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NanoRem Bulletin

CL:AIRE's NanoRem bulletins describe practical aspects of research which have direct application to the characterisation, monitoring or remediation of contaminated soil or groundwater using nanoparticles. This bulletin describes a pilot study to evaluate the nanoscale zero-valent iron remediation of arsenic in groundwater.

NanoRem Pilot Site – Nitrastur, Spain: Remediation of Arsenic in Groundwater Using Nanoscale Zero-valent Iron

1. INTRODUCTION

This bulletin describes a pilot study to evaluate the nanoscale zero-valent iron (nZVI) remediation of arsenic (As) in groundwater. It was undertaken as part of the NanoRem Project (Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment), which was funded through the European Union Seventh Framework Programme.

The Nitrastur site in Asturias, Spain is characterised by high concentrations of As in both soil and groundwater. In groundwater, the two most common form of As are arsenate, As (V) and arsenite, As(III). According to scientific literature both arsenates and arsenites can be fully transformed into metalloid arsenic As(0) by reaction with nZVI (Yan *et al.*, 2012; Ling and Zhang, 2014). As(0) is insoluble, thermodynamically stable, and this reaction is not expected to be reversible. This renders nZVI a potential candidate for *in situ* remediation applications.

The pilot study presented an opportunity for testing the application of nanoparticles (NPs) in real site conditions, focusing on the treatment of dissolved As in groundwater. In order to be able to evaluate the performance of the field application, three objectives were set as part of the injection and monitoring plan:

- Objective 1: To determine the effectiveness of arsenic nano-remediation;
- Objective 2: To determine the temporal and spatial dispersion of nZVI; and
- Objective 3: To assess the potential risks associated with nZVI injection and changing groundwater geochemical conditions.

2. SITE DESCRIPTION

The pilot site is an abandoned 20 hectare, flat brownfield site, located in Asturias (Northern Spain). It was used between 1950 and 1998 for the production of nitrogen-based products such as fertilizers. Currently the site hosts the ruins of the former chemical factory and it is the property of a private electric utility firm. There are no imminent plans for its redevelopment. Figure 1 gives an aerial view of the site and shows the location of the boreholes.

Preliminary intrusive investigations were performed by Deme Environmental Contractors NV and the University of Oviedo in 2009 and 2013 including 100 trial pits, 20 boreholes (all fitted with groundwater monitoring wells) and hydrogeological tests. As a result, high levels of fertilizers, petroleum hydrocarbons and heavy metals were detected both in soil and groundwater and a preliminary Conceptual Site Model (CSM) was defined (see below for further details).

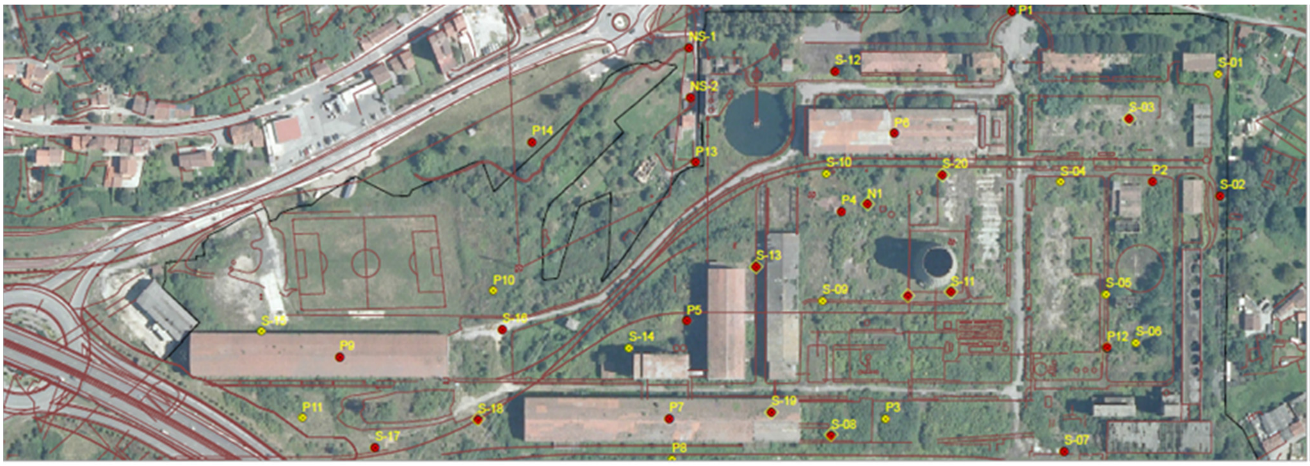

Figure 1. Aerial view of the site showing the location of the boreholes.

