Performance of a permeable reactive barrier for *in situ* removal of ammonium in groundwater

Guohua Hou, Fei Liu, Mingzhu Liu, Xiangke Kong, Shengpin Li, Liang Chen, Patricia J. S. Colberg, Song Jin and Honghan Chen

ABSTRACT

Nitrogen as ammonium (NH_4^+-N) is one of the most common nitrogen contaminants in groundwater; this is particularly true in the industrial and agricultural regions of northern China, where rapid population growth and economic development have stressed public water supplies and reduced groundwater quality. In this study, we report the performance of a zeolite permeable reactive barrier (PRB) designed to remove ammonium from contaminated river water that infiltrates to a groundwater aquifer that serves as a drinking water supply for the city of Shenyang. Groundwater monitoring data obtained over 5 months of operation indicate that ammonium concentrations in the groundwater decreased from 2–10 mg/L to <0.5 mg/L after the PRB was installed in the vicinity. Data suggest that ammonium removal was mainly due to sorption and ion exchange, with NH_4^+ exchanged with Na^+ and K^+ in the zeolite. After more than 1 year of continuous operation, there is no evidence of microbial ammonium oxidation. To our knowledge, this was the first field-scale demonstration of a PRB in China.

Key words | adsorption, ammonium in groundwater, groundwater in China, permeable reactive barrier, PRB, zeolite

Guohua Hou
Fei Liu
Mingzhu Liu (corresponding author)
Shengpin Li
Liang Chen
Honghan Chen
Beijing Key Laboratory of Water Resources and
    Environmental Engineering,
China University of Geosciences, Beijing 100083,
China
E-mail: *liumz@cugb.edu.cn*

Xiangke Kong
Institute of Hydrogeology & Environmental
    Geology, CAGS, Shijiazhuang 050061,
China

Patricia J. S. Colberg
Song Jin
Department of Civil and Architectural Engineering,
University of Wyoming, Laramie, Wyoming 82071,
USA

INTRODUCTION

As groundwater supplies are overdrawn, their contamination with nitrogen compounds (ammonium, nitrite, nitrate) has become a problem in need of urgent remediation. This is particularly true in the industrial regions of northern China, where rapid population growth and economic development have stressed public water supplies and reduced groundwater quality (Ma *et al.* 2013).

Nitrogen as ammonium (NH_4^+-N) is the most common nitrogen contaminant in low redox groundwater (Hinkle *et al.* 2007) as well as in groundwater aquifers located adjacent to surface water supplies (Zhuo *et al.* 2011). There are at least 30 different technologies designed to treat contaminated soils and groundwater (Evanko & Dzombak 1997; Mulligan *et al.* 2001; Khan *et al.* 2004). The permeable reactive barrier (PRB) is one of a few passive-treatment technologies that has been demonstrated to be cost-effective

in remediating nitrogen contaminants in the subsurface (Patterson *et al.* 2004; Robertson *et al.* 2008; Erto *et al.* 2011).

There are several configurations of PRBs, including those designed to optimize adsorption of contaminants to reactive media (Erto *et al.* 2011), to degrade contaminants microbiologically (Careghini *et al.* 2013), and to reduce contaminant concentrations through abiotic reduction (Chen *et al.* 2012). Regardless of the mechanism at work, PRBs can be designed to treat a wide variety of organic and inorganic contaminants, including ammonium (Kong *et al.* 2012), chlorinated solvents (Phillips *et al.* 2010), petroleum hydrocarbons (Chen *et al.* 2011) and heavy metals (Ouellet-Plamondon *et al.* 2011). Contaminants are removed by sorption, biodegradation, precipitation, or the combination of these reactions as the groundwater moves through the PRB (USEPA 1998; Gavaskar 1999; Thiruverikatachari *et al.* 2008).

In the design of PRBs that depend on adsorption reactions, various materials have been used, including zeolite (Vignola *et al.* 2011), granular activated carbon (GAC) (Suponik 2010), limestone (Komnitsas *et al.* 2004), scoria (Zhang *et al.* 2012), blast furnace slag (Kanew *et al.* 2006), and polymer mats (Patterson *et al.* 2004). For example, a PRB filled with GAC was utilized to remediate an aquifer adjacent to a solid waste landfill that was contaminated with tetrachloroethylene (PCE). The numerical model results showed that the barrier consistently removed more than 90% of the PCE and always met Italian regulatory requirements (Nardo *et al.* 2010).

Another type of PRB, the so-called 'bio-PRB', depends on microbial processes to transform organic pollutants or to precipitate inorganic species (USEPA 2004). Teerakun *et al.* (2011) employed a laboratory-scale PRB system composed of three sequential columns (a zero-valent iron [ZVI] PRB, an anaerobic bio-PRB, and an aerobic bio-PRB) to treat high concentrations of trichloroethylene (TCE; 500 mg/L) in synthetic groundwater. The entire system removed approximately 84% of the influent TCE, with 42% of the removal attributed to the ZVI.

