the contaminant plume may spread beyond the radius of influence if the system is not properly designed (OST 2002). Furthermore, like in all methods involving the addition of air or oxygen gas into the aquifer, clogging of the wells can occur. This might be a serious threat in Delhi, where wells already have a clogging problem due to the precipitation of Fe.

### Sequential Reactive Barrier Remediation

Permeable reactive barriers (PRBs) are a widely used in-situ method. The concept of PRBs is to place a permeable reactive material in the subsurface perpendicular to the flow path of contaminated groundwater. Due to the natural hydraulic gradient, the groundwater moves through the material where the contaminants are immobilized or transformed to less harmful species (Thiruvenkatachari et al. 2008, Obiri-Nyarko et al. 2014). This method can be combined with impermeable wings to direct the groundwater flow towards the reactive barrier (funnel and gate principle) to reduce the area of the permeable reactive material.

**Example:** In Perth, Australia, a pilot field-scale trial was carried out to test the application of an RPB for the treatment of an $NH_4^+$ contamination. The test site was located on the Swan Coastal Plain, about 30 m from the shoreline. The contaminant plume in the dune sand aquifer of 11 m thickness originates from leaks of ammonium products at a fertilizer factory about 300 m upgradient of the site. The plume had a thickness of about 6 m and reached from 5 mbgl to the clay aquitard at 11 mbgl. Maximum total N concentrations of 110 mg/L were measured (Patterson et al. 2004).

The principal idea was to trigger nitrification and denitrification processes by installing a sequence of different polymer mats in the subsurface. The first, up-gradient mat (oxygen delivery panel) was used to deliver oxygen to induce the bacterial nitrification of $NH_4^+$ to $NO_2^-$ and $NO_3^-$. The second, down-gradient mat was used to deliver ethanol (ethanol delivery panel) to induce bacterial denitrification of the $NO_3^-$ to $N_2$ gas. The mats were installed in a 0.75 m wide, 1 m long and 7 m deep gravel filled flow-through box. 10 m wide impermeable wings were constructed on either side of the reactive zone. As the wall did not reach down to the aquitard, preferential flow paths below the wall developed, making the $NH_4^+$ removal less efficient with depth. Furthermore, $NH_4^+$ feed concentrations (2−57 mg/L) were about one magnitude lower than measured maximum concentrations in the plume because only the top of the $NH_4^+$ plume was treated. Nevertheless, a substantial decrease in total N concentrations was observed. The average influent $NH_4$-N concentration was 12 mg/L and the average total N concentration after the ethanol addition was 0.5 mg/L (Patterson et al. 2004).

Large scale column experiments indicate that $NH_4^+$ removal using this technique is also efficient at higher concentrations. Total N concentrations decreased from approximately 120 mg N/L to about 10 mg N/L. Oxygen concentration initially increased from 0.05 to 23 mg/L and then decreased to around 1 mg/L within one week and remained at this level throughout the experiment (Patterson et al. 2002).

Aspects to consider in the evaluation of the applicability of this method in Delhi:

This method provides an in-situ remediation over a short time frame or groundwater flow distance, which is an advantage in Delhi where limited space is available between the source of the contamination and the production wells. Pumping is not necessary because the method makes use of the natural hydraulic gradient. This makes the measure cost-effective (once it is installed) compared to long-term above-ground treatment systems. In order to be able to use this advantage, hydraulic conditions have to be well known before the installation of PRBs to ensure that a flow through the reactive barrier will develop and to reduce the risk of preferential flow around the barrier.

At the Delhi field site, it is conceivable to construct a shield around the existing Ranney wells with particularly high $NH_4^+$ concentrations. Because the well screens of the large production wells are located at a depth of about 15 m, it would be important to construct the barrier over the full depth of the aquifer down to the clay aquitard at about 16 mbgl. This makes construction more difficult and would lead to high installation costs. A further difficulty might arise from the uncontrollable drawdown zones caused by private bore wells since the mats seem to be sensitive to changes in redox conditions. However, this probably would not affect the polymer mats in the deeper horizon of the aquifer, where the well screens are located.

Due to limited field scale studies available for this technique of $NH_4^+$ remediation, a pilot study is recommended, which should be accompanied by a research program for further evaluation of the applicability with its advantages and disadvantages. For example, it is important to understand whether competing chemicals exist in the aquifer and in which extent this measure changes the groundwater flow regime. Furthermore, possible negative impacts of groundwater table fluctuations due to groundwater abstraction have to be studied.

### 7.2.3 Pump-and-Treat Methods

Pump-and-treat methods are widely used to treat contaminated groundwater. The contaminated water is extracted from the aquifer and treated in above-ground treatment systems before it is discharged into the sewer system or re-injected into the aquifer. Pump-and-treat measures have two main advantages over in-situ remediation methods: the possibility to hydraulically control the groundwater movement and the availability of a wide range of treatment measures. Therefore, the contaminants can not only be removed from the groundwater efficiently, but the continuous spreading of the plume can be prevented and faster remediation can be achieved, e.g. by increasing the hydraulic gradient through higher pumping rates (Cohen et al. 1994). Pump-and-treat measures can be combined with other measures to further increase the efficiency. In the following section two pump-and-treat remediation methods, which were applied to treat $NH_4^+$ contaminations, are introduced:

(1) Surfactant enhanced pump-and-treat remediation (with ex-situ filtration)
(2) Nutrient enhanced pump-and-treat remediation (ex-situ addition of nutrients)

**Surfactant Enhanced Pump-and-Treat Remediation**

In many cases pump-and-treat remediation alone is not sufficient to remove the required quantities of contaminants from the aquifer to meet the given clean-up objectives and the use of surface-active agents (surfactants) is an option to enhance the efficiency and to speed up remediation (Deitsch and Rockaway 2002). Surfactants should increase the mobility of the pollutants in the aquifer by increasing their desorption from the sediment to enhance their removal through pumping. Surfactants consist of a hydrophopic and hydrophilic moiety and adsorb at the sediment interfaces, reducing the interfacial tension and, therefore, changing the wetting properties of the sediments. Depending on the pollutant, cationic, anionic or nonionic surfactants can be applied (Palmer and Fish 1992). To date, most studies and reviews about surfactant enhanced remediation focus on organic contaminants (e.g. Mulligan et al. 2001, Paria 2008).

Although no scientific publications on the use of surfactants for $NH_4^+$ remediation are available, this method was applied by the company Ivey International. The injection of a surfactant (Ivey-sol® formulation) lowered the surface tension of the groundwater, improving both its wetting and permeability properties and thus making the desorbed $NH_4^+$ hydraulically more available for extraction by pumping (Ivey International Inc. year unkown[a]).

**Example:** For the remediation of $NH_4^+$-contaminated groundwater in western Canada, the Ivey-sol® aided SORBITALL® filtration method (patented by Ivey International Inc.) was applied. The method involves enhanced desorption of $NH_4^+$ in-situ and filtration of the groundwater ex-situ. At the described site, the $NH_4^+$ contamination originated from several spills from a fertilizer facility. Measured $NH_4^+$ concentrations in the 2000 m long plume were in the range of 20 mg/L to 700 mg/L (Ivey International Inc. year unknown).

Several 100 mm diameter injection wells were installed across the plume in an integrated network of 5-spot patterns with nearby extraction wells. Ivey-sol® surfactant was injected bi-weekly to desorb $NH_4^+$ from soil and fractured bedrock surfaces. The contaminated water was then extracted and treated ex-situ with the SORBITALL® filtration system, an ion exchange technique using zeolite (Ivey International Inc. year unknown[b]). After treatment, the water was recharged through infiltration wells outside the plume boundary. Thus, a hydraulic barrier in the local groundwater table was created with the function to minimize the spreading of the $NH_4^+$ plume and to enhance the induced hydraulic gradient towards the extraction wells. An over 96 % reduction in $NH_4^+$ concentration was achieved at the example site, and the remediation was completed within 18 months (Ivey International Inc. year unknown).

Aspects to consider in the evaluation of the applicability of this method in Delhi:

With this method, the time necessary for remediation can be reduced because the injection of surfactant desorbs the $NH_4^+$ from the aquifer matrix. This would be a big advantage in Delhi because it would eliminate the problems that are associated with long term measures (constant maintenance and adjustment). However, the great disadvantage of using this method is the addition of surfactant to the groundwater. Surfactants interact with the sediment surfaces as well as with the dissolved solutes in the water, changing the aquifer characteristics. The effects of surfactants on an aquifer are site-specific and have to be thoroughly tested before application (Harwell et al. 1999). The efficient removal of the surfactants has to be ensured. Although the surfactants applied are reported to be non-toxic and biodegradable (Ivey International Inc. year unkown[a]), they must be designed to remain in the aquifer for a sufficient amount of time to achieve remediation without having to replace too large quantities of the surfactant (Harwell et al. 1999). This means that the aquifer could be influenced by surfactants beyond the period of the remediation measure. Even though the well field currently is no designated drinking water protection zone, the area should be considered as one. The application of chemicals is therefore not advised at the field site to protect drinking water resources.

### Nutrient Enhanced Remediation (Pumping and Reinjection)

Biological enhancement is another option to increase the efficiency of pump-and-treat systems (U.S. Environmental Protection Agency 1996). For the remediation of $NH_4^+$ contaminated sites, the in-situ groundwater nitrification and de-nitrification remediation system (patented by Mailath and Chu) was developed. This method is a pump-and-treat remediation method only in a wider sense because the treatment itself does not take place at the surface but in the subsoil. However, to trigger the in-situ reactions, water is pumped from the aquifer, mixed above-ground with additives and is then re-injected (Mailath and Chu 2005, 2008).

**Example**: In Calgary, Canada, a pilot study was implemented to test the in-situ groundwater nitrification and de-nitrification remediation system (Mailath 2008). The pilot site was located in a contaminated sand and gravel aquifer, which was described in detail by other authors, independently of the pilot study. The aquifer is 6−11 m thick (Lanza 2009) and locally overlain by 2−5 m thick silt and clay glacial deposits (Savage et al. 2006). A former industrial site, which was shut down in 1992, was the main source of the nitrogen. Lanza (2009) reported peak concentrations of 38 mg/L $NO_3$-N and 75 mg/L $NH_4$-N at this site.

Two pairs of wells were installed for the treatment, each consisting of an extraction and an injection well to achieve the nitrification and denitrification step. In both cases the injection well was located upgradient of the extraction well, in order to allow the development of a reaction cell between the injection and the extraction well (Mailath 2008). In general, the reaction cell size depends on aquifer characteristics. It increases with increasing hydraulic conductivity and decreasing hydraulic gradient (Mailath and Chu 2008).

Oxygen and nutrients (typically $PO_4^{3-}$) were added to the extracted water before reinjection to trigger nitrification in the aquifer. The oxic, nutrient-rich water encouraged nitrifying bacteria to develop; the aim was to maintain phosphorous concentrations between 0.2 and 0.8 mg/L and dissolved oxygen concentrations above 1 mg/L. The addition of nutrients, therefore, depended on the existing nutrient concentrations in the groundwater. Denitrification was induced by the second pair of wells to reduce $NO_3^-$ concentrations. Instead of oxygen, carbon and nutrients were added to the extracted groundwater to encourage the growth of denitrifying bacteria. The mass flux of $NO_3^-$ entering the reaction cell can be modeled to determine the stoichiometric carbon equivalent required to reduce the $NO_3^-$ (Mailath and Chu 2005).