Taking **Nano**technological **Rem**ediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment.
This project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no. 309517.

Geology and soil contamination

The site area is covered by a layer of made ground (177,000 m^2) with a variable thickness between 2 m and 9 m. Made ground materials include construction debris, slag from furnaces, wastes from coal washing and partially burned pyrite and pyrite ashes which are typically rich in heavy metals including As. The volume of contaminated made ground was estimated in the 2009 investigation as being as much as 228,904 m^3. Underlying the made ground, there is a layer of Quaternary alluvial deposits about 3 m thick, of sandy gravels with boulders which define the, locally semi-confined, aquifer of the site. Beneath the aquifer, there is less permeable, very hard Carboniferous shale and sandstone.

Table 1 shows heavy metal concentrations found in the made ground for the four metals that were above the Basque (Spanish) soil reference value for industrial use (VIE-B). None of the metals were higher than their respective reference values in the aquifer material, but their concentrations are included for comparison. The maximum As concentration found is 4300 mg/kg.

Table 1. Maximum concentrations of heavy metals detected in made ground and aquifer material.

Contaminant	Basque/Spanish soil reference value for industrial use (VIE-B)	Maximum concentration detected (mg/kg)	
		Made ground	Aquifer material
Arsenic (As)	200	4300	15
Mercury (Hg)	40	120	0.99
Lead (Pb)	1000	11000	34
Zinc (Zn)	10000	11000	290

Hydrogeology and groundwater As contamination

The groundwater level is located close to the contact area between the made ground and the alluvial materials, fluctuating from one level to another (at a depth ranging between 2 m and 6 m below ground level (bgl)). Its flow direction is towards an adjacent perennial river with an average flow of about 55 m^3/s, and its average velocity is around 0.5 m/day. In terms of groundwater quality, from a total of eight heavy metals analysed, six (As, Pb, Zn, Cd, Cu and Ni) were above the Spanish reference value for groundwater, for which the 2000 Dutch Intervention Values are used (Table 2).

Regarding dissolved total As, the maximum concentration found before the injection date was 5527 µg/l (March 2015), i.e. nearly two orders of magnitude above the intervention value for this metalloid (60 µg/l). The highest concentrations were located in the central area of the site and most of the As is in the form of pentavalent As or As(V), with a lesser amount in the trivalent form, As (III).

Table 2. Maximum concentrations of heavy metals detected in groundwater.

Contaminant	Maximum concentration detected in groundwater (µg/l) / Dutch Intervention value (µg/l)
Arsenic (As)	5527 / 60
Lead (Pb)	240 / 75
Zinc (Zn)	19000 / 800
Copper (Cu)	12000 / 75
Cadmium (Cd)	150 / 6
Nickel (Ni)	90 / 75

Geochemical aquifer conditions

According to *in situ* measured geochemical parameters in the groundwater, the pH had a neutral average value (with a minimum recorded value of 5.7), the electrical conductivity was relatively low (1163 µS/cm) and the oxidation-reduction potential (ORP) was approximately +405 Rmv which suggested aerobic, oxic natural conditions.

Conceptual site model – CSM

The main source of As contamination is the made ground of the site, whereas the potential receptors are the aquifer and the adjacent river (there are no human receptors since the site is currently abandoned with limited access to it) and the main pathways for contaminant migration are a) leaching from the made ground to groundwater and b) the downgradient migration of heavy metals in groundwater respectively (Figure 2).