For remediation of groundwater contaminated by mixed pollutants, a sequential PRB first suggested by Van Nooten *et al.* (2008) is an innovative and semi-passive *in situ* technology. Their combined adsorptive and bio-PRB successfully removed more than 90% of NH_4^+-N from landfill leachate (Van Nooten *et al.* 2010). Kong *et al.* (2012) recently reported using a sequential PRB composed of an oxygen-releasing chemical and zeolite to achieve 99% removal of NH_4^+-N in a laboratory column. Our group has recently applied a sequential PRB (ZVI + bio-PRB) and successfully treated groundwater contaminated with TCE, benzene and toluene (Chen *et al.* 2011).

In this paper, we report the design, installation and performance of the first *in situ* PRB installed in China for groundwater remediation. The system was designed to remediate ammonium nitrogen from contaminated river water that infiltrates to a groundwater aquifer that serves as a municipal drinking water supply.

MATERIALS AND METHODS

Site description

The PRB was installed about 150 m from the Hun River (see Figure 1) in a water supply source area for the city of Shenyang in northeastern China. Groundwater in this region is mainly recharged by the river (Yi *et al.* 2006), which is highly contaminated with ammonium that originates from
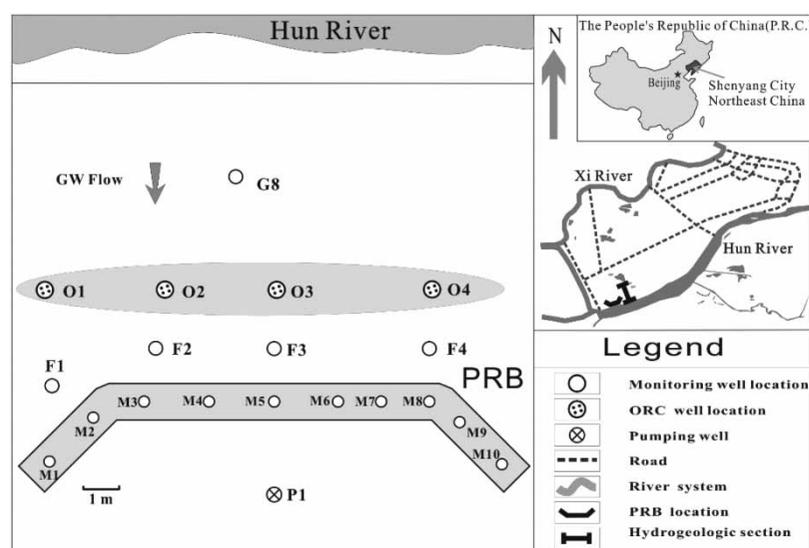
Figure 1 | Hun River remediation site map showing locations of the U-shaped zeolite barrier and various monitoring wells. Monitoring well G8 is located up-gradient of the PRB and was used to monitor baseline concentrations of various analytes; O1–O4 are wells installed for addition of an oxygen-releasing chemical (ORC). Wells F1–F4 are up-gradient wells for monitoring baseline concentrations of ammonium and dissolved oxygen; M1–M10 are wells for monitoring groundwater quality within the zeolite PRB. The well labeled as P1 is a down-gradient well for pumping and monitoring groundwater post-PRB.

the effluent of a nearby wastewater treatment facility and from agricultural activities in the area. The concentration of ammonia as NH_4^+-N in the groundwater is approximately 10 mg/L or 20 times higher than the national regulatory limit of 0.5 mg/L.

The site geology where the PRB was installed is composed of floodplain and first terrace, which is part of the alluvial-pluvial fan of the Hun River. The field stratum consists of a phreatic aquifer and underlying confined aquifer (see Figure 2). The phreatic aquifer, in which contaminated groundwater flows, is mainly composed of medium sand and medium-coarse sand (hydraulic conductivity $\sim 7 \times 10^{-4}$ m/s). The aquitard, located about 40 m under the contaminated area, is made up of clay and silty clay (hydraulic conductivity $\sim 8 \times 10^{-11}$ m/s). The thickness of the aquitard is 4–6 m, and the groundwater table ranges from 10 to 12 m below ground surface. The concentration of ammonia-N in groundwater seasonally ranges from 1 to 8 mg/L, while the NO_3^--N varies from 10 to 20 mg/L and the NO_2-N varies from 0 to 0.4 mg/L. The pH is 6–8, the dissolved oxygen (DO) averages 2–4 mg/L, and the temperature is 12–20 °C.