During in-situ pilot scale testing at the pilot site, $NH_4$-N concentrations were reduced from 58 to 6.0 mg/L in approximately 120 days and $NO_3$-N concentrations were reduced from 66 mg/L to 0.2 mg/L in approximately 14 days (Mailath 2008).

Aspects to consider in the evaluation of the applicability of this method in Delhi:

This method is especially applicable under site conditions where the hydraulic conductivity is relatively high, such as in sand and sandy gravel aquifers, which are the conditions met in the floodplain aquifer in Delhi. In soils with relatively high hydraulic conductivities, the reaction cell size of the injection wells can be maximized, and the number of injection wells can be minimized resulting in lower cost systems (Mailath and Chu 2005). The method can be applied in aquifers, which are at the same time contaminated with $NH_4^+$ and $NO_3^-$. This case can be expected when the river water quality increase once sufficient sewage treatment capacity is installed in Delhi due to high nitrogen guideline values for STP effluents (7.2.1 General Improvement of River Water Quality).

A disadvantage of this method concerning the Delhi field site is that four wells would be required in one line parallel to the groundwater flow direction to complete both, the nitrification and denitrification process. The relatively short flow path from the plume to the production wells, therefore, constitutes a major problem because it seems inefficient to extract groundwater and re-inject it (nitrification step), extract and re-inject it again (denitrification step), and then to extract it 50 m further down gradient in a drinking water production well.

As is common for pump-and-treat methods, this method requires high maintenance and involves high costs (energy costs for operating pumps, costs of nutrients, oxygen). Furthermore, on-site installations (treatment sheds) are required for the pumps and the nutrients mixing facilities.

## 7.3 EFFECTS OF REMEDIATION ON THE AQUIFER

### Redox Zonation in the Aquifer

Changing redox conditions in the river in case of source control will most likely lead to changing redox conditions in the aquifer. Source control measures will probably produce oxidizing conditions in the Delhi section of the Yamuna River throughout the year. Dissolved oxygen concentrations in European rivers of all sizes range between 9 and 11 mg/L (EEA 2001b), and similar values could be expected in Delhi, depending on STP effluent quality. This improvement of source water quality could initiate a change of the redox conditions in the aquifer – depending on the organic matter content in the riverbed sediments and the aquifer material. In the case of high organic matter contents, the oxidation of organic matter could deplete the oxygen in the infiltrating water and lead to highly reducing conditions in the aquifer as is described by Doussan et al. (1997). In the case of lower biodegradable carbon concentrations, two scenarios are possible: The development of a complete aerobic riverbank filtration site without any redox zonation (von Rohr 2014, p.7) or the development of a redox zonation from aerobic to denitrifying to Mn and Fe reducing to $SO_4^{2-}$ reducing conditions. The latter could develop in the form of a vertically stratified zonation as described by Massmann et al. (2008) or horizontally stratified as described by Champ et al. (1979).

The current redox zonation in the aquifer reaches from a sulfate reducing zone close to the river to suboxic (mildly reducing with Fe and Mn available at low concentrations – up to 0.25 mg/L Fe and 0.5 mg/L Mn) redox conditions farther away (chapter 3, Sprenger and Lorenzen 2014). Because the average organic matter content is only 0.6% in the sand and 1.3% in the kankar (chapter 3), strongly reducing conditions are not expected to develop at the field site. However, the development of the redox zonation is also temperature dependent: Massmann et al. (2006) showed that $O_2$ is reduced faster in summer months when temperatures are higher. Because of the high groundwater temperatures around 25 °C throughout the year, a complete aerobic riverbank filtration site without any redox zonation is therefore not likely to develop at the field site. A horizontally stratified zonation is not to be expected because the aquifer is only 14.5−16 m deep. Therefore, the most likely scenario is a vertically stratified redox zonation from oxic conditions to suboxic conditions.

These considerations are supported by the studies conducted at the Palla well field North of Delhi, upstream of Wazirabad barrage, where the river is still uninfluenced by sewage water. Lorenzen et al. (2010) showed that low Fe concentrations between <0.05 and 0.5 mg/L and Mn concentrations of 0.1−0.9 mg/L Mn in the bank filtrate close to the river – approximately 30 m according to Pekdeger et al. (2008) – indicate that reductive dissolution of Fe(hydr)oxides is only limited. Fe and Mn concentrations farther away from the river (distance unknown) tend to increase slightly (up to 1.3 mg/L Fe and 1.0 mg/L Mn), indicating slightly more reducing conditions. Because of a very similar geological and hydrogeological situation at the Palla and the central Delhi field site, it can be assumed that similar conditions will develop in central Delhi when the river water quality improves.

## Arsenic Mobilization and Demobilization

Redox conditions and pH control the chemical form and speciation of arsenic. In water the most common forms of arsenic are arsenate − As(V) − and arsenite − As(III). Strictly speaking, arsenates and arsenites are compounds containing the arsenate oxoanion ($AsO_4^{3-}$) or the arsenite oxoanion ($AsO_3^{3-}$), but the names are often used to refer to pentavalent As or trivalent As. In aqueous solution, arsenate is found in the form of arsenic acid ($H_3AsO_4$) and arsenite is found in the form of arseous acid ($H_3AsO_3$), whereby the dissociation state depends on the pH (Chinn et al. 2002). In groundwater As(V) arsenate predominates in the form of $H_2AsO_4^-$ at pH <7 and in the form of $HAsO_4^{2-}$ at pH >7 under oxidizing conditions. Under reducing conditions, at a pH below 8, As(III) arsenite predominates in the form of non-ionic $H_3AsO_3$ (e.g. Suthersan and Payne 2005).

Although arsenic chemistry is complex and elevated arsenic concentrations can be found in groundwater under oxidizing as well as under reducing conditions (Smedley and Kinniburgh 2002), it is very likely that changing redox conditions at the field site will lead to a substantial decrease in arsenic concentrations. According to numerous studies of arsenic contamination in the Ganga-Brahmaputra Basin (e.g. Nickson et al. 2000, Fendorf et al. 2010, Shah 2014, Mahanta et al. 2015) reducing conditions trigger the release of geogenic arsenic. In the alluvial sediments found in the entire region, the mobility of arsenic is mainly controlled by sorption to Fe oxyhydroxides (McArthur et al. 2001) and Mn oxides (Smedley and Kinniburgh 2002). Both arsenate ions have a much stronger binding to those minerals than the non-ionic form of arsenite, which only can be sorbed through Lewis acid-base interactions (Suthersan and Payne 2005). Therefore, strong redox gradients below surface water bodies lead to the reduction of As(V) to As(III) and to a subsequent desorption of As(III) from Fe and Mn oxides. Furthermore, Fe and Mn reducing conditions in the aquifer leads to the dissolution of Fe and Mn oxides which causes a further increase in As concentrations, because of the fewer sorption sites which are available to bind As in the sediment (Smedley and Kinniburgh 2002, Fendorf et al. 2010).

At the study site, high As concentrations above 0.025 mg/L (permissible limit: 0.05 mg/L) were only found in the reducing zone along the river, along with high Fe and Mn concentrations. Farther away from the river, where suboxic conditions prevail, Fe and As concentrations remain low, indicating that the reductive dissolution of iron oxyhydroxides is the main source of the arsenic pollution at the field site. A change in redox conditions would prevent the reduction of As(V) to As(III) and the dissolution of the Fe and Mn minerals and, therefore, decrease the mobility of arsenic. This is supported by the findings from Lorenzen et al. (2010) who reported As concentrations between <1 and 11 µg/L at the Palla field site, where less reducing conditions prevail. These concentrations are very low compared to the As concentrations of up to 146 µg/L found at the central Delhi field site in the present study.

## Development of Sulfate and Nitrate Concentrations

A change to oxic or suboxic conditions in the current anoxic zone of the aquifer would lead to an increase of $SO_4^{2-}$ concentrations. One reason is that no $SO_4^{2-}$ sink would be available for the $SO_4^{2-}$

in the infiltrating water. Another reason is that additional oxidation of sulfide minerals could take place. Although pyrite was not found in the aquifer material, other sulfide minerals must be present as can be clearly seen from the development of $SO_4^{2-}$ concentrations along the transect (chapter 3). However, the permissible limit of $SO_4^{2-}$ is 400 mg/L (IS 10500: 2012). Therefore, problems regarding drinking water quality requirements are not expected to occur in this respect.

$NO_3^-$ concentrations are expected to increase because the oxidation of the desorbed $NH_4^+$ would occur. This would speed up the flushing of nitrogen out of the aquifer because $NO_3^-$ does not react with the sediment surface at the given pH and is therefore not retarded in the aquifer. Whether or not $NO_3^-$ concentrations above the drinking water requirements would occur depends on the rate of nitrification and mixing with groundwater of lower $NO_3^-$ concentrations.

## 7.4 POST-TREATMENT OPTIONS

Post-treatment measures aim at achieving drinking water quality by removing contaminants and adjusting ion contents and proportions in the raw water according to given standards and guidelines. In the following section, an overview of post-treatment options for raw water containing elevated $NH_4^+$ concentrations is given. These options include:

(1) Physicochemical nitrogen removal
(2) Biological treatment

Because comprehensive compilations of $NH_4^+$ treatment methods were already made by Gauntlett (1980) and Health Canada (2013), the descriptions of the methods are very short and concise and the section focuses on the applicability of the methods under conditions met in Delhi.

### 7.4.1 Physicochemical Nitrogen Removal

Physicochemical processes provide a range of methods for the removal of $NH_4^+$ in drinking water as well as in wastewater treatment. Because high $NH_4^+$ concentrations were found in the groundwater at the studied well field, methods applied in wastewater treatment might be suitable for the use in Delhi. The most common methods are:

- Air stripping of ammonia (applied mostly in wastewater treatment)
- Ion exchange (applied in drinking water and wastewater treatment)
- Breakpoint chlorination (applied in drinking water and wastewater treatment)
- Reverse osmosis (RO) (applied in drinking water treatment)

**Air stripping of Ammonia**

Air stripping of ammonia ($NH_3$) is usually used in wastewater treatment. The principle behind the method is the conversion of $NH_4^+$ to $NH_3$ gas (see Table 1.2) by increasing the pH to about 11 by adding lime or caustic soda. The water containing the $NH_3$ gas is then brought into contact with air in a stripping tower, where the $NH_3$ will be stripped to the air due to the gradient across the gas/liquid interface (Huang and Shang 2006). Subsequently, the $NH_3$ in the off-gas can be removed by passing it through a biofilter for biological removal (EPA 1997, p.64). The space requirement for the stripping towers is large because a volumetric air-to-water ratio of about 3000:1 is required to achieve a sufficient $NH_3$ removal (Gauntlett 1980).

Aspects to consider in the evaluation of the applicability of this method in Delhi:

Due to the low concentrations of $NH_4^+$ usually found in surface and groundwater and to the relatively low Henry's law constant, this method is not expected to be very efficient in drinking water treatment according to Health Canada (2013). However, at the studied well field in Delhi, $NH_4^+$ concentrations between 5.5 and 8 mg/L were measured in one of the production wells and the concentrations are expected to increase. This is far beyond concentrations usually found in source water in industrialized countries. Therefore, this method might after all be suitable for raw water treatment in Delhi.