3. PROJECT MANAGEMENT

3.1 Project Team

The pilot study was managed by Fundación Tecnalia Research & Innovation with the collaboration of five NanoRem project partners:

- University of Stuttgart (VEGAS): Overall coordinator for the NanoRem project.
- Technical University of Liberec: Laboratory testing of NPs.
- Aquatest: Site investigation works.
- Geoplano: Drilling and injection works.
- Nano Iron, s.r.o.: NPs provider.

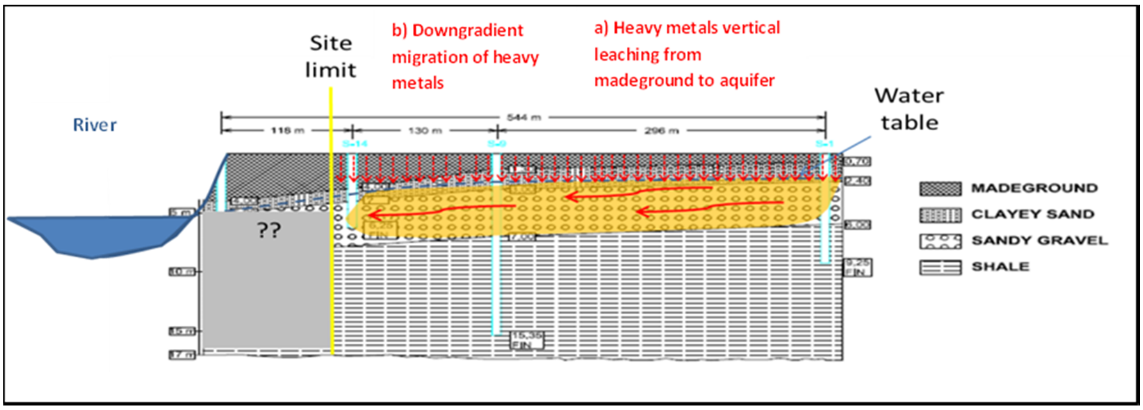

Figure 2. CSM cross section

3.2 Regulatory Approval

In March 2014 the "Gobierno del Principado de Asturias" (Asturias Government) authorised Tecnalia to perform a pilot study with NPs for groundwater remediation at the Nitrastur site. Considering its abandoned status, there were no specific requirements from regulators for this particular site.

4. DESIGN, INSTALLATION AND OPERATION

4.1 Laboratory Testing

Preliminary laboratory work evaluated two types of nanoscale iron oxides as well as a nZVI NP called NANOFER STAR. Laboratory reactivity test results with Nitrastur groundwater samples showed that the concentration of dissolved As from the site decreased significantly in treatments using all the NPs tested. The largest reductions were obtained with NANOFER STAR, hence it was this NP that was taken forward to the field site.

4.2 Injection of NPs

The injection took place at three injection points (IP-1, IP-2 and IP-3) at 1.73 m distance intervals in a triangular configuration, in order to maximise the distribution of nZVI in the subsurface. Injection wells were 3" diameter, PVC tubes, slotted 0.5 m below the groundwater level, into the saturated zone, and packer installed in the made ground:

IP-1 —> slotted interval: 5.00 – 7.00 m bgl
IP-2 —> slotted interval: 3.50 – 7.00 m bgl
IP-3 —> slotted interval: 4.30 – 7.00 m bgl

The injection process was controlled in eight additional monitoring wells or control points (CP-1 to CP-7 and MW-1), all drilled down to bedrock Lutite (7 m bgl) slotted above the piezometric level.

Injection works were performed in collaboration with Geoplano. During 4 days, from February 23rd to 27th 2016, a total of 250 kg of NANOFER STAR were injected in the pilot area, at low pressure (< 5 bars) and a flow rate of approximately 0.6-1 m³/hour. Together with the nZVI, a lithium chloride tracer (LiCl at 50 mg/l) was added to check the theoretically limited NPs transport against a more mobile element.

Figure 3 (a, b and c) shows a schematic of the injection pilot test set up, the locations of the monitoring wells / injection points and a photo of the site works, respectively.