Barrier installation and design

The *in situ* PRB was composed of an adsorption-biodegradation wall filled with commercial zeolite filings obtained locally (3–5 mm diameter; Faku County, Liaoning Province,

PRC). The chemical composition of the zeolite was: SiO_2 67.09%, Al_2O_3 12.44%, Fe_2O_3 0.78%, Na_2O 0.26%, MgO 1.22%, CaO 8.81%, K_2O 1.20%, and others 13.32%. The adsorption capacity for ammonium was about 4.74 mg/g. The PRB was installed vertically in the ground to a depth of 40 m (see Figure 1). The zeolite reaction barrier, with a permeability (hydraulic conductivity $\sim 7 \times 10^{-3}$ m/s) one order of magnitude greater than the aquifer permeability, was instrumented with several monitoring wells located about 1 meter apart (M1–M10 in Figure 1).

The PRB was designed to protect well P1 rather than treating whole plumes, and was U-shaped (3 m + 9 m + 3 m long) with two side wings bending towards well P1 in an effort to increase groundwater flow through the PRB. Access to the monitoring wells installed in the zeolite barrier was via manholes located at the surface. The oxygen-releasing chemical wells (400 mm i.d.) were parallel to and up-gradient from the PRB; they were constructed of polyvinyl chloride (PVC, 1.9 cm i.d.) with 30- or 45-cm long screens which were completed between 14 and 35 m below ground surface. The oxygen-releasing chemical wells were included in the design in order to add an oxygen-releasing chemical if needed to maintain aerobic conditions for microbial ammonia removal; however, the concentration of influent NH_4^+-N was quite low during the monitoring period, and the oxygen-releasing amendments were never made during the study.
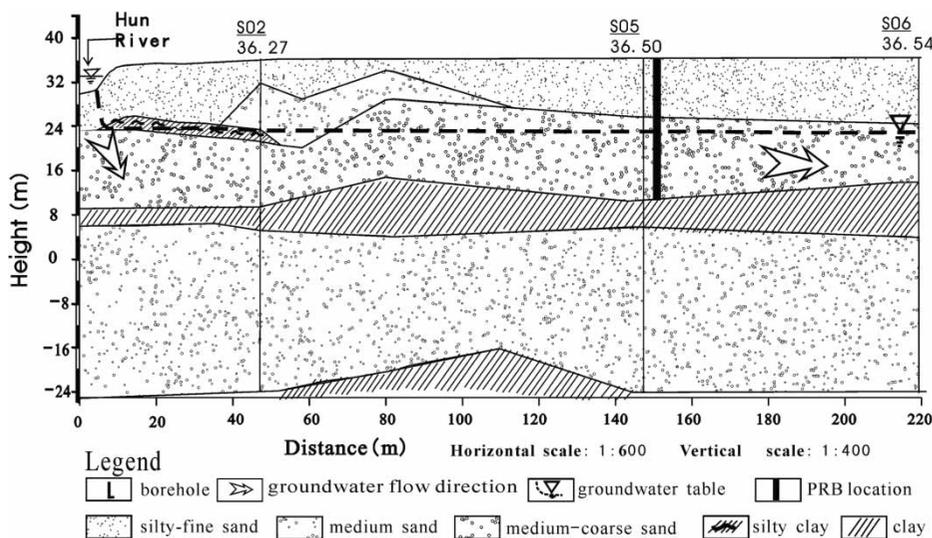

Figure 2 | Hydrogeologic profile of the remediation site adjacent to the Hun River near the city of Shenyang in northeast China.

Groundwater could naturally flow through the PRB (15 m long × 1 m wide × 40 m deep zeolite wall) by gravity at a velocity of approximately 0.63 m/d, and then the water could be pumped by well P1. The depth of the PRB was chosen to be in a zone of lower hydraulic permeability, which consists of a continuous stiff clayey layer beneath a medium-coarse sand which acts as an aquitard to groundwater flow. The water table at the site is ∼12 m below ground level with an underlying aquifer at 10 m below ground level.

Appropriate design and placement of monitoring wells are critically important to ensure effective assessment of system performance. Monitoring wells (200 mm diameter, 40 m deep) were positioned upstream and downstream of the reactive barrier as well as within the zeolite wall. There were also four monitoring wells installed between the zeolite barrier and the oxygen-releasing chemical wells in order to monitor DO and evaluate the performance of the oxygen-releasing chemical if added (see Figure 1). Groundwater sampling was conducted monthly for the following parameters: pH, Eh, DO, alkalinity, NH_4^+-N, NO_3^--N, and NO_2^--N, total dissolved solid, and major cations and anions. In addition to the permanent monitoring wells, temporary sampling wells were utilized to increase the spatial resolution of the data.