(Gauntlett 1980) described this method as energy intensive but regarding the equipment it is cost-effective because, once installed, these systems usually work for a long time (Huang and Shang 2006). Extensive data on this technique are available because it has been widely applied for $NH_4^+/NH_3$ removal in the last years. The warm climate in Delhi would be a major advantage for the application of this method. High temperatures increase the efficiency of the method because the $NH_3$ to $NH_4^+$ proportion increases and the solubility of $NH_3$ gas in water decreases (Huang and Shang 2006). Data from the India Meteorological Department show that in Delhi monthly average minimum temperatures are above 20 °C in six months of the year, and average monthly maximum temperatures above 30 °C occur in eight months of the year (IMD year unknown).

Critical issues regarding the application in Delhi include scaling problems and the varying $NH_4^+$ concentrations at the well field. Due to high Fe and $HCO_3^-$ concentrations in the raw water, the precipitation of Fe-oxides and carbonate minerals is expected to occur. They would form an insoluble scale, reducing the efficiency of the mass transfer (Huang and Shang 2006). Design calculations for air stripping units are complicated and the inlet water quality has to be well known to be able to make correct assumptions (Huang and Shang 2006). The high variations in $NH_4^+$ concentrations at the field site and the expected increase in the production wells could lead to high uncertainties in those calculations. Furthermore, re-carbonation or another neutralization technique would have to be adopted to make the water suitable for drinking purposes and an efficient handling of the stripped $NH_3$ gas is necessary.

### Ion Exchange

Ion exchange is widely applied in the treatment of drinking water. The method involves the process of displacing ions of one species from an insoluble solid phase by ions of another species in solution. Natural zeolites are used as ion exchange material for ion removal from polluted water (Metcalf & Eddy Inc. 2014). The zeolite clinoptilolite is selective for the $NH_4^+$ ion in preference to other ions occurring in the water (EPA 1997) and $NH_4^+$ is removed when water is passed through a bed of clinoptilolite. 86–99 % $NH_4^+$ removal can be achieved depending on $NH_4^+$ concentrations and water composition. Weatherley and Miladinovic (2004) showed that clinoptilolite has removal efficiency rates over 80 % at $NH_4$-N concentrations of 70 mg/L in the inlet water and over 98 % at concentrations of 10 mg/L. At this concentration, the $NH_4^+$ sorption capacity of the clinoptilolite was 1.26 mg/g (0.07 meq/g). Efficiency of ion exchange increases by 20−40%, if the zeolite is heat-treated before use (El-Hady et al. 2001).

Aspects to consider in the evaluation of the applicability of this method in Delhi:

The ion exchange process has no sensitivity to fluctuation in $NH_4^+$ influent concentrations (Rahmani and Mahvi 2006), which is an advantage in Delhi, where $NH_4^+$ fluctuations are high. The method seems to be simple and cost-effective because clinoptilolite can be easily and economically re-generated by the use of NaCl (El-Hady et al. 2001) or by biological regeneration (Rahmani and Mahvi 2006). However, the presence of $Ca^{2+}$ reduces $NH_4^+$ adsorption onto the zeolite (Weatherley and Miladinovic 2004). This might be an issue in Delhi because the groundwater of the floodplain aquifer has high $Ca^{2+}$ concentrations due to calcite dissolution. Therefore, laboratory batch and column experiments are recommended to determine the removal capacity and removal rates for the central Delhi groundwater.

High input concentrations require large volumes of zeolites (Li et al. 2011) and the method is not practicable for WTPs with a treatment capacity >18 MGD (80,000 $m^3$/d) because of the large space requirement (Kurama et al. 2002). Most WTPs in Delhi have a capacity >40 MGD (180,000 $m^3$/d) (Planning Department 2011), and therefore, this method is not suitable to retrofit existing WTPs. It could be used for treating $NH_4^+$ contaminated groundwater by clustering a few wells and installing a treatment facility for $NH_4^+$ treatment before conventional treatment.

### Breakpoint Chlorination

Breakpoint chlorination refers to the process at which sufficient chloride is added to react with all oxidizable compounds in the solution until additional chloride occurs as free chlorine (Metcalf & Eddy Inc. 2014). Typically, hypochlorous acid (HOCl), a highly active oxidizing substance, is used. When added to water containing nitrogen in form of $NH_4^+$ or $NH_3$, the following stepwise reaction occurs (EPA 1997):

$$NH_4^+ + HOCl \rightarrow NH_2Cl + H_2O + H^+$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$$

$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O$$

Temperature, pH, contact time and the Cl:$NH_3$ ratio are factors influencing these reactions (Metcalf & Eddy Inc. 2014). After the formation of monochloramine ($NH_2Cl$) the process proceeds by forming dichloramine ($NHCl_2$) and then by decomposing $NHCl_2$. Trichloramine ($NCl_3$) is formed as an intermediate product throughout the entire decomposition of the chloramines (Health Canada 2013). The deconstruction of the chloramines takes place by oxidizing them to nitrous oxide ($N_2O$) and nitrogen ($N_2$) and reducing the chlorine to chloride ion (Metcalf & Eddy Inc. 2014).

Theoretically, a stoichiometric $Cl_2$:$NH_3$-N ratio of 7.6:1 will achieve a 95−99 % conversion to $N_2$. Experiments by Takó and Laky (2012) show that a $Cl_2$:$NH_4$-N dose ratio of 9−11:1 is required in the presence of Fe, Mn and organic matter. Dechlorination of the water might be necessary (EPA 1997), since the method increases the chloride content of the treated water.

This method is adopted in many currently planned and operating water treatment plants, but not with the aim to reduce $NH_4^+$ concentrations but for disinfection purposes: The chloramines which form as a consequence of the presence of $NH_4^+$ act as a potential disinfectant (Donnermair and Blatchley III 2003).

Aspects to consider in the evaluation of the applicability of this method in Delhi:

Breakpoint chlorination is used as a disinfection step in many WTPs in India. For the effective removal of $NH_4^+$ with this method, close monitoring and determination of the breakpoint is required, including the measurement of $NH_4^+$ concentrations and the several forms of chlorine (Health Canada 2013). Because of the frequent variations in raw water quality, chlorine dosage has to be constantly adjusted to achieve breakpoint chlorination. In high concentrations chloramines can lead to an unpleasant odor of the treated water. Additionally, the chlorine in the water can react with organic material and might result in the formation of undesirable by-products like tri-halo methane (THM) and adsorbable organic halides (AOX) which are carcinogenic and mutagenic. To remove these by-products the treatment has to be followed by carbon adsorbers (Takó and Laky 2012) making the process relatively expensive.

The use of chlorine for $NH_4^+$ removal can only be recommended for water with less than 1 mg/L of $NH_4^+$ (Gauntlett 1980). Therefore, this method is not suitable for the treatment of $NH_4^+$-contaminated groundwater. In Delhi, it might even be difficult to reach treatable concentrations in the raw water even when mixing groundwater with surface water before treatment. Although the $NH_4^+$ concentration in the surface water of the Yamuna River at the intake of Wazirabad water works is 0.39 mg/L on average, concentrations of up to 3.55 mg/L have been measured at that location (CPCB 2006). Mixing groundwater with surface water is, therefore, not always sufficient to reduce the high $NH_4^+$ concentrations in the raw water to treatable limits. The challenges of breakpoint chlorination of Yamuna River water are described by (Kumar 2013).

### Reverse Osmosis

Reverse osmosis (RO) is a membrane filtration technology that is mainly used for seawater desalination processes (Fritzmann et al. 2007), but is also applied in water treatment systems (Radjenović et al. 2008). RO involves semi-permeable membranes which are permeable for water and not permeable for dissolved substances. The water is forced to permeate through the membrane by the application of pressure that is higher than the osmotic pressure. Ionic species (e.g. $NH_4^+$) are held back as they cannot pass the membrane. RO usually requires pre-filtration to remove particulate matter as well as other pre-treatment steps, such as disinfection to limit bacterial activity and the addition of anti-scaling agents or pH-adjustment to inhibit scale formation (Fritzmann et al. 2007).

During RO, water with a high mineral content is converted to water with a very mineral content. In full scale tests with feed N concentrations of 33 mg/L (comprising ionized and unionized ammonia), >94 % ammonia rejection were achieved (Bellona et al. 2008). In other studies, $NH_4^+$ rejection factors of >96 % (Kurama et al. 2002) and >98 % (Bódalo et al. 2005) were obtained.

Aspects to consider in the evaluation of the applicability of this method in Delhi:

As with the ion exchange technique, varying $NH_4^+$ concentrations do not affect the treatment process. The low start-up times and the continuous and automatic operation of this system (Kurama et al. 2002) are other advantages, this technique shares with the ion exchange method. However, compared to the ion exchange technique, this method only has small space requirements and few temperature effects. Despite its high efficiency and various other advantages, the investment and operating costs of RO are high (Kurama et al. 2002) making it impracticable to use this process for regular $NH_4^+$ treatment in Delhi. Furthermore, RO requires an extensive pre-treatment of the water, including the removal of particulate matter and the addition of chemicals to prevent scaling and fouling of the membranes. A post-treatment is necessary to re-mineralize the water to adjust it to drinking water standards (Fritzmann et al. 2007).

The membrane technique could be used as an intermediate solution to treat peak $NH_4^+$ concentrations if there is a significant variation in water quality throughout the year and one technique alone would not be able to fulfill all requirements.

### 7.4.2 Biological Filters

This method works through the accumulation of nitrifying bacteria through natural attachment to solid particles, forming so called biofilms. $NH_4^+$ and biodegradable organic matter (BOM) present in the raw water are removed simultaneously through microbial metabolism in the biofilm (Yu et al. 2007). The $NH_4^+$ removal occurs in two steps: First, $NH_4^+$ is oxidized to $NO_2^-$ by ammonium oxidizing bacteria (mainly *Nitrosomonas*), and then $NO_2^-$ is oxidized to $NO_3^-$ by nitrite oxidizing bacteria (mainly *Nitrobacter*) (Andersson et al. 2001). Both oxidation reactions use oxygen as an electron acceptor, and sufficient oxygen has to be supplied through an aeration step before biological filtration (Lytle et al. 2012).

Depending on the filter material, biological granular activated carbon filters (GAC) and biological rapid sand filters are distinguished. The latter represent a mixture of rapid sand filtration for particle removal and biological treatment (Lee et al. 2014). While both filter material types are widely used in water treatment plants, nitrifying trickling filters are preferred for wastewater treatment plants (Chaudhary et al. 2003).

It is essential to understand the processes occurring in the filter to operate a biofilter facility effectively. These are the attachment, growth and detachment of microorganisms (Chaudhary et al. 2003). Studies by Lee et al. (2014) showed that the efficiency of $NH_4^+$ removal depends on the $NH_4^+$ loading rate and is independent of the flow and the influent $NH_4^+$ concentrations. But because of their comparatively low inflow $NH_4$-N concentrations of <2 mg/L the transferability of these results to sites with much higher $NH_4^+$ concentrations might be limited. Removal rates >90 % were achieved with feed $NH_4^+$ concentrations below 4.4 mg/L (Health Canada 2013) and Yu et al. (2007) described the successful application of biofilters with feed water containing up to 5.3 mg/L $NH_4$-N. Two possibilities to increase the efficiency of biofilters are to correct the loading rate downwards or to increase the filter area. Incomplete $NH_4^+$ removal can be caused by operating outside the optimum temperature range (Andersson et al. 2001), insufficient oxygen supply (Lytle et al. 2012), inadequate design (Lopato 2011) and maybe even nutrient (phosphorous) limitations (de Vet et al. 2010). Temporary incomplete nitrification can also occur due to a sudden increase in BOM concentrations (Manem and Rittmann 1992) and fluctuations in feed $NH_4^+$ concentrations (Rittmann 1990)

Aspects to consider in the evaluation of the applicability of this method in Delhi:

Although it is a cost-effective method for $NH_4^+$ removal (Yu et al. 2007) and suitable for Indian climatic conditions the treatment with biological filters can be recommended only with certain restrictions. Biological filters rely on the microbial oxidation processes ($NH_4^+$ to $NO_2^-$ to $NO_3^-$). Therefore, enough oxygen has to be supplied in the feed water, which can be difficult in case of $NH_4^+$ concentrations >1.5 mg/L (Lytle et al. 2013). Pilot studies with aerated biofilters and $NH_4^+$ influent concentrations between 1.5 and 3.3 mg/L were conducted. Although complete nitrification was achieved, keeping up a constant high oxygen supply was challenging (Lytle et al. 2013).

