CL:AIRE
AB 1
(October 2014)
ADVOCATE bulletin

CL:AIRE's ADVOCATE bulletins describe practical aspects of research which have direct application to the characterisation, monitoring or remediation of contaminated soil or groundwater. This bulletin describes laboratory studies to evaluate reactive materials to treat contaminated groundwater in a permeable reactive barrier.

Remediation of TCE contaminated groundwater using permeable reactive barriers

1. Introduction

Chlorinated solvents, such as: trichloroethylene (TCE) and tetrachloroethylene (PCE) are primary contaminants of concern common in aquifers in Europe and North America. They have been widely used for a variety of industries (ammunition, electronics, automotive parts, textile and dry cleaning) as cleaning and degreasing solvents (Mccarty, 2010). TCE, PCE and their daughter products are considered to be a health concern and are included in the list of probable carcinogens to humans (ATSDR, 1997). Chlorinated solvents have densities higher than water, thus they can penetrate deeper into an aquifer forming dense (relative to water) non-aqueous phase liquid (DNAPL) plumes. These compounds have relatively low solubility in water, which means that their loss by dissolving in water is rather a slow process. Additionally, they demonstrate low sorption affinity indicating that they do not sorb strongly into aquifer solids (Mccarty, 2010). Because of their characteristics, chlorinated solvents are among the contaminants that have proved to be difficult to remediate, representing a technical and economic challenge to engineers (Gavaskar *et al*., 2000).

Permeable reactive barriers (PRB) may offer a low cost and efficient option to treat groundwater contaminated with chlorinated solvents. The main objective of this technology is to intercept and remediate dissolved contaminants passing through the barrier with a reactive material (ITRC, 2011). The technology has gained popularity because of its efficient and low cost removal of pollutants from groundwater compared to active remediation technologies with high operation and maintenance costs (e.g. 'pump and treat') (USEPA, 2001). One key step in the design of the PRB is the selection of the appropriate reactive material to treat the contaminants of interest. To date, zero valent iron (ZVI) is the most worldwide used reactive material for the removal of chlorinated solvents from groundwater. Although significant removal efficiencies of chlorinated solvents have been demonstrated, the formation of mineral precipitates may limit the long-term performance of the PRB with ZVI by decreasing reactivity and permeability (Bone, 2012). Therefore, this research includes the selection and use of alternative reactive materials, such as: compost and brown coal to treat groundwater contaminated with chlorinated solvents to overcome the problems that ZVI possesses.

2. Site Description

The contaminated site is located in southeast Poland in the vicinity of the town of Nowa Deba (Fig.1). Chlorinated solvents (TCE and PCE) have been detected in some of the waterworks' wells with concentrations up to 6,130 µg/L and 694 µg/L, respectively, exceeding Polish standards for drinking water and giving to the aquifer a "poor" groundwater chemical status (Kret *et al*., 2011). Due to the risk these contaminants represent to human health, urgent measures are needed to stop the further spread of contaminants within the aquifer and to the remaining wells. Previous studies have concluded that natural attenuation (NA) will take more than 60 years to clean up the groundwater and have underlined the necessity to evaluate an alternative remediation strategy. On the contrary, a feasibility study has indicated that the installation of a PRB system may be effective to reduce TCE and PCE concentrations, diminishing the environmental risk and achieving a 'good' groundwater chemical status according to the Water Framework Directive (Directive 2000/60/EC). Furthermore, it is anticipated that the combination of a PRB with appropriately designed operational regime of the waterworks in Nowa Dęba may allow meeting the drinking water standards according to the Polish regulation (Dz.U.2010.72.466).

3. Permeable Reactive Barrier Technology

Permeable reactive barrier -PRB- is an *in situ* passive remediation technology which consists of placing a reactive cell perpendicular to the groundwater flow to intercept and treat the contaminant plume (ITRC, 2011). The contaminant removal occurs by physical, chemical or biological processes such as: oxidation, reduction, biodegradation, sorption and precipitation (Carey *et al*., 2002).