Groundwater analysis

Groundwater samples (500 mL per well collected via peristaltic pump over ∼10 min) were obtained from the monitoring wells and analyzed for NH_4^+-N, NO_3^--N, and NO_2^--N. Ammonium concentrations were determined by a flow injection analyzer (Lachat-QC8000, Hach, Loveland, CO, USA) using a salicylate spectrophotometric method. Nitrate (NO_3^--N) and nitrite (NO_2^--N) concentrations were quantified by ion chromatography (DX-600, DIONEX Co., Sunnyvale, USA). The detection limit for each analyte was 0.1 mg/L; the standard deviation for replicate samples was ±10%. The DO, pH, Eh, temperature and specific conductance were measured in the field with portable multi-parameter meters (HQ40d, Hach, Loveland, CO, USA) with three successive readings within ±1% for DO, ±0.02 for pH, ±0.1 mV for Eh, ±0 °C for temperature, and ±0.5% for specific conductance. Major metals and cations were analyzed by Inductively Coupled Plasma Atomic

Emission Spectrometry (IRIS Intrepid, Thermo Elemental, Maryland, USA). Anion samples were unfiltered and unacidified; analyses were performed with an ion chromatograph (DX-600, Dionex, USA).

RESULTS AND DISCUSSION

Baseline ammonium-N concentrations

As in Figure 3, there is a positive correlation in NH_4^+-N concentrations between the Hun River and the groundwater sampled at the up-gradient monitoring well (G8). As the concentration of ammonium-N fluctuated in the river, it also varied in the local subsurface water supply. These data clearly demonstrate the hydraulic connection between the river and groundwater at this location.

Removal of NH_4^+-N after installation of PRB

Figure 4 graphically follows the changes in ammonium concentrations after installation of the PRB in an up-gradient well (G8), in three of the wells located within the zeolite barrier (M1, M5 and M9), and in well P1 that is located down-gradient of the PRB. Ammonium concentrations decreased to less than 0.5 mg/L in all wells down-gradient of the PRB by August 2012, and remained consistently below this level throughout the monitoring period. There were fluctuations in the ammonium concentrations at M1 and M5, M9 in July 2012 when PRB was just constructed
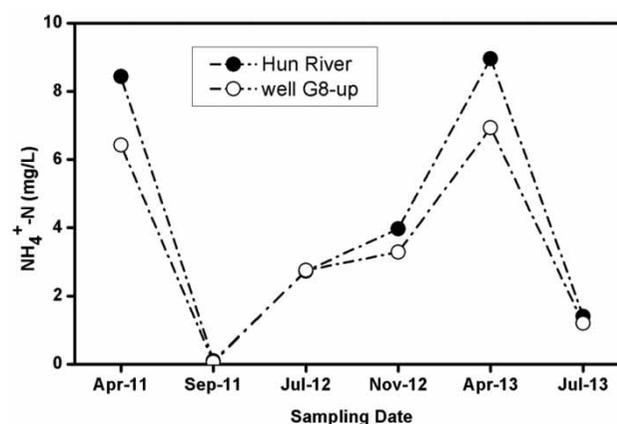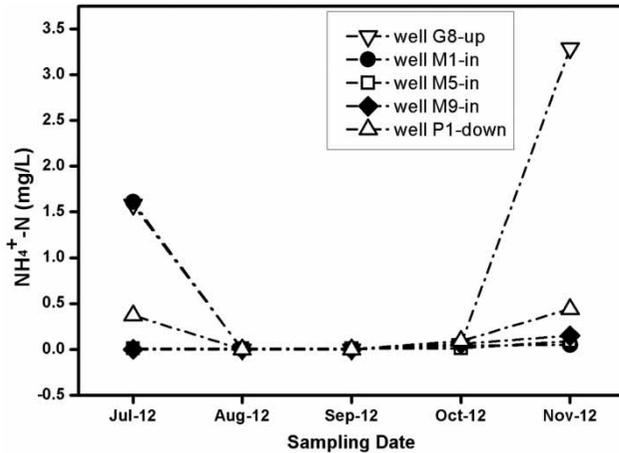