4.3 Sampling and Monitoring Programme

During the injection works, real-time (at 5 minute intervals), *in situ* (at 5 m bgl) geochemical parameters were measured: pH, electrical conductivity (EC), ORP, temperature (T) and dissolved oxygen (DO). Additionally, 1 day before and during 6 months after the injection,

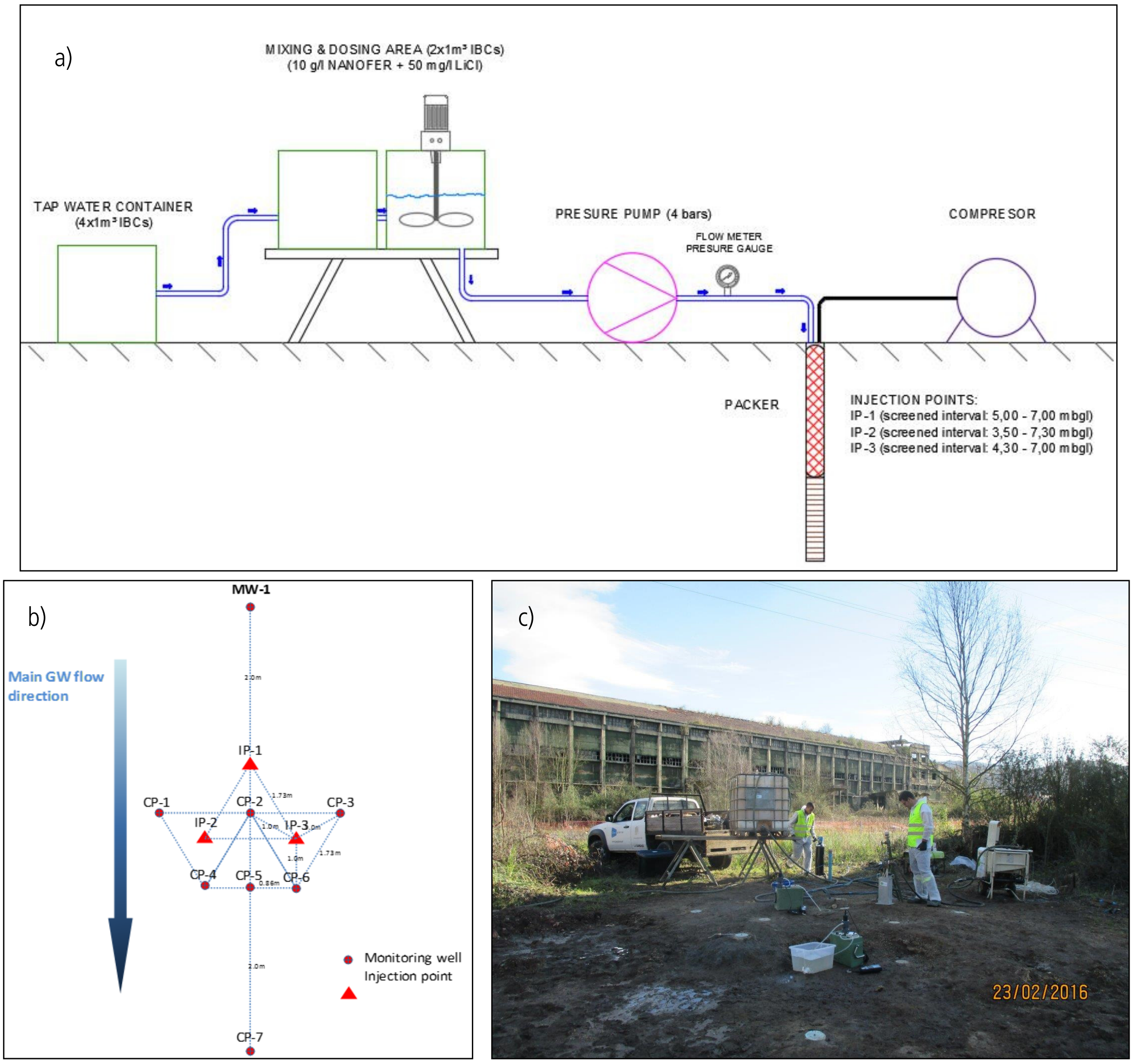

Figure 3. a) Schematic of the injection process, b) Pilot test monitoring well and injection point layout, and c) General site overview.

groundwater samples were periodically taken and basic parameters were measured for a total of 13 sampling campaigns[1]: 3, 5, 9, 12, 16, 19, 23 and 30 days after the injection and monthly for the following 5 months (180 days).