The technology has been studied since the early 1990s and to date a wide range of contaminants including but not limited to chlorinated solvents, BTEX, PAHs, heavy metals, nitrates, sulphates can be treated by this technology. PRB is a technology that has been evolving since its inception. New reactive materials have been tested to broaden the spectrum of contaminants that can be treated; the design has evolved from a single wall to treat a single contaminant to use combined media to either treat diverse contaminants by sequential walls, or to enhance the removal efficiency of a single material in PRB systems (Bone, 2012). The success of this technology, however, depends on the effectiveness of the reactive materials used and the hydraulic performance of the barrier, both of which can be investigated in the laboratory (batch and column studies) and in the field (ITRC, 2011).

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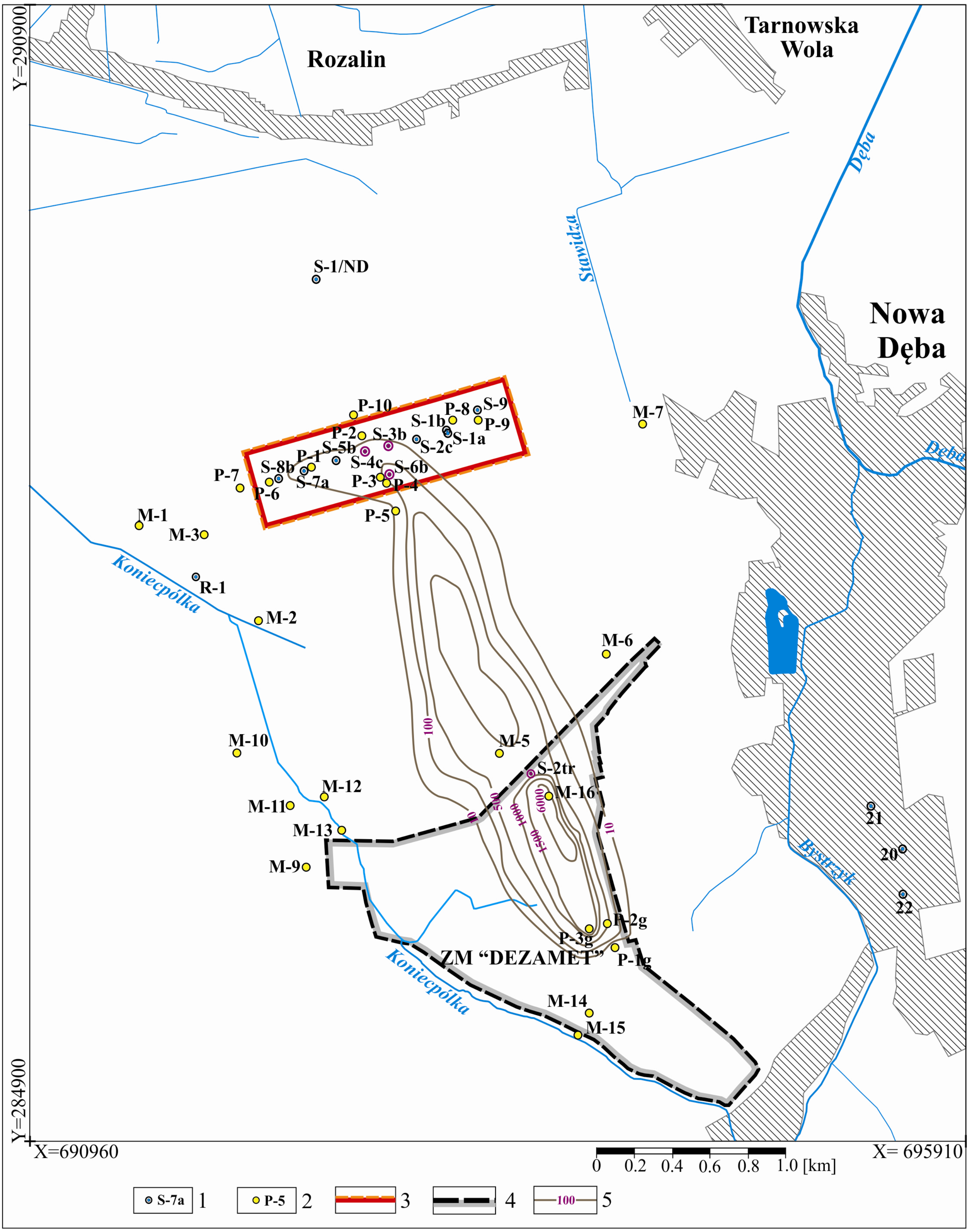