The Ranney well P3 already exceeds these concentrations and it is expected that $NH_4^+$ concentrations in other wells at the Delhi site will increase in future. Therefore, surface water or uncontaminated groundwater would have to be mixed with the contaminated groundwater before treatment. Because of the temporal variations in $NH_4^+$ concentrations in the groundwater, the proportions of mixing would have to be adjusted constantly to achieve stable feed concentrations. This might be challenging because surface water composition also varies throughout the year (Chapter 3) and the biomass in the filters requires several hours to days adjustment time to changes in input concentrations (Rittmann 1990). It is recommended to conduct pilot and full scale studies to find optimum operating conditions for the specific local requirements.

Colonization of the biofilters to obtain complete nitrification takes about 70 days (Lytle et al. 2007). In case of complications, down-times of the system could, therefore, be long. Malfunctions can only be detected through regular, very accurate sampling of the influents and effluents. Furthermore, a denitrification unit might be necessary in the case of high $NH_4^+$ concentrations to meet the Indian Standard Drinking Water Specification requirment for $NO_3^-$ of 45 mg/L (IS 10500: 2012).

## 7.5 DISCUSSION AND RECOMMENDATIONS

In the long term, it is essential to improve the river water quality by implementing sufficient sewage treatment capacity. As this has been widely recognized, several new STPs are planned or under construction. Five STPs with a designed capacity of 89 MGD are likely to be commissioned in 2014−15 (DJB 2014) and river water quality is expected to get better. Still, elevated $NH_4^+$ concentrations will prevail for decades after source water quality improves (Chapter 6). Therefore, it is essential to develop a remediation or post-treatment scheme if the central Delhi well field should be used for the water supply of Delhi in medium−long term.

### 7.5.1 Recommended Remediation

$NH_4^+$ remediation options are complex and expensive. In Delhi, remediation is further complicated by the fact that wells are spread along an extended stretch of the river. Remediation measures would have to be installed over vast areas making any measure extremely costly. However, remediation would restore a good groundwater quality. This would benefit the small-scale groundwater users, who abstract water from private wells in addition to public water supply or because they do not have access to public water supply.

In case remediation measures should be implemented, it is not recommended to use any option involving the injection of chemicals or additives other than oxygen into the aquifer. Although those methods usually are characterized by a faster removal of $NH_4^+$, there is a risk of unwanted secondary reactions and formation of by-products, which might not get degraded on the short flow paths to the production wells. Special precaution should be taken because the well field is used for drinking water production. The BIOXWAND (patented by the Berlin water supplier Berliner Wasserbetriebe) only involves the injection of oxygen gas into the aquifer and would be a method which meets the prerequisites for use in this sensitive area.

If it is decided to develop such a remediation concept, it is of utmost importance to observe the following recommendations:

- Installation of multi-level observation wells at the site including leveling survey. Regular measurements water levels when wells are operating and when they are switched off. Creation of groundwater contour maps for the different seasons.
- Development of a detailed groundwater flow model. The hydraulic conditions at the well field have to be well known to be able to decide on a concept. It is especially important to understand how the wells influence the flow regime.
- Flow and reactive transport modeling of different remediation scenarios prior to decision-making.
- Implementation of groundwater quality monitoring by regular groundwater sampling at the observation wells. To be able to evaluate remediation measures, groundwater quality has to be known and documented before the start of remediation measures.
- Implementation of an accompanying groundwater monitoring during remediation.

### 7.5.2 Recommended Post-Treatment

In case the well field should be used in medium–long term, it is advised to set up an adapted post-treatment concept, designed specifically for the groundwater parameters of the central Delhi well field. Such an adapted site-specific post-treatment would have the advantage that it not only reduces elevated $NH_4^+$ concentrations caused by the infiltration of sewage water, but it would also allow to treat other (geogenic) parameters of concern, for example As.

Two steps have already been taken in this direction. (1) The construction of the Common Wealth Games Village WTP, a 1 MGD WTP that treats the water from one Ranney well and bore wells located on the central Delhi floodplain. (2) The construction of a 6 MGD nitrification plant in Okhla to treat $NH_4^+$ contaminated groundwater from the floodplain (currently not operating). Although biological filters, as were used in the Okhla nitrification plant, are a common and cost-efficient option to remove $NH_4^+$ from raw water, most studies about biofilters for drinking water treatment were not conducted under conditions met in India and the results cannot directly be transferred. Challenges to be met with this technique in Delhi include:

- Supply enough oxygen to cope with the high $NH_4^+$ concentrations.
- Monitor both inlet and outlet concentrations closely and adapt the hydraulic loading to stabilize nitrogen loading and thus achieve complete nitrification.

Lee et al. (2014) described stable $NH_4^+$ removal in new, less concentration-sensitive biological filters. However, the tested range of $NH_4^+$ concentrations is an order of magnitude lower than those found in the raw water of the Ranney wells in Delhi. Therefore, pilot and full scale studies to find optimum operating conditions for the specific local requirements are strongly recommended if the application of this technique should be further enhanced in India. As an alternative to biological filters, a method with more robustness towards fluctuating input parameters and less downtime in case of failures should be considered, such as ion exchange using zeolites.

## 7.6 CONCLUSION

This chapter gives an overview of remediation and post-treatment options available for $NH_4^+$ contaminated groundwater or raw water. Both approaches have advantages and disadvantages. Remediation measures would lead to an improvement of groundwater quality for all groundwater users, but most likely at extremely high costs. Post-treatment measures could be implemented in short—medium term and would show fast results but people, who are dependent on water from handpumps or private bore wells would continue to be affected by the groundwater contamination. If this option is chosen, the improvement of the public water supply is vital to terminate private groundwater abstraction.

The available data is not sufficient to give final recommendations about which strategy should be pursued. Besides hydrogeological and technical issues which have to be further investigated, cost analyses and long-term plans of the water supplier have to be considered.

# Chapter 8

# Summarizing Conclusion and Outlook

The present thesis is a comprehensive investigation of the transport and fate of $NH_4^+$ at a well field in central Delhi, where RBF at a sewage-contaminated river is practiced. This subject is of importance because:

- The permissible limits of the drinking water specification have to be met.
- Elevated $NH_4^+$ concentrations can lead to problems with drinking water chlorination, which is necessary for disinfection.
- Drinking water resources in the metropolis are stressed, and the growing water demand might require unconventional solutions and innovative approaches to water supply.

Field investigations showed that infiltrating Yamuna River water is the main source of the $NH_4^+$ in the alluvial sand and kankar aquifer, while agricultural use does not contribute significantly to the contamination. Laboratory column experiments revealed that the transport of $NH_4^+$ in the aquifer is retarded, and retardation in the kankar is significantly higher than in the sand. This results in a slower plume migration in the kankar, which forms a 1−2 m thick layer above the underlying aquitard, and can explain the different $NH_4^+$ concentrations measured at different depths in the aquifer.

The breakthrough of $NH_4^+$ can be currently observed in well P3, which is the production well closest to the Yamuna River (at 500 m distance to the riverbank). Field observations and interviews led to the assumption that the well screens of the large horizontal collector wells at the field site are located in the kankar layer. Therefore, the kankar characteristics determine the development of $NH_4^+$ concentrations in the well and a slow increase in $NH_4^+$ concentrations can be expected in the coming years until concentrations of 20−35 mg/L will be reached.

A 1D reactive transport model of 500 m length demonstrated that it takes 61 years until the 100 % $NH_4^+$ breakthrough occurs in the studied well, but concentrations above 10 mg/L can be expected after about 19 years. This is only a first estimate. Many assumptions of model parameters had to be made (hydraulic conductivities and flow velocities) because only this studies' laboratory data were available for this layer. Pumping tests and field-scale tracer tests in this unit would greatly improve the accuracy of the reactive transport models. Long-term river water quality data and observation wells in the kankar layer would even provide an option for model calibration: The well field was constructed in 1973 and started operation around 1975, but at that time river water quality might have still been good. The identification of the start of severe river water quality deterioration would improve the understanding of the contamination.

Simple 2D flow models gave impressions of possible well field management strategies. But again, limited data availability (especially missing data about abstraction rates and groundwater levels) only allowed for qualitative results. Nevertheless, the importance of the well P3 for water production was demonstrated as it produces the lowest decline in groundwater levels in the eastern floodplain at high abstraction rates.

Many scenarios for the future use of the central Delhi well field are conceivable. The three following options are examples of three fundamentally different approaches:

**Option 1** would be to operate the well field as it is currently done and to successively switch off wells as $NH_4^+$ concentrations rise in the raw water. This solution would “buy time” as distances between the wells are between 500 and 700 m long and $NH_4^+$ transport is slow. Natural attenuation, in this case nitrification, can be expected to occur to some extent, reducing $NH_4^+$ concentrations along the flow path. The main advantages of this option are that no further investment would be necessary and that contaminated water would not be used for drinking water production. The big disadvantage of this option is the resulting decrease in water production. If abstraction rates in wells farther away from the river are increased to make up for the loss, they produce a larger groundwater decline in the eastern part of the aquifer. A calibrated reactive transport model would help predict when the $NH_4^+$ plume will reach other wells.

**Option 2** comprises the operation of the well field as it is (without switching off any wells) and the implementation of remediation or post-treatment measures. With this strategy, the water abstraction of the well field would remain constant, and the remediation or post-treatment measures would have to be planned to fit the existing conditions (e.g. abstraction rates, $NH_4^+$ concentrations). For this, a calibrated flow and reactive transport model of the entire well field is necessary because the expected scenarios have to be known beforehand to be able chose appropriate treatment or remediation schemes.

**Option 3** is to develop the central Delhi well field to fit the requirement of a treatment unit. As a first step, a post-treatment strategy for groundwater with high $NH_4^+$ concentrations adapted to the local conditions has to be established. In a second planning step, a well field management is to be set up to be able to provide the treatment facility with the required water in quantity and quality. Depending on the capacity of the planned treatment unit, it could be advantageous to increase the water production at the well field. This could be achieved by placing additional wells even closer to the river in the form of a well gallery. Besides the increase in water supply, the main advantage of this option is that it gives more freedom in choosing a post-treatment method. Furthermore, existing infrastructure (pipelines) could be used, reducing overall investment costs.

Compared to the Palla well field in the North where the Yamuna riverbed shifts over several 100 m per decade, the river in central Delhi stays at a relatively constant location owing to the numerous embankments. This makes well field management easier than in Palla. However, several issues have to be considered: (1) How much Yamuna River water can be abstracted according to the water sharing agreement with the other basin states? (2) Are there any legal issues? (3) Would this measure be socially accepted?