Figure 3 │ NH_4^+-N concentrations in well G8 (located up-gradient from PRB) and in the Hun River monitored from April 2011 to July 2013.
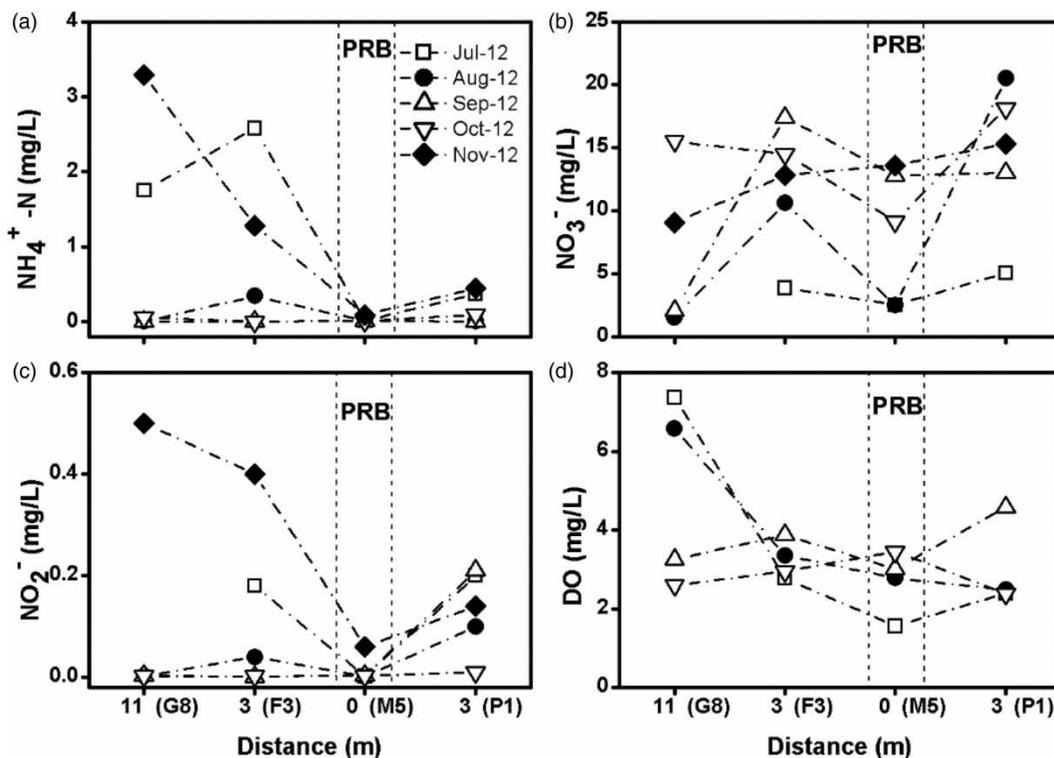
Figure 4 │ Ammonium-N concentrations in up-gradient well G8, in wells within the PRB (M1, M5, M9), and in down-gradient well P1 monitored from July 2012 to November 2012.

and its performance was not stable yet. However, the concentrations of ammonium became stable at less than 0.5 mg/L after the initial phase. The ammonium concentrations in well P1, which was located down-gradient of the PRB, were

also always less than 0.5 mg/L. This represents a overall removal efficiency of about 80%, which is even greater than the 70% achieved for ammonium removal from rainfall runoff using an above-ground limestone–zeolite PRB (Srinivasan *et al.* 2008). These results clearly demonstrate that a zeolite PRB is an effective way to treat groundwater *in situ* that is contaminated with ammonia nitrogen.

Concentration profiles for NH_4^+-N, NO_3^--N, NO_2^--N and DO are plotted spatially in Figure 5, starting from two up-gradient monitoring wells (G8 and F3), through the zeolite barrier (M5), and then down-gradient of the PRB (P1). Although there appears to be some experimental variability in July 2012 in the initial phase of PRB, as ammonium-N concentrations in the PRB decrease, there were corresponding slight reductions in nitrate concentrations in a warm season from August to October, the values of nitrite are always at a low level, and the variability of DO (2–4 mg/L) is not obvious. Because the low levels of influent ammonium (~3.5 mg/L) would have been readily adsorbed to the zeolite, very little ammonium would have been available for
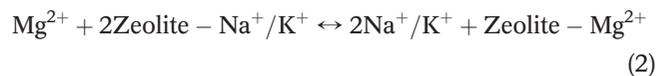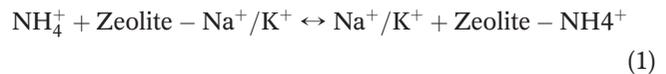

Figure 5 │ Concentrations of ammonium (NH_4^+-N), nitrate (NO_3-N), nitrite (NO_2-N) and DO in well G8 (up-gradient of the PRB), well F3 (up-gradient of the PRB), well M5 (within the PRB) and well P1 (down-gradient of the PRB) from July 2012 to November 2012.

microbial nitrification. Microbial denitrification might exist in the PRB and was responsible for the observed nitrate reduction. However, the reaction was expected to be less significant due to DO (>2 mg/L) and elevated Eh (>400 mV), both being unfavorable for microbial nitrate or nitrite reduction (Paredes *et al.* 2007). Nitrate and nitrite were most likely transformed to nitrogen gas under the redox condition observed in the PRB. This is consistent with the data from historic surveys in this region, that ammonium is mainly from effluent of a municipal waste water treatment plant and local agricultural activities.