Figure 1: Map of the study site (1- wells; 2- piezometers; 3- waterworks; 4- metal works and suspected contaminant source; 5- TCE concentrations)

4. Reactive materials

Several different types of reactive media are available for use in PRBs. Activated carbon and zeolite are the most frequently used sorptive media in PRBs. Among a variety of reactive materials, zero valent iron (ZVI) has shown the greatest efficiency for reducing chlorinated compounds in groundwater (e.g. Baciocchi and Boni, 2003; Lai *et al.*, 2006; Dries *et al.*, 2002; Muegge, 2008). Although ZVI effectiveness to remove TCE is proven, its use has evidenced some problems that include the formation of mineral precipitates in the iron surface leading to the clogging of the barrier and consequently loss of reactivity and permeability (Gillham *et al.*, 2002; Henderson and Demond, 2007; Wilkin *et al.*, 2002).

To overcome some problems evidenced by the use of ZVI as a reactive material, there is an increasingly recognized use of organic substrates that promote the reductive dechlorination of chlorinated solvents (Henry *et al.*, 2003; Shen and Wilson, 2007; Seo and Bishop, 2008; Wei and Seo, 2010). These materials, generally include a bulk source of plant material (e.g. wood mulch) as a long-term carbon source, materials for enrichment or supplying nutrients (e.g. compost, sludge), and coarse sand or pea gravel to maintain permeability and to prevent compaction. Other local agricultural or industrial waste products that may be suitable as wall materials, include for example: cotton gin trash, mushroom compost, chitin (Henry *et al.*, 2008; ITRC, 2011). These materials can be readily obtained at low costs compared to other media used so far in PRBs.

For the present study low cost alternative materials were pre-selected to be tested as possible candidates for the PRB. These materials are: compost, brown coal, zeolite, diatomaceous earth and mulch.

5. Laboratory studies for the selection of reactive materials to treat TCE

Laboratory studies are essential to support the selection of the reactive material during the design process of a PRB. The test results can provide information on the material ability to remove the contaminant of interest and predict shortcomings in the operation of the barrier.

Laboratory studies include batch and column tests. Batch tests are limited to assess the best performing reactive material compared to others materials tested. Column tests provide more information on how the material is likely to perform in the field, however are still limited by the test constraints (e.g. scale).

For the present study, a series of batch tests were performed to pre-select the reactive materials to be placed in the barrier. Initially, four reactive materials and four materials combinations (i.e. compost, brown coal, zeolite, diatomaceous earth, compost + brown coal, compost + mulch, compost + zeolite, diatomaceous earth + mulch) were evaluated. ZVI was used as a 'control' for its proven ability to effectively remove TCE (i.e. the ability of the tested materials to remove TCE was compared to that of ZVI).

Results from the tests show that the four selected reactive materials exhibited removal efficiencies higher of that of ZVI (80%); brown coal, however, was the reactive material which presented the highest removal efficiency (97%) followed by zeolite (87%), compost (86%) and diatomaceous earth (82%). Regarding the combination of reactive materials, the four evaluated mixtures (1:1 solid to solid ratio) exhibited significantly lower removal efficiency than that of the materials when evaluated individually (Fig. 2).