The results of the study can be used as a basis for the evaluation of water quality problems at the central Delhi well field. The results might support decision-makers in planning next steps regarding water resources and well field management.

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# Appendix

# A1

## M.Sc. and B.Sc. theses written in the frame of the Delhi case study

### M.Sc.

Frommen T. (2015) Transport of Ammonium in Porous Media under Oxic and Anoxic Conditions: Development of an Optimized Laboratory Column Design and Quality Assurance of Related Experimental Data. M.Sc. Thesis, Freie Universität Berlin, Institute of Geological Sciences

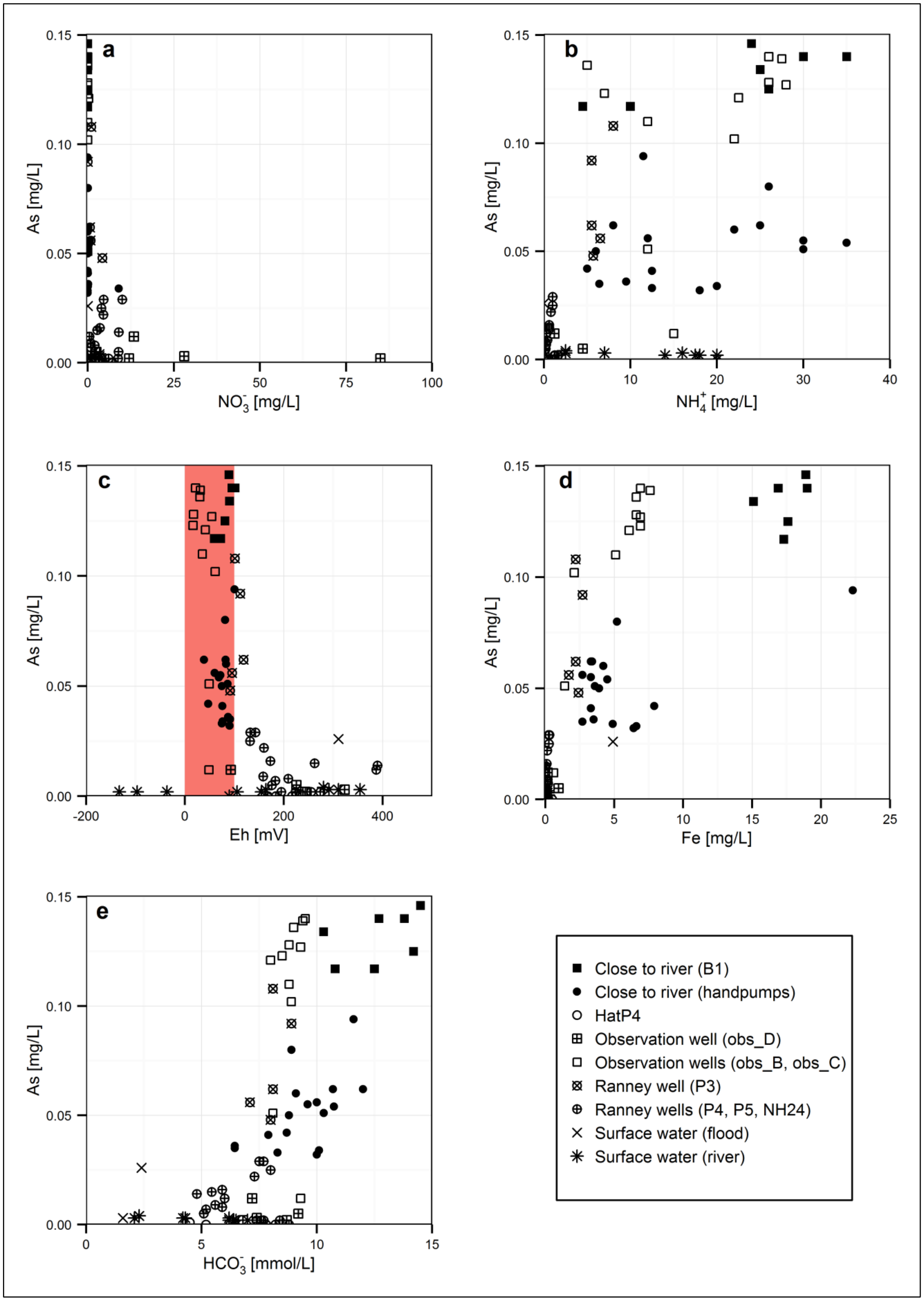
### B.Sc.

Eybing M. (2014) Charakterisierung eines alluvialen Grundwasserleiters in Delhi (Indien): Sedimentanalysen von Bohrungen an einem Uferfiltrationsstandort am Yamuna. (Characterization of an alluvial aquifer in Delhi, India: Sediment analyses of samples from drillings at a riverbank filtration site at the Yamuna River). B.Sc. Thesis, Freie Universität Berlin, Institute of Geological Sciences

Krömer L.I. (2014) Column Tests of Sediment Samples from the Yamuna Flood Plain in Delhi (India): Examination of Sediment Characteristics with Regard to Ammonium Retention, Mobilization and Degradation. B.Sc. Thesis, Freie Universität Berlin, Institute of Geological Sciences

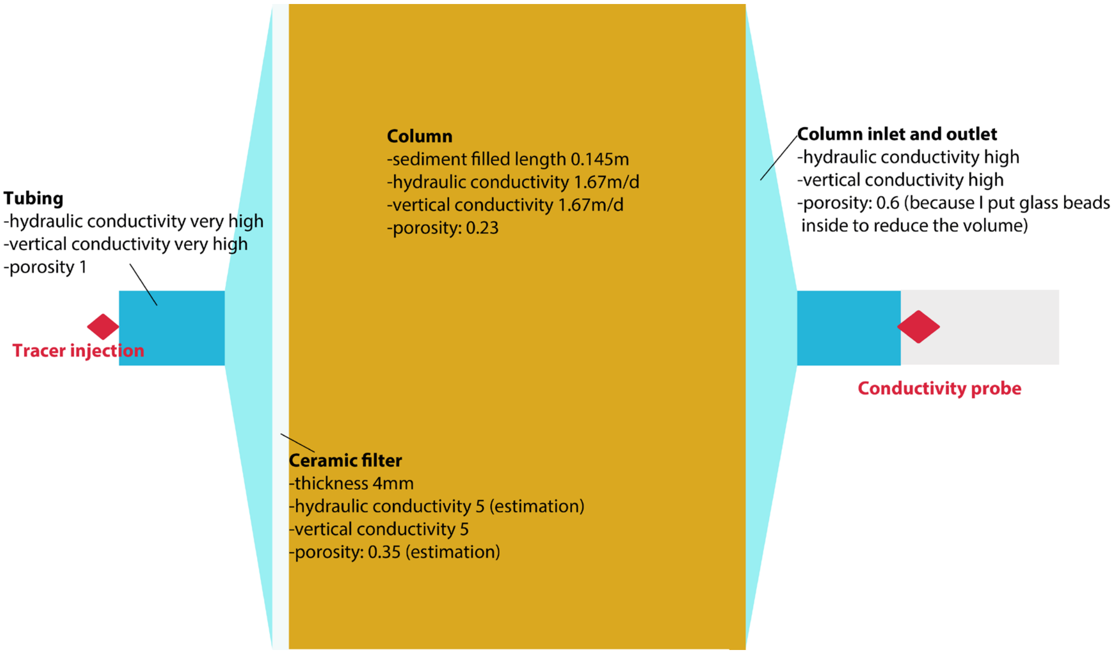
# A2

## Relation of As to $NO_3^-$, $NH_4^+$, E*h*, Fe and $HCO_3^-$



## A3

### Model set-up for the tracer test transport model of sediment B2_35



# A4.1

## PHREEQC-Input file for 1D field site modeling: Adsorption of $NH_4^+$ in the sand layer, 278 cells

```
Database C:/phreeqc/database/amm.dat
TITLE Transport and cation exchange in sand: Adsorption experiment
SOLUTION 0 displacing solution: SW from Niza (NI-SW) sample 10042 December 2012
units mg/kgw
temp 20.5
pH 7.6
Na      171
K       15.4
Mg      33.7
Ca      65.4
Cl      218
S(6)     125 as SO4
#S(-2) 0
C(4)     6.5e-3 mol/kgw as HCO3 charge
Amm     20 as AmmH
N(3)    0.02 as NO2
N(5)    0 as NO3
#Fe     0.07
#Mn     0.3

SOLUTION 1-278 Initial solution: Background solution from HatP4 sample 10081 Dec
2013
units mg/kgw
temp 26.2
pH 7.58     # charge
#redox pe # N(-3)/N(3) #S(-2)/S(6)
Na      19.9
K       5.4
Mg      14
Ca      63.7
Cl      6
C(4)    5.2e-3 mol/kgw as HCO3 charge
Amm     0 as AmmH
N(3)     0.005 as NO2 #0.005
N(5)    0.0
Fe      0.09
Mn      0.09
S(6)    2 as SO4
S(-2)   0 as H2S
END

EXCHANGE_MASTER_SPECIES
X X-

EQUILIBRIUM_PHASES 1-278
Calcite 0.3  10     #slightly oversaturated
Fe(OH)3(a)  0  10

EXCHANGE_SPECIES #adjusted selectivity coefficients
X- = X-
-log_k 0.0

X- + Na+ = NaX # reference reaction
-log_k 0.0

2X- + Ca+2 = CaX2
-log_k 0.18
```

```
X- + K+ = KX
-log_k 0.98

2X- + Mg+2 = MgX2
-log_k -0.09

X- + AmmH+ = AmmHX
-log_k 0.81
#-gamma      2.5    0.0    0.3

2X- +  Fe+2 = FeX2
-log_k -2.48

EXCHANGE 1-278
-equilibrate 1
X- 0.05418 # how many exchange places per cell, calculated for 1kg water? --> takes
CEC and porosity into account. CEC is 0.0125 meq/kg, effective porosity is 0.21 and
7.781 kg sediment is needed to fill the pore volume ne with 1 kg of water

TRANSPORT
-cells 278 # This model was set up with 278 cells
-lengths 1.8
-shifts 5560
-time_step 172800 # (2d in each cell) --> flow velocity of 0.9 m/d
-flow_direction forward
-boundary_conditions flux flux
-diffusion_coefficient 0.0e-9 #
-dispersivities 5 #depends on the scale (1/10-1/100 of total length)
-correct_disp true
-punch_cells  278 # 1 5 10 15   # written in selected output file
-punch_frequency 20 #50
-print_cells 1 278  # written in output file
-print_frequency 20

SELECTED_OUTPUT
-file 1D_field_site_cell278_sand_ammdat_adsorption.xls
-reset false
-step  true
-time true
-solution true
-distance true
-pe true
-ph true
-molalities AmmHX

USER_PUNCH
-headings Pore_vol NH4_mg/L Na_mg/L K_mg/L Ca_mg/L Mg_mg/L NH4X_meq CaX2_meq/kg
MgX2_meq NaX_meq KX_meq
-start
10 PUNCH (STEP_NO + .5) / cell_no
20 PUNCH TOT("Amm")*18*1000 # Totals are in mole
30 PUNCH TOT("Na")*23*1000
40 PUNCH TOT("K")*39*1000
50 PUNCH TOT("Ca")*40*1000
60 PUNCH TOT("Mg")*24.3*1000
70 PUNCH MOL("AmmHX")*1000
80 PUNCH MOL("CaX2")*1000*2
90 PUNCH MOL("MgX2")*1000*2
100 PUNCH MOL("NaX")*1000
110 PUNCH MOL("KX")*1000
-end
END
```