5. RESULTS AND DISCUSSION

The field data collected from the 6 month sampling programme was collated and interpreted. It is presented below according to the three main objectives of the study.

- Determination of the effectiveness of arsenic nanoremediation (Objective 1);
- Determination of the temporal and spatial dispersion of nZVI (Objective 2); and
- Assessment of the potential risks associated with nZVI injection and changing groundwater geochemical conditions (Objective 3).

5.1 Determination of the effectiveness of arsenic nanoremediation (Objective 1)

According to the field data, total dissolved As[2] reduction in groundwater and therefore the technology efficiency can be explained by two consecutive geochemical phases (Figure 4, Figure 5 and Figure 6 summarise As concentration, pH factor and redox potential spatial and temporal evolution respectively, before the injection and 180 days (6 months) after):

Geochemical Phase 1: From injection to +14 days after the injection

In all wells total dissolved As concentration reduced during the first 7 days after the injection and in some wells (MW-1, CP-2 and CP-6) As concentrations continued to decrease for at least one week more (16 days after the injection). In other wells As concentrations remained steadily low. This low total dissolved As period characterises the first geochemical phase.

During this phase, measured redox potential was at its lowest recorded value, between -400 and -500 mV for most wells, except for MW-1 (control well) and CP-7 (furthest control point). There was also a pH increase in most wells to a maximum recorded value of 9.41 in CP-2 (except for the upgradient well MW-1) until 3 days after the end of the injection, when the pH started to fluctuate, but at a higher register than the original measured values.

Geochemical Phase 2: From 28 days to 180 days (6 months) after the injection

During this phase, As levels fluctuated significantly with no clear chemical trend for all wells. 34 days after nZVIs injection, As levels increased in almost all wells (in CP-6 As concentration rose from 36 µg/l up to 880 µg/l), including the upgradient well MW-1. The only exception to this general behaviour was at CP-3, where As levels continued to decrease, and CP-2 and CP-5 where As concentrations remained slightly below initial levels during the entire geochemical phase 2.

At the 61 days sampling campaign, not all wells exhibited the same behaviour, most likely due to differences in the hydrogeological setting of each well in that the aquifer is characterised by the presence of gravels and boulders with a variable permeability.

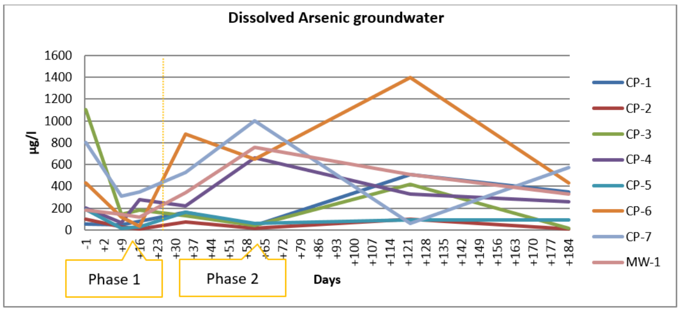

Figure 4. The evolution of total dissolved As concentration (days before and after the injection application)

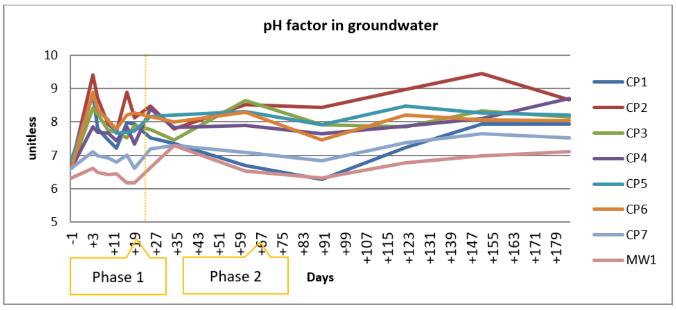

Figure 5. pH evolution (days before and after the injection application).

