F Gomez Universidad Politecnica de Valencia, Spain
R Gomez Martin University of Granada, Spain
D Goulias University of Maryland, USA
K G Goulias Pennsylvania State University, USA
F Grandori Politecnico di Milano, Italy
W E Grant Texas A & M University, USA
S Grilli University of Rhode Island, USA
R H J Grimshaw Loughborough University, UK
D Gross Technische Hochschule Darmstadt, Germany
R Grundmann Technische Universitat Dresden, Germany
A Gualtierotti IDHEAP, Switzerland
O T Gudme stad University of Stavanger, Norway
R C Gupta National University of Singapore, Singapore
J M Hale University of Newcastle, UK
K Hameyer Katholieke Universiteit Leuven, Belgium
C Hanke Danish Technical University, Denmark
K Hayami University of Toyko, Japan
Y Hayashi Nagoya University, Japan
L Haydock Newage International Limited, UK
A H Hendrickx Free University of Brussels, Belgium
C Herman John Hopkins University, USA
I Hideaki Nagoya University, Japan
D A Hills University of Oxford, UK
W F Huebner Southwest Research Institute, USA
J A C Humphrey Bucknell University, USA
M Y Hussaini Florida State University, USA
W Hutchinson Edith Cowan University, Australia
T H Hyde University of Nottingham, UK
M Iguchi Science University of Tokyo, Japan
D B Ingham University of Leeds, UK
L Int Panis VITO Expertisecentrum IMS, Belgium
N Ishikawa National Defence Academy, Japan
J Jaafar UiTm, Malaysia
W Jager Technical University of Dresden, Germany
Y Jaluria Rutgers University, USA
C M Jefferson University of the West of England, UK
M K Jha Morgan State University, USA
P R Johnston Griffith University, Australia
D R H Jones University of Cambridge, UK
N Jones University of Liverpool, UK
N Jovanovic CSIR, South Africa
D Kaliampakos National Technical University of Athens, Greece
N Kamiya Nagoya University, Japan
D L Karabalis University of Patras, Greece
A Karageorghis University of Cyprus
M Karlsson Linkoping University, Sweden
T Katayama Doshisha University, Japan
K L. Katsifarakis Aristotle University of Thessaloniki, Greece
J T Katsikadelis National Technical University of Athens, Greece
E Kausel Massachusetts Institute of Technology, USA
H Kawashima The University of Tokyo, Japan
B A Kazimie Washington State University, USA
S Kim University of Wisconsin-Madison, USA
D Kirkland Nicholas Grimshaw & Partners Ltd, UK
E Kita Nagoya University, Japan
A S Kobayashi University of Washington, USA
T Kobayashi University of Tokyo, Japan
D Koga Saga University, Japan
S Kotake University of Tokyo, Japan
A N Kounadis National Technical University of Athens, Greece
W B Kratzig Ruhr Universitat Bochum, Germany
T Krauthammer Penn State University, USA
C-H Lai University of Greenwich, UK
M Langseth Norwegian University of Science and Technology, Norway
B S Larsen Technical University of Denmark, Denmark
F Lattarulo Politecnico di Bari, Italy
A Lebedev Moscow State University, Russia
L J Leon University of Montreal, Canada
D Lesnic University of Leeds, UK
D Lewis Mississippi State University, USA
S lghobashi University of California Irvine, USA
Water Pollution XI

Editor

C.A. Brebbia
Wessex Institute of Technology, UK
Preface

This Volume contains most of the papers presented at the 11th International Conference on Modelling, Monitoring and Management of Water Pollution, held in the New Forest Campus of the Wessex Institute of Technology. The Meeting was sponsored by the WIT Transactions on Ecology and the Environment and the International Journal of Sustainable Development and Planning and the International Journal of Computational Methods and Experimental Measurements.

The Meeting has always been very successful and provides a friendly forum for the discussion and exchange of information between scientists, managers and academics from different areas of water contamination.

The Water Pollution Conference started in Southampton in 1991 and has been held in Milan, Italy, in 1993; Porto Carras, Greece, in 1995; Lake Bled, Slovenia, in 1997; Lemnos, Greece, in 1999; Rhodes, Greece, in 2001; Cadiz, Spain, in 2003; Bologna, Italy, in 2006; Alicante, Spain, in 2008; and Bucharest, Romania, in 2010.

Water Pollution problems are essentially multidisciplinary and require specialists from different areas to work together on a wide variety of issues. The Conference created an international arena for the discussion and dissemination of work related to water quality and environmental problems caused by the increase of pollution loads and the inappropriate management of water resources.