# A4.2

## PHREEQC-Input file for 1D field site modeling: Desorption of $NH_4^+$ in the sand layer, 556 cells

```
Database C:/phreeqc/database/amm.dat
TITLE Transport and cation exchange in sand: Desorption experiment
SOLUTION 0 displacing solution: SW from Palla (PA-SW) sample 136
units mg/kgw
temp 22.3
pH 8.56
Na     35
K      9
Mg     14
Ca     44
Cl     38
S(6)    46 as SO4
S(-2)  0
C(4)    3.1e-3 mol/kgw as HCO3 charge
Amm    0.1 as AmmH
N(3)   0.2 as NO2
N(5)   6 as NO3
Fe     0.62
Mn     0.05

SOLUTION 1-556 Initial solution: Background solution from B1 sample 10085
units mg/kgw
temp 25.2
pH 6.93
#redox pe # N(-3)/N(3) #S(-2)/S(6)
Na     97
K      17.3
Mg     38.7
Ca     126.5
Cl     141
C(4)   12.7e-3 mol/kgw as HCO3 charge
Amm    35 as AmmH
N(3)    0.005 as NO2
N(5)   0.00001
Fe     16.9
Mn     0.42
S(6)   5 as SO4
S(-2)  0.04 as H2S
END

EXCHANGE_MASTER_SPECIES
X X-

EQUILIBRIUM_PHASES 1-556
Calcite 0.3  10     #is slightly saturated with calcite
Fe(OH)3(a) 0 10

EXCHANGE_SPECIES #Adjusted selectivity coefficients of the sand
X- = X-
-log_k 0.0

X- + Na+ = NaX # reference reaction
-log_k 0.0

2X- + Ca+2 = CaX2
-log_k 0.18
```

```
X- + K+ = KX
-log_k 0.98

2X- + Mg+2 = MgX2
-log_k -0.09

X- + AmmH+ = AmmHX
-log_k 0.81
#-gamma      2.5    0.0    0.3

2X- +  Fe+2 = FeX2
-log_k -2.48

EXCHANGE 1-556
-equilibrate 1 #equilibrate with background solution
X- 0.05418 # how many exchange places per cell(1kg of water) --> takes CEC and
porosity into account. CEC is 0.0125 meq/kg, effective porosity is 0.21 and 7.781
kg sediment is needed to fill the pore volume ne with 1 kg of water

TRANSPORT
-cells 556 # This model was run with 556 cells. Shifts had to be adjusted
accordingly to reach the assumed linear gw flow velocity
-lengths 0.9
-shifts 11120 # 11120/556= 20 pore volumes --> 4125 min --> 2.86 d
-time_step 86400 # (1d in each cell) --> flow velocity of 0.9 m/d
-flow_direction forward
-boundary_conditions flux flux
-diffusion_coefficient 0.0e-9 -dispersivities 5 #depending on the scale (1/10-1/100
of total lenght)
-correct_disp true
-punch_cells  556 # 1 5 10 15   # selected output file
-punch_frequency 50 #50
-print_cells 1 556  # output file
-print_frequency 50

SELECTED_OUTPUT
-file 1D_field_site_cell556_sand_ammdat.xls
-reset false
-step  true
-time true
-solution true
-distance true
-pe true
-ph true
-molalities AmmHX

USER_PUNCH
-headings Pore_vol NH4_mg/L Na_mg/L K_mg/L Ca_mg/L Mg_mg/L NH4X_meq CaX2_meq/kg
MgX2_meq NaX_meq KX_meq
-start
10 PUNCH (STEP_NO + .5) / cell_no
20 PUNCH TOT("Amm")*18*1000 #totals are given in mole
30 PUNCH TOT("Na")*23*1000
40 PUNCH TOT("K")*39*1000
50 PUNCH TOT("Ca")*40*1000
60 PUNCH TOT("Mg")*24.3*1000
70 PUNCH MOL("AmmHX")*1000
80 PUNCH MOL("CaX2")*1000*2
90 PUNCH MOL("MgX2")*1000*2
100 PUNCH MOL("NaX")*1000
110 PUNCH MOL("KX")*1000
-end
 END
```

# A4.3

## PHREEQC-Input file for 1D field site modeling: Adsorption of $NH_4^+$ in the kankar, 139 cells

```
Database C:/phreeqc/database/amm.dat
TITLE Transport and cation exchange in kankar: Adsorption experiment
SOLUTION 0 displacing solution: SW from Niza (NI-SW) sample 10042 Dec 2012
units mg/kgw
temp 20.5
pH 7.6
Na     171
K      15.4
Mg     33.7
Ca     65.4
Cl     218
S(6)    125 as SO4
#S(-2) 0
C(4)    6.5e-3 mol/kgw as HCO3 charge
Amm    20 as AmmH
N(3)   0.02 as NO2
N(5)   0 as NO3

SOLUTION 1-139 Initial solution: Background solution from P4 sample 10080 December
2013
units mg/kgw
temp 26.4
pH 7.4
redox pe # N(-3)/N(3) #S(-2)/S(6)
pe 2.96 # O2(g) -0.68 # pe Formel: 16.9*Eh[V] # ORP =-121 mV
Na     67.5
K      6.8
Mg     23
Ca     80
Cl     78
C(4)   5.9e-3 mol/kgw charge
Amm    0.6 as AmmH
N(3)    0.03 as NO2 #0.005
N(5)   3.5
Fe     0.1
Mn     0.3
S(6)   53 as SO4
S(-2)  0.0 as H2S
END

EXCHANGE_MASTER_SPECIES
X X-

EQUILIBRIUM_PHASES 1-139
Calcite 0.3  10     #slightly oversaturated
Fe(OH)3(a)  0  10

EXCHANGE_SPECIES #Adapted selectivity coefficients for the kankar
X- = X-
-log_k 0.0

X- + Na+ = NaX # reference reaction

2X- + Ca+2 = CaX2
-log_k 0.10

X- + K+ = KX
-log_k 0.67
```

```
2X- + Mg+2 = MgX2
-log_k -0.28

X- + AmmH+ = AmmHX
-log_k 0.55

2X- +  Fe+2 = FeX2
-log_k -1.90

EXCHANGE 1-139
-equilibrate 1
X- 0.21 # how many exchange places per cell (for 1 kg water)?

TRANSPORT
-cells 139
-lengths 3.6
-shifts 7645 #
-time_step 345600 # (4d in each cell) --> flow velocity of 0.9 m/d
-flow_direction forward
-boundary_conditions constant flux
-diffusion_coefficient 0.0e-9 nett)
-dispersivities 50 # depends on scale (1/10-1/100 of the total length)
-correct_disp true
-punch_cells  139 # 1 5 10 15   # selected output file
-punch_frequency 50 #50
-print_cells 139  # output file
-print_frequency 50

SELECTED_OUTPUT
-file 1D_field_site_cell139_gravel_ammdat_adsorption_80a.xls
-reset false
-step  true
-time true
-solution true
-distance true
-pe true
-ph true
-molalities AmmHX
-totals Amm Na K Ca Mg  # da werden die totals in mol geschrieben

USER_PUNCH
-headings Pore_vol NH4_mmol/L Na_mmol/L K_mmol/L Ca_mmol/L Mg_mmol/L NH4X_meq
CaX2_meq/kg MgX2_meq NaX_meq KX_meq
-start
10 PUNCH (STEP_NO + .5) / cell_no
20 PUNCH TOT("Amm")*1000
30 PUNCH TOT("Na")*1000
40 PUNCH TOT("K")*1000
50 PUNCH TOT("Ca")*1000
60 PUNCH TOT("Mg")*1000
70 PUNCH MOL("AmmHX")*1000
80 PUNCH MOL("CaX2")*1000*2
90 PUNCH MOL("MgX2")*1000*2
100 PUNCH MOL("NaX")*1000
110 PUNCH MOL("KX")*1000
-end
 END
```

# A4.4

## PHREEQC-Input file for 1D field site modeling: Desorption of $NH_4^+$ in the kankar, 139 cells

```
Database C:/phreeqc/database/amm.dat
TITLE Transport and cation exchange in kankar: Desorption experiment
SOLUTION 0 displacing solution: SW from Palla (PA-SW) sample 136
units mg/kgw
temp 22.3
redox pe
pH 8.56
pe 4.53 #nach Formel 16.9*Eh[V]
Na     35
K      9
Mg     14
Ca     44
Cl     38
S(6)    46 as SO4
S(-2)  0
C(4)    3.1e-3 mol/kgw as HCO3 charge
Amm    0.1 as AmmH
N(3)   0.2 as NO2
N(5)   6 as NO3
Fe     0.62
Mn     0.05

SOLUTION 1-139 Initial solution: Background solution from H250 sample 10086
units mg/kgw
temp 24.3
pH 7.23    # charge
redox pe # N(-3)/N(3) #S(-2)/S(6)
pe 1.42 # O2(g) -0.68 # pe Formel: 16.9*Eh[V] # ORP =-121 mV
Na     79.7
K      13.2
Mg     24.8
Ca     89.1
Cl     115
C(4)   9.5e-3 mol/kgw charge
Amm    26 as AmmH
N(3)    0.005 as NO2 #0.005
N(5)   0.05
Fe     5.2
Mn     0.27
S(6)   4 as SO4
S(-2)  0.0 as H2S
END

EXCHANGE_MASTER_SPECIES
X X-

EQUILIBRIUM_PHASES 1-139
Calcite 0.3  10
Fe(OH)3(a)  0  10

EXCHANGE_SPECIES #Adjusted selectivity coefficients of the kankar
X- = X-
-log_k 0.0

X- + Na+ = NaX # reference reaction
-log_k 0.0

2X- + Ca+2 = CaX2
```

```
-log_k 0.10

X- + K+ = KX
-log_k 0.67

2X- + Mg+2 = MgX2
-log_k -0.28

X- + AmmH+ = AmmHX
-log_k 0.55

2X- +  Fe+2 = FeX2
-log_k -1.90

EXCHANGE 1-139
-equilibrate 1
X- 0.21 # how many exchange places per cell (1kg Water)? --> takes CEC and porosity
into account.

TRANSPORT
-cells 139
-lengths 3.6
-shifts 7645 #
-time_step 345600 # (4d in each cell) --> flow velocity of 0.9 m/d
-flow_direction forward
-boundary_conditions constant flux
-diffusion_coefficient 0.0e-9 #
-dispersivities 50 # (1/10-1/100 of total length)
-correct_disp true
-punch_cells  139 # 1 5 10 15   # selected output file
-punch_frequency 50 #50
-print_cells 139  # output file
-print_frequency 50

SELECTED_OUTPUT
-file 1D_field_site_cell139_gravel_ammdat_half_80a.xls
-reset false
-step  true
-time true
-solution true
-distance true
-pe true
-ph true
-molalities AmmHX

USER_PUNCH
-headings Pore_vol NH4_mmol/L Na_mmol/L K_mmol/L Ca_mmol/L Mg_mmol/L NH4X_meq
CaX2_meq/kg MgX2_meq NaX_meq KX_meq
-start
10 PUNCH (STEP_NO + .5) / cell_no
20 PUNCH TOT("Amm")*1000
30 PUNCH TOT("Na")*1000
40 PUNCH TOT("K")*1000
50 PUNCH TOT("Ca")*1000
60 PUNCH TOT("Mg")*1000
70 PUNCH MOL("AmmHX")*1000
80 PUNCH MOL("CaX2")*1000*2
90 PUNCH MOL("MgX2")*1000*2
100 PUNCH MOL("NaX")*1000
110 PUNCH MOL("KX")*1000
-end
END
```