Geochemical indicator parameters

In addition to nitrogen and DO, influent and effluent samples were routinely analyzed for major metal cations (see Figure 6). The influent groundwater concentrations of Na^+, K^+, Ca^{2+} and Mg^{2+} were 30, 4, 38, and 12 mg/L, respectively. After passing through the zeolite PRB, the concentrations of K^+ and Na^+ increased, suggesting a partial release of these cations from the zeolite (see Figures 6(a)

and 6(b)). The concentration of Mg^{2+} in the effluent decreased significantly to ~4 mg/L (see Figure 6(d)), while Ca^{2+} concentrations generally remained unchanged (see Figure 6(c)). The increases in Na^+ and K^+ concentrations and the decreases in ammonium and Mg^{2+} in the PRB suggest that the NH_4^+-N and Mg^{2+} are primarily exchanged with Na^+ and K^+ present in the zeolite crystal structure. As expected, Ca^{2+} cations were neither retained nor released in the PRB system. The reactive process can be mainly carried out by the following ion-exchange reaction:

$$NH_4^+ + Zeolite - Na^+/K^+ \leftrightarrow Na^+/K^+ + Zeolite - NH4^+ \tag{1}$$

$$Mg^{2+} + 2Zeolite - Na^+/K^+ \leftrightarrow 2Na^+/K^+ + Zeolite - Mg^{2+} \tag{2}$$

Huang *et al.* (2010) also reported that the order of the effect of metal cations on NH_4^+ ion removal was $Na^+ > K^+ > Ca^{2+} > Mg^{2+}$ at the same concentration. In this paper the low level of influent ammonium limited the ion
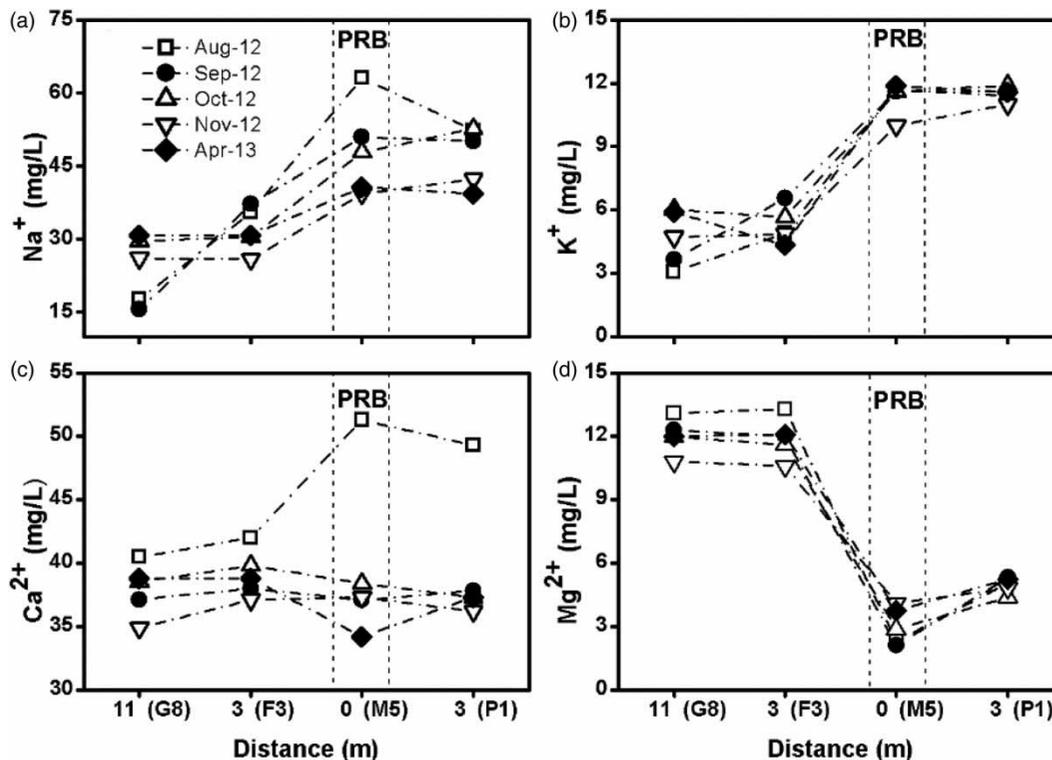

Figure 6 | Concentrations of Na^+, K^+, Ca^{2+} and Mg^{2+} in wells G8 and F3 (up-gradient of the PRB), in well M5 (within the PRB), and in well P1 (down-gradient of the PRB) from August 2012 to April 2013.

exchange reactions with other metal cations in the region except for the Na$^+$ ions. Similar results have been reported by others (Wang *et al.* 2007). The driving force of the influent concentration of metal cations promoted the ion exchange reaction between them and the redistribution of metal cations in the solid–liquid phase in the PRB.