This book contains a series of important contributions, grouped together in the following sections:

- Water Quality
- Lakes and Rivers
- Groundwater and Aquifer Issues
- Pollution and Oil Spills
The Editor is grateful to all members of the International Scientific Advisory Committee and other colleagues who helped to review the contributions included in this book. He is also indebted to all authors for their excellent papers.

The success of the Meeting will ensure that the Conference is reconvened in 2014.

The Editor
The New Forest, 2012

Note: All papers presented at prior Water Pollution Conferences since 1993 are archived in the Institute’s eLibrary (http://library.witpress.com). WIT Conferences are listed on the Institute’s website at www.wessex.ac.uk/conferences
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Remediation of groundwater polluted by gasoline-derived compounds with biobarriers

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Abstract

Biobarriers (BBs) are a new type of in situ technology for the remediation of contaminated groundwater.

In this work results of laboratory experiments on a BB system are discussed. First, a proper filling material for BB applications was selected among four possible granular materials (perlite, pumice, expanded clay, activated carbon), based on the physical-chemical properties affecting the BB performance and the bacterial adhesion capacity. Based on the results, pumice was selected as the filling material for the second part of the work, during which a laboratory column test was carried out without inoculation. Physical-chemical parameters (temperature, dissolved oxygen concentration, pH and specific electric conductivity) and pollutant concentrations (BTEX, MTBE, tert-butyl alcohol, 1,2,4-trimethylbenzene, naphthalene) were measured in water samples collected from eight piezometers uniformly distributed along the column length. Molecular microbiological analyses were also carried out on pumice before and after the treatment to assess the differences in the bacterial community.

Different decreasing trends in the pollutant concentration along the column were observed for the different groups of contaminants that found explanation in the distribution of the different microbial populations throughout the column.

Keywords: groundwater remediation, biobarrier, monoaromatic solvents, methyl tert-butyl ether, gasoline-derived compounds.
1 Introduction

Permeable Reactive Barriers (PRBs) are an in situ remediation technology for groundwater based on the replacement of part of the aquifer with reactive materials that intercept and treat dissolved plumes of contaminants. Based on the selected filling material and the removal mechanism, different organic or inorganic pollutants can be treated (e.g., chlorinated solvents, petroleum hydrocarbons, heavy metals, etc.) [1, 2].

Biobarriers (BBs) are an innovative type of PRBs based on the biodegradation of organic pollutants. BBs can overcame problems related to the traditional biostimulation or bioaugmentation treatments (soil heterogeneity, poor hydraulic conductivity or biomass distribution). However, a critical issue is the selection of a proper filling material to ensure high hydraulic conductivity, long-term chemical-physical and structural stability, good biomass adhesion properties, environmental compatibility and cheapness. The BB efficiency strictly depends on the configuration and the location of the barrier, the residence time of the contaminated water within the reactive zone and the maintenance of proper conditions for the biomass [3].

In this work, laboratory experiments on a BB system to treat groundwater contaminated with gasoline-derived pollutants are presented.

2 Materials and methods

2.1 Filling material

Four filling materials were tested based on their physical-chemical properties affecting BB performances and the existing literature [4, 5]: activated carbon (PK 3-5 – NORIT), perlite (PEROIL T – Perlite Italiana), volcanic pumice (Euroterriflora) and expanded clay (Termolite-Laterite). Grain size distribution (ISO 11277:2009), porosity [6], bulk density (ISO 11272:1998), hydraulic conductivity (ISO 17312:2005) and organic carbon content (UNI EN 15169:2007) were measured for all materials.

The capacity of some selected materials of being colonized was tested by using two bacteria strains: Pseudomonas sp. CXP452 and Rhodococcus sp. E252. The inoculum (50 ml, 0.1 optical density at 540 nm) was added to 15 g d.w. of material and left for 24 h at 30°C. The amount of bacteria sorbed on the materials were quantified by dilution and plating on rich agar medium.