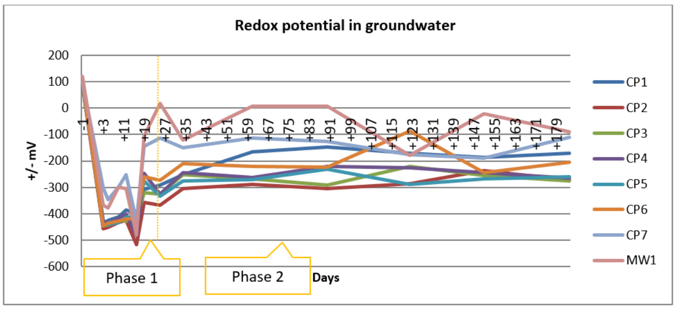

Figure 6. Redox potential evolution (days before and after the injection application).

According to ORP recorded values, during this second chemical phase, there was first an initial partial increase in all wells, followed by a steady situation, with no significant variations. 180 days after the injection application, redox values remained below pre-injection conditions (all wells showed negative ORP values as opposed to positive original ones, except for the control well, MW-1).

In terms of pH, at the end of the monitoring period, the pH was stable and still higher than original values in most wells (close to or higher than 8.0). MW-1, the control well, showed a pH value closest to the initial one.

5.2 Determination of the temporal and spatial dispersion of nZVI (Objective 2)

In order to understand nZVI NPs distribution, iron (Fe total, Fe(II) and Fe(III)) and the lithium (Li) tracer were measured periodically in groundwater.

According to the field data shown in Figure 7, Figure 8 and Figure 9 changes in lithium, ferrous iron and ferric iron concentrations respectively can be explained in two consecutive geochemical phases that are similar to those of the dissolved As (explained in the previous section):

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[1] Chemical analyses were performed by AGROLAB laboratory (www.agrolab.com/en/).

[2] Total dissolved arsenic includes both As(III) and As(V).

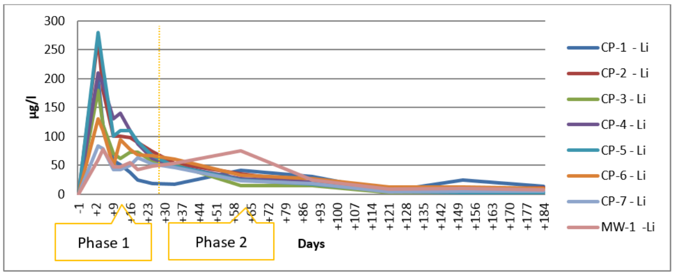

Figure 7. Li levels in monitoring wells and sampling campaigns (µg/l)

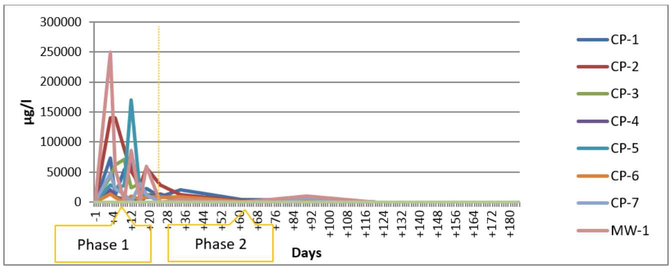

Figure 8. Fe(II) in monitoring wells and sampling campaigns (µg/l)

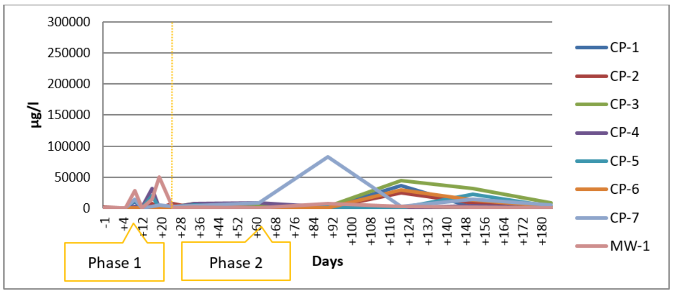

Figure 9. Fe(III) in monitoring wells and sampling campaigns (µg/l)

Geochemical Phase 1: From injection to 24 days after the injection

According to lithium distribution, the injection radius of influence covered the entire pilot test area (20 m² from MW-1 down to CP-7) in a short time, 3 days, due to the relatively high groundwater velocity (0.5 m/day). As expected, the lithium concentration was higher in CP-2 and CP-5, which matches well with the main groundwater flow direction towards the closest river, and decreased gradually as groundwater flowed into the pilot test zone from upgradient areas and rainfall infiltration recharged the aquifer.