CONCLUSIONS

This paper summarizes results from an operating zeolite PRB designed and installed for the *in situ* remediation of groundwater contaminated with ammonium nitrogen originating from river water infiltrating to a drinking water aquifer. Ammonium concentrations in the groundwater decreased from 2–10 mg/L to <0.5 mg/L after the PRB was installed. Results suggest that ammonium removal was mainly due to sorption and ion exchange. After more than 1 year of continuous operation, there is no evidence of microbial ammonia oxidation. To our knowledge, this is the first field-scale PRB in China. Data collected to date indicate that the PRB technology may offer a cost-effective solution to a widespread problem of surface–groundwater contamination in China; however, additional research is required to determine ways to regenerate the zeolite *in situ* and/or enhance its performance by inducing microbial nitrification and denitrification in an effort to extend the longevity of this technology in the field.

ACKNOWLEDGMENTS

REFERENCES

Careghini, A., Saponaro, S. & Sezenna, E. 2013 Biobarriers for groundwater treatment: a review. *Water Science and Technology* 67 (3), 453–468.

Chen, L., Liu, F., Liu, Y., Dong, H. & Colberg, P. J. S. 2011 Benzene and toluene biodegradation down gradient of a zero-valent iron permeable reactive barrier. *Journal of Hazardous Materials* 188 (1–3), 110–115.

Chen, L., Jin, S., Fallgren, P. H., Swoboda-Colberg, N. G., Liu, F. & Colberg, P. J. S. 2012 Electrochemical depassivation of zero-valent iron for trichloroethene reduction. *Journal of Hazardous Materials* 239, 265–269.

Erto, A., Lancia, A., Bortone, I., Di Nardo, A., Di Natale, M. & Musmarra, D. 2011 A procedure to design a permeable adsorptive barrier (PAB) for contaminated groundwater remediation. *Journal of Environmental Management* 92 (1), 23–30.

Evanko, C. R. & Dzombak, D. A. 1997 *Remediation of Metals-Contaminated Soils and Groundwater*, Technology Evaluation Report TE-97-01, Ground-Water Remediation Technologies Analysis Center, Pittsburgh, PA, USA.

Gavaskar, A. R. 1999 Design and construction techniques for permeable reactive barriers. *Journal of Hazardous Materials* 68 (1–2), 41–71.

Hinkle, S. R., Bohlke, J. K., Duff, J. H., Morgan, D. S. & Weick, R. J. 2007 Aquifer-scale controls on the distribution of nitrate and ammonium in ground water near La Pine, Oregon, USA. *Journal of Hydrology* 333 (2–4), 486–503.

Huang, H., Xiao, X., Yan, B. & Yang, L. 2010 Ammonium removal from aqueous solutions by using natural Chinese (Chende) zeolite as adsorbent. *Journal of Hazardous Materials* 175 (1–3), 247–252.

Kanew, S. R., Choi, H., Kim, J. Y., Vigneswaran, S. & Shim, W. G. 2006 Removal of arsenic(III) from groundwater using low-cost industrial by-products: blast furnace slag. *Water Quality Research Journal of Canada* 41 (2), 130–139.

Khan, F. I., Husain, T. & Hejazi, R. 2004 An overview and analysis of site remediation technologies. *Journal of Environmental Management* 71 (2), 95–122.

Komnitsas, K., Bartzas, G. & Paspaliaris, I. 2004 Efficiency of limestone and red mud barriers: laboratory column studies. *Minerals Engineering* 17 (2), 183–194.

Kong, X., Ma, J., Yang, Y., Liu, F. & Bi, E. 2012 Laboratory column study for evaluating a bio-chemical permeable reactive barrier to remove ammonium from groundwater. *Environmental Science & Technology* 35 (12), 1–5.

Ma, J., Shi, Y., Chen, X. & Wang, H. X. 2013 Nitrogen load from rural non-point source pollution in suburb area of Shenyang: a case study of Damintun town. *Advanced Materials Research* 610, 3277–3281.

Mulligan, C. N., Yong, R. N. & Gibbs, B. F. 2001 Remediation technologies for metal-contaminated soils and groundwater: an evaluation. *Engineering Geology* 60 (1–4), 193–207.

Nardo, A. D., Natale, M. D., Erto, A., Musmarra, D. & Bortonea, I. 2010 Permeable reactive barrier for groundwater PCE remediation: the case study of a solid waste landfill pollution. *Computer Aided Chemical Engineering* 28, 1015–1020.