2.2 Column test

A column test was carried out in a Teflon-coated basin (250 cm long, 10 cm wide) filled with 15 cm of pumice. The lowest 10 cm were saturated with water and involved in water flow during the test. Above the pumice layer, 10 cm of activated carbon (Norit GF 40) were placed to avoid vapor emissions. Eight piezometers (“A” to “H”) were uniformly distributed along the column, with the last one 240 cm far from the beginning of the column. Figure 1 shows the scheme of the column test and some set up steps.
Tap water was artificially contaminated with commercial gasoline and used as the inflow solution; fresh free gasoline was maintained over the water level in the input tank to keep the pollutant dissolved concentrations constant over time. Benzene, toluene, ethylbenzene and xlenes (BTEXS), methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), tert-butyl alcohol (TBA), 1,2,4-trimethylbenzene and naphthalene were quantified under steady state conditions; Table 1 summarizes the average concentrations in the input solution.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration (mg/l)</th>
<th>Compound</th>
<th>Concentration (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTBE</td>
<td>96 ± 19</td>
<td>TBA</td>
<td>7.9 ± 6.7</td>
</tr>
<tr>
<td>Toluene</td>
<td>78 ± 19</td>
<td>Ethylbenzene</td>
<td>3.5 ± 0.9</td>
</tr>
<tr>
<td>Benzene</td>
<td>18.2 ± 3.7</td>
<td>1,2,4-Trimethylbenzene</td>
<td>0.9 ± 0.5</td>
</tr>
<tr>
<td>m+p-Xylenes</td>
<td>11.6 ± 4.8</td>
<td>ETBE</td>
<td>0.07 ± 0.02</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>7.9 ± 2.9</td>
<td>Naphthalene</td>
<td>0.05 ± 0.02</td>
</tr>
</tbody>
</table>

Before starting the test, a commercial oxygen-release compound (EHC-O, Adventus, 0.3% on dry weight basis of pumice) was uniformly distributed throughout the saturated layer of pumice to ensure aerobic conditions. Nitrogen (27.7 g of NH₄NO₃) and phosphorous (2.1 g of H₂KPO₄ and 2.7 g of HK₂PO₄) were also added.

The average flow rate and the duration of column test were 3 l/d and 43 days respectively, based on typical pollutant velocity in gravel aquifers.

Water samples were collected from all piezometers twice a week. Samples were analyzed to measure the pollutant concentrations, temperature, the pH value...
(electronic pH-meter XS pH 6, Oakton), the dissolved oxygen – DO (OXI 340i probe, WTW) and the specific electric conductivity – SEC (LM 8, EH Conducta). The pollutants in the water samples were extracted by solid-phase microextraction and quantified in GS-MS (UNICHIM 1210:1997).

At the end of the test, some samples of activated carbon were collected and analyzed (C2S extraction and GS-MS analysis, ISO 16200-1:2001) to evaluate the pollutant loss due to volatilization.

Pumice samples were also collected before and at the end of the test and analyzed by denaturing gradient gel electrophoresis (DGGE) to assess the microbial communities attached to the filling material. Samples were kept at -20°C until DNA extraction from 0.5 g of pumice using a commercial soil kit FastDNA® Spin (BIO 101 Inc., Vista, CA). The V3-V5 hypervariable regions of the 16S rRNA gene were amplified in DGGE analysis through 357F primer using a 40 pb GC-clamp and 907R primer [7]. For each sample, two PCR were carried out in 75 µl reaction volume by using the GoTaq® Green Master Mix (Promega Corporation, Madison, WI) and 1.30 µM of each primer. Reaction conditions were those described in Sass et al. [7]. DGGE was carried out in a D-Code System (Bio-Rad Laboratories, Hercules, CA, USA) using a 16x16 cm gel containing 7% of acrylamide:bis-acrylamide (37.5:1) and 2% of glycerol and a denaturing gradient between 40 and 55%. Electrophoresis was carried out for 5 h at 60°C using a 200 V constant voltage. Gels were marked with ethidium bromide and analyzed. Selected bands were excised, purified according to the protocol described in Sambrook and Russell [8] and sequenced at the end of electrophoresis run. The Ribosomal Database Project (RDP) classifier was used for the taxonomic assignment of the sequenced bands [9]. The Quantity One software (Bio-Rad Laboratories, Hercules, CA) was used for identification and calculation of band intensity. The dissimilarity “Bray-Curtis” index was calculated based on the relative intensity of each band using the EsimatesS software [10]. The software Statistica™ was used for cluster analyses by the single linkage method.

3 Results

3.1 Filling material

Figure 2 shows the particle size distribution of the tested materials. Due to excessive particle size dispersion, pumice was sieved to select the particle size range 6-10 mm. Table 2 summarizes the other physical-chemical properties. Activated carbon, pumice and expanded clay exhibited a high hydraulic conductivity. Perlite was unsuitable for BB applications due to the weak mechanical behavior exhibited during the tests.