In terms of nZVI spatial distribution, despite the delayed transport mentioned above, iron particles were detected in all wells mainly as ferrous iron, Fe(II), including CP-7, 3 m downgradient from the injection zone, covering an area of 20 m^2, within the first 24 days after the injection application. Control point MW-1, CP-2 and CP-5 showed the highest iron concentrations during this period and CP-7, the most downgradient well, showed high levels of ferrous iron (48 mg/l) in the first campaign after the injection (3 days after).

Geochemical Phase 2: From 24 to 180 days (6 months) after the injection

During this phase, lithium concentrations remained low (<50 µg/l), and decreased gradually with time until the end of the monitoring process (6 months after the injection application).

In terms of NPs presence, after 24 days, total, ferrous and ferric iron concentrations decreased significantly and remained persistently low or even non-detectable as NPs were consumed and their oxides precipitated, until day 90. At that sampling campaign, a ferric iron (Fe(III)) level increase (from 8.6 mg/l up to 83 mg/l) is noticed in control well CP-7, and subsequently, in day 120, in almost all wells including MW-2 (located 15 m downgradient from the injection zone), except CP-4, ferric iron levels increase. All the total iron detected during this second geochemical phase is in the form of ferric iron, Fe(III), which correlates with the *in situ* geochemical parameters measured in all wells during this phase: i.e. higher redox conditions (although still lower than original values) and higher dissolved oxygen values. In this case, Fe(III) content is probably indicative of some degree of upgradient NPs corrosion.

Interpretation of results from Objectives 1 and 2

The existence of similar time evolution profiles for dissolved As, lithium, iron and basic parameters such as redox potential, pH or dissolved oxygen, allows for the following interpretation of the geochemical processes taking place in both of the identified phases. The boundary between them is a diffuse time period between 2 to 4 weeks after the injection application:

Geochemical Phase 1 (0-24 days after NPs application): this stage is characterised by the presence of low As concentrations, high levels of iron (total and ferrous), lowest values of redox potential (between -400 and -500 mV), lowest levels of dissolved oxygen and alkaline conditions, in all wells. Iron particles were detected in all wells mainly as ferrous iron, Fe(II), including CP-7, 3 m downgradient from the injection zone, covering an area of 20 m^2, within the first 24 days after the injection application. All these factors suggest that NPs were effectively reducing As into metalloid arsenic As(0).

Geochemical Phase 2 (24–180 days after NPs application): during this stage, NPs were oxidised and precipitated, shaping a reductive zone. The As response to this zone is variable. Locally, in CP-2, CP-3 or CP-5, As levels, constantly low, reveal the adsorption effect of the iron oxides during the entire monitoring period (180 days); whereas in other control points, such as CP-4 and CP-6, As levels are probably indicative of some degree of desorption and transport taking place 60 to 120 days after the injection application. These local differences in As content may be related to differences in the hydrogeology. Additionally NPs corrosion is noticed as an Fe(III) increase in that period.

5.3 Assessment of the potential risks associated with nZVI injection and changing groundwater geochemical conditions (Objective 3)

Considering the main geochemical mechanisms responsible for the removal of arsenate and their interaction with the soil's mineral ions in the aquifer, potential side effects of a nZVI application have been identified: i) mobilisation of other metals, ii) enlargement of the contaminant plume, iii) increased desorption of As from nZVI and its corrosion products iv) increased toxicity due to nZVI's presence. Evaluation of these will allow a better understanding of the remediation process and to integrate the necessary measures to control potential risks in the monitoring programme. Data for the first of these potential side effects is presented in this bulletin.