Ouellet-Plamondon, C., Lynch, R. & Al-Tabbaa, A. 2011 Metal retention experiments for the design of soil-mix technology

permeable reactive barriers. *CLEAN – Soil, Air, Water* **39** (9), 844–852.

Paredes, D., Kuschk, P., Mbwette, T., Stange, F., Müller, R. & Köser, H. 2007 New aspects of microbial nitrogen transformations in the context of wastewater treatment: a review. *Engineering in Life Sciences* **7** (1), 13–25.

Patterson, B. M., Grassi, M. E., Robertson, B. S., Davis, G. B., Smith, A. J. & McKinley, A. J. 2004 Use of polymer mats in series for sequential reactive barrier remediation of ammonium-contaminated groundwater: field evaluation. *Environmental Science & Technology* **38** (24), 6846–6854.

Phillips, D., Nooten, T. V., Bastiaens, L., Russell, M., Dickson, K., Plant, S., Ahad, J., Newton, T., Elliot, T. & Kalin, R. 2010 Ten year performance evaluation of a field-scale zero-valent iron permeable reactive barrier installed to remediate trichloroethene contaminated groundwater. *Environmental Science & Technology* **44** (10), 3861–3869.

Robertson, W., Vogan, J. & Lombardo, P. 2008 Nitrate removal rates in a 15-year-old permeable reactive barrier treating septic system nitrate. *Ground Water Monitoring & Remediation* **28** (3), 65–72.

Srinivasan, R., Hoffman, D. W., Wolfe, J. E. & Prcin, L. J. 2008 Evaluation of removal of orthophosphate and ammonia from rainfall runoff using aboveground permeable reactive barrier composed of limestone and zeolite. *Journal of Environmental Science and Health Part A: Toxic/Hazardous Substances and Environmental Engineering* **43** (12), 1441–1450.

Suponik, T. 2010 Adsorption and biodegradation in PRB technology. *Environment Protection Engineering* **36** (3), 43–57.

Teerakun, M., Reungsang, A., Lin, C. J. & Liao, C. H. 2011 Coupling of zero valent iron and biobarriers for remediation of trichloroethylene in groundwater. *Journal of Environmental Sciences* **23** (4), 560–567.

Thiruverikatachari, R., Vigneswaran, S. & Naidu, R. 2008 Permeable reactive barrier for groundwater remediation. *Journal of Industrial and Engineering Chemistry* **14** (2), 145–156.

USEPA 1998 *Permeable Reactive Barrier Technologies for Contaminant Remediation*, EPA 600-R-98-125, US Environmental Protection Agency, Washington, DC, USA.

USEPA 2004 *Technologies for Treating MtBE and Other Fuel Oxygenates*, EPA 542-R-04-009, US Environmental Protection Agency, Washington, DC, USA.

Van Nooten, T., Diels, L. & Bastiaens, L. 2008 Design of a multifunctional permeable reactive barrier for the treatment of landfill leachate contamination: laboratory column evaluation. *Environmental Science & Technology* **42** (23), 8890–8895.

Van Nooten, T., Diels, L. & Bastiaens, L. 2010 Microbially mediated clinoptilolite regeneration in a multifunctional permeable reactive barrier used to remove ammonium from landfill leachate contamination: laboratory column evaluation. *Environmental Science & Technology* **44** (9), 3486–3492.

Vignola, R., Bagatin, R., D'Auris, A. D. F., Flego, C., Nalli, M., Ghisletti, D., Millini, R. & Sisto, R. 2011 Zeolites in a permeable reactive barrier (PRB): one year of field experience in a refinery groundwater. Part 1: the performances. *Chemical Engineering Journal* **178**, 204–209.

Wang, Y., Kmiya, Y. & Okuhara, T. 2007 Removal of low-concentration ammonia in water by ion-exchange using Na-mordenite. *Water Research* **41** (2), 269–276.

Yi, S., Chi, B., Wu, F. & Zhou, Y. 2006 Research on numerical simulation and evaluation of riverside source field: a case study of Liguanpu riverside source field in Shenyang City. *Journal of Natural Resources* **21** (1), 154–160.

Zhang, Y., Zhang, Y. L., Zhang, S. Y., Song, F., Huang, J. Y., Zhang, Y. & Bai, X. D. 2012 Utilization of scoria as PRB reactive media for the removal of petroleum hydrocarbon from groundwater. *Advanced Materials Research* **535–537**, 2457–2461.

Zhuo, N., Cuiyun, Z. & Sheng, Z. 2011 Study of groundwater contamination of ammonium and its nitrogen isotope. *South-to-North Water Transfers and Water Science and Technology* **9** (3), 129–132.