Figure 3 shows the percentage of bacteria sorbed on the materials at the end of the attachment test compared to the amount of bacteria in the initial inoculum. About 60% of Pseudomonas sp. CXP45 and more than 70% of Rhodococcus sp. CXP45 were retained on pumice. On the contrary, activated carbon and expanded clay did not exhibit significant attachment properties towards the
Table 2: Physical-chemical properties of the tested materials (n = number of replicates).

<table>
<thead>
<tr>
<th></th>
<th>Activated carbon</th>
<th>Perlite (6-10 mm)</th>
<th>Pumice (6-10 mm)</th>
<th>Expanded clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity (-)</td>
<td>0.67 ± 0.02 (n = 5)</td>
<td>0.55 ± 0.08 (n = 10)</td>
<td>0.62 ± 0.01 (n = 5)</td>
<td>0.47 ± 0.01 (n = 5)</td>
</tr>
<tr>
<td>Bulk density (kg d.w./m^3)</td>
<td>248 ± 8 (n = 5)</td>
<td>106 ± 7 (n = 10)</td>
<td>338 ± 22 (n = 5)</td>
<td>337 ± 22 (n = 5)</td>
</tr>
<tr>
<td>Hydraulic conductivity (m/s)</td>
<td>4.4 · 10^{-4} ± 1.2 · 10^{-4} (n = 6)</td>
<td>6.3 · 10^{-4} ± 0.5 · 10^{-4} (n = 8)</td>
<td>5.2 · 10^{-4} ± 1.3 · 10^{-4} (n = 4)</td>
<td>4.1 · 10^{-4} ± 0.7 · 10^{-4} (n = 4)</td>
</tr>
<tr>
<td>Organic carbon content (% g C /g d.w.)</td>
<td>-</td>
<td>0.34 ± 0.02 (n = 4)</td>
<td>2.11 ± 0.06 (n = 4)</td>
<td>0.05 ± 0.01 (n = 4)</td>
</tr>
</tbody>
</table>

Figure 2: Particle size distribution of the tested materials.

Figure 3: Bacterial adhesion on the support materials.
inoculated biomass. Based on these results, pumice was selected as the filling material for the column test.

3.2 Column test

From day 1 to 10 of the test, the pH value increased along the column length up to a maximum value of 9.4 in the piezometer H; during the remaining part of the test, pH values of about 7.5-8.0 were measured throughout the entire column length. A similar trend was observed for SEC, with values up to 2000 μS/cm in the last piezometer within ten days of test and a constant value of 750 μS/cm in the following period in all the piezometers. The DO confirmed aerobic conditions along the column for the entire duration of the test (5.7 ± 0.5 mg/l). The trend of the physical-chemical parameters measured in the water samples was related to the oxygen-releasing compound added before starting the test.

Table 3 reports the theoretical pollutant retardation factor and velocity in the column test [11, 12]. The pollutant average residence times were between 5 and 70 days; steady state conditions were reached during the experiment duration for all contaminants but 1,2,4-trimethylbenzene and naphthalene.

Table 3: Retardation factor and pollutant velocity in the column test.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Retardation Factor (-)</th>
<th>Pollutant velocity (cm/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTBE</td>
<td>1.1</td>
<td>46</td>
</tr>
<tr>
<td>TBA</td>
<td>1.5</td>
<td>35</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>1.6</td>
<td>32</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.8</td>
<td>29</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.9</td>
<td>28</td>
</tr>
<tr>
<td>ETBE</td>
<td>2.7</td>
<td>19</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>4.6</td>
<td>11</td>
</tr>
<tr>
<td>m+p-Xylenes</td>
<td>5.3</td>
<td>9.6</td>
</tr>
<tr>
<td>1,2,4-Trimethylbenzene</td>
<td>11.6</td>
<td>4.4</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>15.5</td>
<td>3.3</td>
</tr>
</tbody>
</table>

MTBE and toluene concentrations over time in the piezometers C and H (93.6 and 240 cm far from the column inlet) are shown in Figure 4. Figure 5 shows the average concentration of these compounds under steady state conditions in the piezometers along the column. The removal efficiency (referred to the average concentration measured in the input solution) in the piezometers C and H were 42% and 72% for MTBE, and 78% and 97% for toluene. MTBE removal was proportional to the distance travelled in the column up to the piezometer C; MTBE concentration was nearly constant between C and F and decreased in G and H. The removal rate of toluene was very high in the first part of the column, while it significantly decreased toward the end of the column. ETBE trend was similar to MTBE, with decreasing concentrations up to C and constant values in the remaining part of the column. The concentrations of BEX, 1,2,4-trimethylbenzene and naphthalene had trends similar to toluene. The
Figure 4: Concentrations over time of MTBE (a) and toluene (b) in the inflowing water and in water collected from piezometers C and H.