Mobilisation of other metals

Metals other than As can be grouped as redox sensitive or insensitive according to their redox-dependent solubility. Redox-sensitive metals (e.g. Cr, Cu, Hg, Fe and Mn) can change their oxidation state forming low solubility hydroxides-oxides. Redox-insensitive metals (e.g. Al, Ba, Cd, Pb, Ni, Zn) can, in the presence of reactants, under reducing conditions, form carbonates, phosphates, sulphates and hydroxides-oxides whose solubility depends more on pH than on redox potential.

In the pilot area, eight heavy metals dissolved in the groundwater were monitored prior to and after nZVI injection: As, Cd, Cu, Cr total, Hg, Ni, Pb and Zn. Some of the metal concentrations increased after the application of nZVI, exceeding their reference value for groundwater (Dutch intervention value). This was the case for Hg (redox sensitive), total Cr (redox sensitive) and Pb (redox insensitive). On the other hand, at the last sampling campaign (6 months after injection) concentrations for these metals were again below the intervention reference value for groundwater.

Dissolved Cu, redox sensitive, did not undergo a variation in concentration, despite the redox potential reduction after NPs application and some of the redox insensitive metals were either mobilised or their concentration was reduced after NPs application (Pb, Zn and Cd), so other mechanisms must control their stabilisation.

It is important to point out that at this site, the mobilisation of metals does not impose a significant impact since groundwater is already contaminated with dissolved metals and no sensitive receptors have been identified.

6. CONCLUSIONS AND LESSONS LEARNED

The Nitrastur pilot study presented an opportunity for testing the application of NPs in real site conditions, focusing on the treatment of dissolved As in groundwater. In order to be able to evaluate the performance of the nanoremediation field application, three objectives were set as part of the injection and monitoring plan. The main conclusions obtained for each of the objectives are described below:

Objective 1. To determine the effectiveness of arsenic nanoremediation – main conclusions

- ⇒ Arsenic remediation at the pilot test site was divided into two distinctive stages, where different geochemical processes seem to be taking place:
  - Geochemical Phase 1 (0-24 days after NPs application): Geochemical factors suggest that NPs are effectively reducing As into metalloid arsenic As(0).
  - Geochemical Phase 2 (24-180 days after NPs application): During this chemical stage, most NPs have been oxidised and have precipitated, forming a reactive zone in which dissolved As behaves differently: locally the metalloid gets adsorbed into it during the entire monitoring period (CP-2, CP-3 or P-5), or undergoes desorption mechanisms 2 to 4 months after the injection application (CP-4, CP-6 or CP-7), probably related to different local hydrogeological settings and/or also to some degree of NPs corrosion.
- ⇒ Although in general terms results are encouraging, additional long-term laboratory tests and technology modelling tools for predicting the effects of the technology are recommended for future applications, particularly considering the possibility of arsenic partial desorption.

Objective 2. To determine the temporal and spatial dispersion of nZVI – main conclusions

- ⇒ Regarding the spatial distribution of nZVI in the subsurface, iron particles were detected in all wells, mainly in the form of Fe(II), covering an area of about $20m^2$, 24 days after the injection application.
- ⇒ Following the first 24 days, iron concentration decreased significantly and remained persistently low or even non-detectable as NPs were consumed and their oxides precipitated.
- ⇒ From day 90 onwards, some ferric iron (Fe(III)) level increase was noticed in almost all wells including MW-2 (located 15 m downgradient from the injection zone). Fe(III) content is probably indicative of some degree of upgradient NPs corrosion.
- ⇒ Although in general terms NPs dispersion has been explained, other monitoring and tracing tools than groundwater sampling are recommended for future applications.

Objective 3. To assess the potential risks associated with nZVI injection and changing groundwater geochemical conditions – main conclusions

- ⇒ Mobilisation of other metals:
  - While some of the analysed metal concentrations increased initially after the application of nZVI (e.g. Hg, total Cr and Pb), the final sampling campaigns concentrations for these metals fell back below the corresponding intervention reference value for groundwater. However, it is considered necessary to investigate at laboratory-scale the effect of NPs application on mixtures of dissolved heavy metals.

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