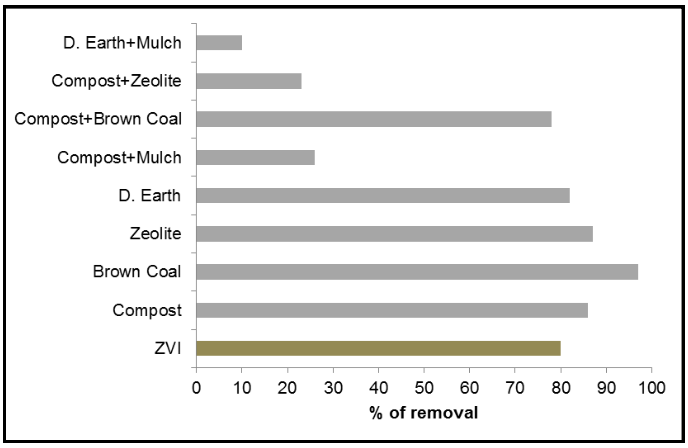

Figure 2: Sustainability assessment framing

The TCE removal efficiency for compost-brown coal mixture (1:1) was of 78%, while the other combinations showed removal efficiencies lower than 50%. These results were opposite to the expected increase of the removal efficiency due to synergic effects of materials combinations. Mulch and compost mixture has shown to be effective for treating chlorinated solvents (Öztürk *et al.*, 2012; Henry *et al.*, 2003) and in some cases its performance better than that of the ZVI-wall (AFCEE, 2008). Likewise, the addition of diatomaceous earth (i.e. generated from the distillery brewery industries) to mulch was expected to exhibit similar results of that of compost-mulch mixture (i.e. a readily degradable source of organic carbon and nitrogen was combined with a long term carbon source).

Further tests included the selection of an appropriate solid to solid ratio for the combinations, batch leaching test to assess the potential impact of the reactive materials on the groundwater environment and finally a test to evaluate the various mechanisms by which the contaminants are removed. The results from these tests however are not included in this document.

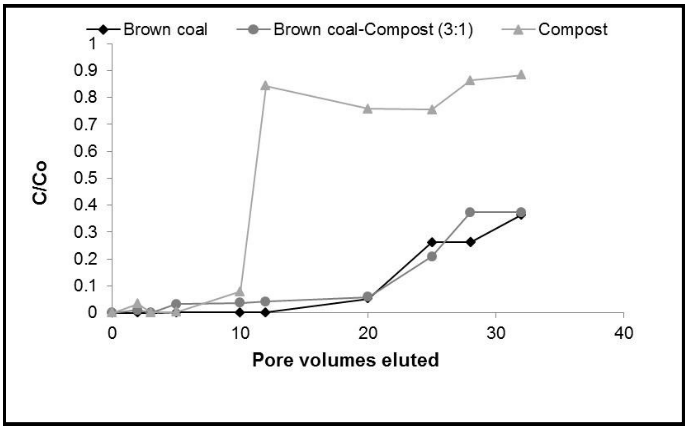

Figure 3: TCE Breakthrough curves for brown coal, compost and brown coal-compost

Following the batch tests two materials were selected for column testing—these are compost, brown coal and brown coal + compost (3:1). A comparison of the breakthrough curves of the materials (Fig. 3) shows that brown coal is the most efficient in removing TCE followed by brown coal-compost (3:1). The ability of compost to retain TCE was exhausted early after only 5 pore volumes.

Additionally, tracer tests and permeability tests were performed to derive the physical properties and transport parameters of the materials. From these tests it is worth mentioning the retardation factor. A retardation factor of 12 was obtained for compost and of 32 for the case of brown coal and the mixture brown coal-compost (3:1). These values indicate that sorption of TCE to the materials plays a major role in the contaminant removal.

The laboratory studies have shown that both compost and brown coal are successful in remediating TCE. The combination of compost and brown coal is promising but further tests have to be performed with different solid to solid ratios to derive the best performing conditions.

This research is in close cooperation with the research of the ADVOCATE fellow Franklin Obiri-Nyarko who is evaluating PRB technology for the treatment of heavy metals by the same approach described in this document (see ADVOCATE Bulletin AB2). The compilation of the results from both research projects will allow the design of a single PRB to treat TCE and heavy metals.

6. Acknowledgements

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7. References

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