Figure 5: Average concentrations of MTBE (a) and toluene (b) under steady state conditions in water collected from the piezometers.

concentration of TBA was very variable over time in all piezometers, but also in the input solution; this behavior was ascribed to microbial activity on MTBE in the input tank, with the production of TBA as a catabolic intermediate.
Table 4 reports the percentage of pollutants captured in the activated carbon above the pumice referred to the mass entered the column during the test. In general volatilization was not significant, though for BTE and MTBE ranged between 11% and 16%.

Table 4: Percentage of pollutants in the activated carbon.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Pollutant loss due to volatilization (% w./w.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>16</td>
</tr>
<tr>
<td>MTBE</td>
<td>13</td>
</tr>
<tr>
<td>Toluene</td>
<td>11</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>11</td>
</tr>
<tr>
<td>m+p-Xylene</td>
<td>2.9</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>1.7</td>
</tr>
<tr>
<td>1,2,4-Trimethylbenzene</td>
<td>-</td>
</tr>
<tr>
<td>ETBE</td>
<td>-</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>-</td>
</tr>
<tr>
<td>TBA</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 6: DGGE gel of pumice samples before (PUM) and after the column test at different locations (piezometers from A to H).

Figure 6 shows the DGGE gel of the pumice samples collected before (PUM) and after the column test at different locations (piezometers from A to H). Two bands were detected in PUM, whereas 6 to 11 bands were identified at the end of the treatment. Bands 1 to 4 and 7 were related to bacterial populations located in the first part of the column, whereas bands 8 and 9 to those in the second part of the column. Bacterial populations of bands 5 and 6 were detected in all samples.
The population of band 2 was classified as *Comamonas* (Table 5). Microrganisms belonging to *Comamonas* genus have been reported to be able to degrade BTEX under aerobic conditions [13]. The population of band 6 was classified as *Hydrogenophaga*, whose *Hydrogenophaga flava ENV735* is able to degrade MTBE as pure culture [14]. Band 8 was related to *Thauera*, whose *Thauera Aromatica k172* is able to degrade aromatic hydrocarbons under both denitrifying and aerobic conditions [15].

Table 5: Taxonomic classification (family and gender) of microorganisms in the bands (confidence level in brackets).

<table>
<thead>
<tr>
<th>Band</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Xanthomonadaceae [60%], Silanimonas [23%]</td>
</tr>
<tr>
<td>2</td>
<td>Comamonadaceae [100%], Comamonas [99%]</td>
</tr>
<tr>
<td>3</td>
<td>Xanthomonadaceae [100%], Thermomonas [100%]</td>
</tr>
<tr>
<td>4</td>
<td>Comamonadaceae [100%], Acidovorax [99%]</td>
</tr>
<tr>
<td>5</td>
<td>Comamonadaceae [99%], Acidovorax [49%]</td>
</tr>
<tr>
<td>6</td>
<td>Comamonadaceae [100%], Hydrogenophaga [100%]</td>
</tr>
<tr>
<td>7</td>
<td>Xanthomonadaceae [100%], Luteimonas [92%]</td>
</tr>
<tr>
<td>8</td>
<td>Rhodocyclaceae [100%], Thauera [100%]</td>
</tr>
<tr>
<td>9</td>
<td>Rhodocyclaceae [37%], Azovibrio [9%]</td>
</tr>
</tbody>
</table>

Figure 7: Cluster analysis based on DGGE results.

Figure 7 shows the dendrogram resulting from the cluster analysis. Bacterial communities after treatment differed from those detected in pumice before the treatment. Moreover, two different clusters along the column could be identified, the first one grouping samples from A to C and the second one those from D to H.
4 Conclusions

With the exception of perlite, which was excluded due to its weak mechanical behavior, the tested materials had proper physical-chemical properties for BB treatments. Pumice in the particle size range 6-10 mm had the best attachment capacity of biomass and was selected as the filling material for the column test.

During the column test, DO concentrations ensured aerobic conditions throughout the column for the entire duration of the test. The pollutant removal efficiency at the end of the column was about 70% for MTBE and ETBE, 90% for benzene and xylenes and more than 97% for toluene and ethylbenzene; volatilization had a minor effect. The microbial analyses carried out on pumice samples collected at the end of the test pointed out two different clusters in microbial populations, which explained the different pollutant behaviors along the column.

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References