| Sampling | Date | Lab ID | Temp | EC | pH | ORP | NH4 | NO2 | NO3 | Na | K | Mg | Ca | Cl | HCO3 | SO4 | HS | As | CBE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| point | | | °C | µS/cm | | mV/cm | mg/L | | | | | | | | | | | | % |
| NI-B1 | 29-Okt-13 | 10069 | 26.2 | 1486 | 6.92 | -111.7 | 25 | 0.005 | 0 | 99.3 | 15.3 | 32.3 | 108 | 130 | 10.30 | 6.8 | 0.04 | 0.134 | 1.50 |
| NI-B1 | 29-Mrz-12 | 10005 | | 1895 | 6.99 | -129.6 | 10 | 0.005 | 0 | 123.5 | 14.7 | 34.1 | 106 | 189 | 10.80 | 0.7 | 0.03 | 0.117 | -4.43 |
| NI-B1 | 07-Dez-12 | 10037 | 24.6 | 1917 | 6.98 | -113.1 | 24 | 0.05 | 0 | 150 | 19.1 | 40.1 | 142 | 171 | 14.50 | 0 | 0 | 0.146 | -0.27 |
| NI-B1 | 27-Jun-13 | 10050 | 25.9 | 1609 | 6.9 | -106.6 | 30 | 0.005 | 0 | 96 | 18.3 | 40.1 | 142 | 119 | 13.80 | 0.5 | 0.02 | 0.14 | -0.01 |
| NI-B1 | 23-Jun-12 | 10019 | 26.7 | 1673 | 7.14 | -142.5 | 4.5 | 0 | 0 | 145 | 15.7 | 37.7 | 113.6 | 195 | 12.50 | 0.6 | NA | 0.117 | -5.51 |
| NI-B1 | 22-Okt-12 | 10026 | 25.3 | 1830 | 6.95 | -121.1 | 26 | 0.005 | 0 | 144 | 18.2 | 38.7 | 134 | 168 | 14.20 | 0 | 0 | 0.125 | -1.14 |
| NI-H1 | 28-Jun-13 | 10051 | 24.7 | 1442 | 7.22 | -127.2 | 12.5 | 0.005 | 0 | 131 | 10.8 | 30.2 | 114 | 192 | 8.30 | 47 | 0.04 | 0.033 | 1.43 |
| NI-H1 | 07-Dez-12 | 10038 | 24.6 | 1584 | 7.29 | -125.8 | 20 | 0.012 | 9 | 143 | 14.9 | 29.4 | 107 | 172 | 10.10 | 0 | NA | 0.034 | 2.02 |
| NI-H1 | 23-Jun-12 | 10018 | 26.7 | 1292 | 7.31 | -155.1 | 5 | 0 | 0 | 101 | 9.5 | 26.9 | 113 | 162 | 8.70 | 18 | NA | 0.042 | -2.38 |
| NI-H1 | 29-Mrz-12 | 10006 | 24.2 | 1151 | 7.24 | -127.5 | 6 | 0.012 | 0 | 96 | 10.2 | 24.5 | 91.3 | 122 | 8.80 | 18 | 0.06 | 0.05 | -4.18 |
| NI-H1 | 29-Okt-13 | 10068 | | 956 | 7.35 | -114.8 | 9.5 | 0.012 | 0.1 | 103 | 8 | 16.5 | 62.3 | 79 | 6.45 | 38 | 0.04 | 0.036 | 2.13 |
| NI-H1 | 22-Okt-12 | 10024 | 25.5 | 1559 | 7.18 | -111.8 | 18 | 0.012 | 0 | 138 | 14.5 | 28.7 | 114.4 | 172 | 10.00 | 17 | 0.03 | 0.032 | 1.96 |
| NI-H1 | 02-Dez-13 | 10076 | 23.9 | 1013 | 7.27 | -126.1 | 12.5 | 0.005 | 0.06 | 101 | 9.7 | 20.3 | 71.2 | 101 | 7.90 | 24 | 0.04 | 0.041 | -2.01 |
| NI-H1 | 09-Dez-13 | 10083 | 23.9 | 770 | 7.4 | -110.7 | 6.4 | 0.005 | 0.06 | 69.5 | 7.5 | 14.9 | 54 | 39 | 6.45 | 21 | 0 | 0.035 | -1.95 |
| NI-H250 | 10-Dez-13 | 10086 | 24.3 | 1153 | 7.23 | -120.9 | 26 | 0.005 | 0.05 | 79.7 | 13.2 | 24.8 | 89.1 | 115 | 8.90 | 4 | 0 | 0.08 | -0.64 |
| NI-H3 | 22-Okt-12 | 10025 | 26.2 | 1707 | 7.33 | -118.6 | 22 | 0.02 | 0 | 150 | 17.2 | 38.3 | 102 | 162 | 9.10 | 125 | 0 | 0.06 | 1.80 |
| NI-H3 | 11-Dez-13 | 10091 | 24.1 | 1703 | 7.34 | -115.9 | 30 | 0.012 | 0.06 | 166.8 | 17.7 | 34.2 | 89.6 | 217 | 10.30 | 7.3 | 0.02 | 0.051 | 1.60 |
| NI-H3 | 28-Jun-13 | 10052 | 25.9 | 1618 | 7.36 | -130.1 | 30 | 0.02 | 0 | 171 | 17.2 | 32.5 | 87 | 234 | 9.60 | 0.4 | 0.012 | 0.055 | 2.38 |
| NI-H3 | 07-Dez-12 | 10039 | 25.1 | 1736 | 7.39 | -120 | 25 | 0.05 | 0.2 | 152 | 15.6 | 36.6 | 105.8 | 206 | 12.00 | 0.2 | NA | 0.062 | -2.09 |
| NI-H3 | 10-Apr-12 | 10012 | 26.4 | 1664 | 7.35 | -141.8 | 12 | 0.005 | 0.6 | 180 | 16.1 | 34.8 | 98 | 258 | 10.00 | 0.8 | 0.06 | 0.056 | -0.69 |
| NI-H3 | 23-Jun-12 | 10017 | 28.2 | 1616 | 7.48 | -163.6 | 8 | 0 | 0 | 166 | 16.7 | 28 | 84 | 200 | 10.70 | 0.5 | NA | 0.062 | -4.26 |
| NI-H3 | 13-Nov-13 | 10075 | 25 | 1644 | 7.33 | -133.1 | 35 | 0.05 | 0.26 | 167 | 18 | 35.5 | 93 | 232 | 10.75 | 0.5 | 0.02 | 0.054 | 1.08 |
| NI-H35 | 09-Dez-13 | 10084 | 23.9 | 1477 | 6.95 | -101.9 | 11.5 | 0.005 | 0 | 117 | 11.9 | 32 | 120.7 | 143 | 11.60 | 0.4 | 0 | 0.094 | -2.12 |
| NI-H4 | 11-Apr-12 | 10013 | 24.5 | 1690 | 7.27 | -145.3 | 5.25 | 0.012 | 0 | 158 | 13.5 | 31.4 | 102 | 254 | 9.60 | 0 | 0.02 | 0.099 | -3.83 |
| NI-H5 | 11-Apr-12 | 10014 | 23.3 | 1387 | 7.48 | -123.4 | 6.5 | 0.005 | 0 | 146 | 11.1 | 27.8 | 76.9 | 195 | 8.10 | 0 | 0.04 | 0.106 | -0.72 |
| NI-HatP4 | 30-Okt-13 | 10071 | 27.1 | 449 | 7.53 | 32 | 0 | 0.005 | 0 | 18.4 | 4.8 | 12.8 | 58.9 | 6 | 4.50 | 6.8 | 0 | 0.001 | 2.31 |
| NI-HatP4 | 09-Dez-13 | 10081 | 26.2 | 495 | 7.58 | -44.9 | 0 | 0.005 | 0 | 19.9 | 5.4 | 14 | 63.7 | 6 | 5.20 | 2 | 0 | 0 | 0.57 |
| NI-HW | 10-Dez-13 | 10087 | 24.4 | 1682 | 7.47 | -86 | 3 | 0.04 | 1.4 | 166.8 | 12.5 | 34.6 | 138 | 180 | 8.50 | 175 | 0 | 0.022 | 1.52 |
| NI-NH24 | 27-Mrz-12 | 10004 | 25.4 | 1305 | 7.54 | 71.9 | 1.3 | 0.048 | 6 | 117.7 | 10.1 | 32.2 | 103 | 89 | 7.60 | 126 | 0.02 | 0.002 | 2.21 |
| NI-NH24 | 23-Jun-12 | 10015 | 28.7 | 1203 | 7.23 | -34.1 | 1.3 | 0 | 4.5 | 108 | 9.6 | 31.8 | 104 | 86 | 7.80 | 126 | NA | 0 | 0.32 |
| NI-NH24 | 07-Dez-12 | 10040 | 24.4 | 1240 | 7.38 | -18.3 | 1 | 0.4 | 3.1 | 109 | 9.9 | 32.1 | 103.9 | 69 | 8.80 | 101 | 0.02 | 0 | 0.72 |
| NI-NH24 | 01-Nov-12 | 10032 | 26.4 | 1198 | 7.39 | 53.3 | 1.65 | 0.24 | 4 | 109 | 9.9 | 32.6 | 106 | 69 | 8.40 | 105 | 0.1 | 0.002 | 2.53 |
| NI-NH24 | 26-Jun-13 | 10047 | 28.8 | 1183 | 7.21 | -7 | 1.2 | 0.03 | 2.4 | 105 | 9.3 | 32.8 | 107 | 83 | 7.70 | 122 | 0 | 0.002 | 1.92 |
| NI-NH24 | 09-Dez-13 | 10082 | 22.7 | 1151 | 7.34 | 14.4 | 1.2 | 0.56 | 7.2 | 100.5 | 10 | 32.1 | 104 | 77 | 8.20 | 122 | 0.02 | 0 | -1.35 |
| NI-NH24 | 29-Okt-13 | 10067 | | 1163 | 7.04 | 21.5 | 1.2 | 0.05 | 8.8 | 103 | 9.5 | 31.8 | 106 | 76 | 7.40 | 120 | 0 | 0.002 | 2.50 |
| NI-obs_A | 02-Nov-12 | 10033 | 25.7 | 1309 | 7.94 | -200.7 | 1.3 | 0 | 0 | 284 | 4.9 | 10.3 | 14.7 | 70 | 10.00 | 95 | 0.12 | 0.003 | 1.08 |
| NI-obs_A | 05-Jul-13 | 10058 | 26.2 | 1249 | 7.89 | -81.7 | 0.4 | 0.02 | 0 | 292 | 4.1 | 10.7 | 7.9 | 30 | 10.50 | 115 | 0.01 | 0.002 | 1.67 |
| NI-obs_A | 18-Dez-12 | 10044 | 25.6 | 1300 | 8.12 | -165.5 | 0.7 | 0.0025 | 0 | 286 | 4.1 | 8.7 | 12.2 | 38 | 10.00 | 100 | 0.2 | 0.005 | 3.17 |
| NI-obs_A | 24-Okt-13 | 10066 | 26 | 1217 | 7.84 | -192.4 | 0.4 | NA | 0 | 305 | 3.4 | 7.4 | 10.5 | 0 | 9.80 | 0 | NA | 0.003 | -71.83 |
| NI-obs_B | 23-Okt-12 | 10028 | 25.3 | 1563 | 7.24 | -180.6 | 26 | 0.012 | 0 | 136 | 14.1 | 30 | 108.4 | 193 | 9.50 | 0 | 0 | 0.14 | 3.29 |
| NI-obs_B | 11-Dez-12 | 10043 | 25.2 | 1515 | 7.19 | -171.9 | 5 | 0.005 | 0 | 126 | 14.2 | 28.6 | 107 | 194 | 9.00 | 0 | 0.05 | 0.136 | -1.03 |
| NI-obs_B | 24-Okt-13 | 10065 | 25.2 | 1579 | 7.23 | -170.9 | 27.5 | 0.005 | 0 | 150 | 14.8 | 28.3 | 107 | 209 | 9.40 | 4 | 0.06 | 0.139 | 3.45 |
| NI-obs_B | 04-Jul-13 | 10057 | 24.9 | 1439 | 7.2 | -140.8 | 22 | 0.005 | 0 | 127 | 14.7 | 26.3 | 103 | 180 | 8.90 | 0.5 | 0.04 | 0.102 | 2.83 |

| Sampling | Date | Lab ID | Temp | EC | pH | ORP | NH4 | NO2 | NO3 | Na | K | Mg | Ca | Cl | HCO3 | SO4 | HS | As | CBE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| point | | | °C | µS/cm | | mV/cm | mg/L | | | | | | | | | | | | % |
| NI-obs_C | 03-Jul-13 | 10055 | 25.4 | 1284 | 7.25 | -153 | 12 | 0.005 | 0 | 114 | 16 | 21.4 | 107 | 163 | 8.10 | 3.6 | 0.02 | 0.051 | 2.93 |
| NI-obs_C | 20-Dez-12 | 10046 | 25 | 1504 | 7.34 | -185.7 | 7 | 0.005 | 0 | 123 | 15.2 | 27.9 | 103.4 | 188 | 8.50 | 0 | 0.04 | 0.123 | 0.61 |
| NI-obs_C | 25-Okt-12 | 10031 | 25.1 | 1482 | 7.21 | -166.8 | 12 | 0.005 | 0 | 140 | 13.9 | 28.1 | 100.8 | 176 | 8.80 | 10 | NA | 0.11 | 2.91 |
| NI-obs_C | 23-Okt-13 | 10064 | 25.1 | 1488 | 7.24 | -184.7 | 26 | 0.05 | 0 | 139 | 14 | 25.9 | 102 | 192 | 8.80 | 0.3 | 0.04 | 0.128 | 4.07 |
| NI-obs_D | 23-Okt-13 | 10063 | 25.2 | 2000 | 6.99 | 41.7 | 0.05 | 0.32 | 85 | 183 | 8.7 | 46 | 167 | 295 | 6.80 | 135 | 0 | 0.002 | 0.05 |
| NI-obs_D | 04-Jul-13 | 10056 | 24.6 | 1131 | 7.24 | -109.1 | 1.2 | 0.03 | 13.4 | 84 | 11.2 | 27.7 | 110 | 100 | 7.20 | 72 | 0.02 | 0.012 | 0.57 |
| NI-obs_D | 20-Dez-12 | 10045 | 25 | 1301 | 7.2 | 23.5 | 4.5 | 0.02 | 2.5 | 133 | 12.1 | 30.5 | 94.5 | 113 | 9.20 | 68 | 0.03 | 0.005 | 0.00 |
| NI-obs_D | 25-Okt-12 | 10030 | 24.8 | 1346 | 7.01 | 36.4 | 2 | 0.005 | 12 | 124 | 7.7 | 34.4 | 112 | 122 | 8.70 | 38 | 0 | 0.002 | 3.70 |
| NI-P3 | 24-Okt-12 | 10029 | 24.8 | 1450 | 7.25 | -90.3 | 5.5 | 0.005 | 0 | 145 | 10.4 | 30.8 | 105.5 | 169 | 8.90 | 5 | 0.02 | 0.092 | 4.08 |
| NI-P3 | 09-Dez-13 | 10079 | 24.4 | 1370 | 7.24 | -110.8 | 5.7 | 0.06 | 4.2 | 125 | 9.4 | 31.3 | 99.1 | 169 | 8.00 | 51.7 | 0.02 | 0.048 | -0.77 |
| NI-P3 | 23-Jun-12 | 10020 | 30.1 | 1302 | 7.27 | -106.9 | 6.5 | 0 | 0.8 | 129 | 10 | 27.1 | 95 | 175 | 7.10 | 26 | NA | 0.056 | 3.27 |
| NI-P3 | 26-Mrz-12 | 10001 | 24.2 | 1415 | 7.1 | -101 | 8 | 0.4 | 1 | 130.7 | 9.8 | 29.1 | 95.9 | 172 | 8.10 | 27 | 0.02 | 0.108 | 0.98 |
| NI-P3 | 11-Jul-13 | 10061 | 27.4 | 875 | 7.29 | -98.2 | 1.2 | 0.03 | 3.8 | 64 | 6.9 | 22.1 | 87.8 | 62 | 5.80 | 87 | 0.02 | 0.019 | -0.38 |
| NI-P3 | 04-Dez-12 | 10034 | 23.9 | 1320 | 7.28 | -83.4 | 5.5 | 0.025 | 0.6 | 134 | 10 | 28.8 | 99.3 | 160 | 8.10 | 19 | 0 | 0.062 | 3.50 |
| NI-P4 | 30-Okt-13 | 10070 | 27 | 770 | 7.25 | 60 | 0.6 | 0.02 | 2.7 | 62.1 | 6.4 | 20.9 | 75.6 | 61 | 5.45 | 46 | 0 | 0.015 | 2.05 |
| NI-P4 | 04-Dez-12 | 10035 | 24.8 | 1332 | 7.34 | -59.2 | 1 | 0.05 | 10 | 134 | 7.7 | 31.2 | 105.5 | 139 | 7.70 | 72 | 0 | 0.029 | 2.50 |
| NI-P4 | 22-Okt-12 | 10027 | 25.7 | 1298 | 7.28 | -70.2 | 1 | 0.04 | 4.6 | 128 | 7.4 | 30 | 102.7 | 126 | 7.50 | 61 | 0.02 | 0.029 | 4.34 |
| NI-P4 | 23-Jun-12 | 10021 | 27.1 | 1277 | 7.4 | -70.3 | 1 | 0 | 3.9 | 129 | 7.2 | 29.1 | 98 | 147 | 8.00 | 81 | NA | 0.025 | -2.31 |
| NI-P4 | 27-Mrz-12 | 10003 | 25.8 | 1286 | 7.34 | -42.2 | 0.8 | 0.04 | 4.5 | 124.4 | 7 | 27.7 | 95.1 | 139 | 7.30 | 76 | 0.01 | 0.022 | -0.39 |
| NI-P4 | 06-Jul-13 | 10059 | 26.8 | 749 | 7.35 | 187.3 | 0.6 | 1.2 | 9 | 58 | 5.8 | 19 | 67.4 | 61 | 4.80 | 49 | 0 | 0.014 | -0.22 |
| NI-P4 | 09-Dez-13 | 10080 | 26.4 | 893 | 7.4 | -29.2 | 0.6 | 0.03 | 3.5 | 67.5 | 6.8 | 23 | 80 | 78 | 5.90 | 53 | 0 | 0.016 | -0.58 |
| NI-P5 | 01-Nov-13 | 10074 | 26.9 | 821 | 7.25 | -19 | 0.25 | 0.012 | 0.9 | 64.8 | 6.1 | 20.6 | 86.7 | 55 | 5.20 | 89 | 0 | 0.007 | 3.00 |
| NI-P5 | 02-Apr-12 | 10010 | 27.1 | 1030 | 7.44 | -43.6 | 0.4 | 0.02 | 0.8 | 78.3 | 5.8 | 20.5 | 80.7 | 63 | 5.60 | 90 | 0.02 | 0.009 | 0.88 |
| NI-P5 | 23-Jun-12 | 10016 | 30.3 | 906 | 7.36 | 6.7 | 0.2 | 0 | 2 | 75 | 6.2 | 21 | 84 | 69 | 5.90 | 108 | NA | 0.008 | -3.28 |
| NI-P5 | 26-Jun-13 | 10048 | 27.5 | 830 | 7.43 | -26 | 0.2 | 0.05 | 8.9 | 58 | 5.8 | 20.8 | 87.7 | 52 | 5.10 | 102 | NA | 0.005 | -0.23 |
| NI-P5 | 07-Dez-12 | 10036 | 24.9 | 956 | 7.46 | 185 | 0.3 | 0.0012 | 0.5 | 71 | 6.7 | 23.1 | 95.6 | 61 | 6.00 | 93 | 0 | 0.012 | 2.26 |
| NI-SW1 | 02-Apr-12 | 10008 | 28.8 | 1760 | 7.33 | -335 | 14 | 0.03 | 0 | 187 | 17 | 34 | 68.5 | 250 | 7.00 | 96 | NA | 0.002 | -0.16 |
| NI-SW2 | 21-Okt-12 | 10022 | 26.8 | 1624 | 7.62 | -298.9 | 18 | 0.012 | 0 | 183 | 16.1 | 35.9 | 66.2 | 210 | 7.00 | 78 | 0 | 0.002 | 4.88 |
| NI-SW3 | 21-Okt-12 | 10023 | 26.9 | 1621 | 7.61 | -238.3 | 20 | 0.005 | 0 | 191 | 16.3 | 36.2 | 65.1 | 254 | 6.50 | 115 | 0 | 0.002 | 1.30 |
| NI-SW4 | 08-Dez-12 | 10041 | 19.7 | 1566 | 7.47 | -96.5 | 17.5 | 0.005 | 0 | 170 | 15.1 | 33.9 | 64.5 | 211 | 6.40 | 124 | NA | 0.002 | 0.71 |
| NI-SW5 | 08-Dez-12 | 10042 | 20.5 | 1588 | 7.6 | -112.3 | 20 | 0.02 | 0 | 171 | 15.4 | 33.7 | 65.4 | 218 | 6.50 | 125 | NA | 0 | 0.40 |
| NI-SW8 | 31-Okt-13 | 10072 | 25.5 | 1069 | 7.54 | 152.3 | 7 | 0.5 | 0 | 109 | 9.3 | 26.8 | 60.7 | 137 | 4.20 | 89 | 0 | 0.003 | 4.45 |
| NI-SW9 | 31-Okt-13 | 10073 | 24.9 | 1058 | 7.63 | 89.6 | 7 | 0.56 | 0.8 | 109 | 9.1 | 27.3 | 59.8 | 146 | 4.30 | 95 | 0 | 0.003 | 1.91 |
| NI-SWatP4 | 06-Jul-13 | 10060 | 31.6 | 275 | 7.74 | 108.4 | 0 | 0.005 | 0 | 5.7 | 8 | 6.7 | 36.4 | 6.5 | 2.40 | 16 | 0 | 0.026 | 1.83 |
| NI-SWatP5 | 26-Jun-13 | 10049 | 32 | 210 | 8.8 | 23.5 | 0 | 0.02 | 0 | 4.6 | 6.1 | 6.1 | 25.4 | 4.8 | 1.60 | 22 | 0 | 0.003 | 1.97 |