The ADVOCATE Project

ADVOCATE MARIE CURIE ACTIONS

Newsletter no.4: June 2014

The ADVOCATE Project

The June 2014 newsletter introduces the Fellows involved in delivering Work Package 4 and 5 of the Advocate Project. Their work is focused on developing in situ treatment strategies for heavy metals and mixed contaminants. This issue presents the latest results of their research.

Franklin Obiri-Nyarko's project is titled as: 'Evaluating reactive materials for permeable barriers to remediate groundwater contaminated with BTEX and heavy metals'. His research is assessing the most effective reactive materials for Permeable Reactive Barriers (PRBs) used in the remediation of groundwater contaminated with a mixture of BTEX and heavy metals. These reactive materials are now used in a pilot field-scale experiment designing PRB treatment in Tomaszów Mazowiecki, Poland.

The project **Oksana Voloshchenko** is working on investigates the transformation of ammonium within constructed wetlands (CWs). Through studying the changes of nitrogen forms, Oksana's research focuses on understanding chemical mechanisms for the removal of complex pollutants in wetland systems, and the role of aerobic and anaerobic zones within the root section of plants present. Field-scale studies have been constructed and developed at Leuna, Germany.

Johana Grajales is undertaking research titled "Identify the most effective strategy for in-situ sustainable remediation of groundwater contaminated with chlorinated solvents using Permeable Reactive Barriers (PRB)". Johana's research is directly linked to Franklin's, performing laboratory studies in order to select the most effective reactive material for the design of PRBs for chlorinated solvent treatment. This design is then installed within a pilot field-scale PRB, while modelling tools are used to validate conceptual models of contaminant migration and to evaluate the in situ performance of the PRB system.

The Advocate team invites all interested parties to the upcoming 'In Situ Remediation '14' conference and workshop in London, organised and supported by the Advocate network. For further details and registration please visit our conference website at:

www.theadvocateproject.eu/conference/main.html

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Franklin Obiri-Nyarko (Hydrogeotechnika, Poland)

Franklin graduated with a BSc in Agriculture (Soil Science major) from the University of Ghana and an MSc in Geosciences (Environmental Geology and Geohazards) from the University of Oslo. Prior to his graduate studies, he worked as a teaching and research assistant at the Department of Soil Science, University of Ghana where he assisted academic staff in their duties.

Franklin has always desired a professional career in academia, and the ADVOCATE Project gave him an excellent chance in 2011, when he joined the team. He is doing his PhD at Hydrogeotechnika Sp. Z o.o in Poland in Work Package 5, together with Johana Grajales and Oksana Voloshchenko.

Introduction

The objective of Franklin's research is to assess reactive materials for permeable reactive barriers (PRBs) to remediate groundwater contaminated with a mixture of BTEX and heavy metals. A PRB is an in-situ remediation technology that may offer a cost-effective alternative to other groundwater treatment methods (such as pump and treat). PRBs involve the emplacement of a reactive medium in the subsurface to intercept the contaminant plume, and to transform the contaminant(s) into environmentally acceptable forms (Figure 1). A key component of the PRB system is the reactive media used to remove or treat the contaminants. Zero valent iron (ZVI) is the most commonly used PRB material. Contaminants such as heavy metals are easily removed by ZVI via mechanisms such as (co)precipitation and/or reduction, but others such as BTEX are not easily degraded. Various other reactive materials have also been tested in PRBs, but they are expensive, inaccessible or ineffective in removing both groups of contaminants within a mixture.

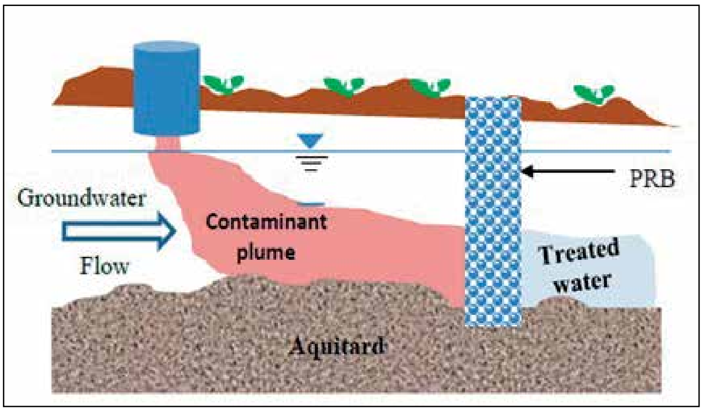


Fig 1 A schematic diagram of a PRB

Laboratory studies

Laboratory batch and column studies were conducted to evaluate a number of low-cost materials, which included ZVI (as control), compost, brown coal, diatomaceous earth, zeolite, mulch and combinations of these materials. The evaluation and selection of the most appropriate reactive media is based on a number of factors, such as biological and chemical reactivity, permeability, environmental compatibility, physical stability, availability and cost. During the experiments, attention was given primarily to Pb and benzene because of their following properties (in combination): ubiquity, mobility in groundwater and toxicity effects on humans and other aquatic life. Laboratory batch tests were first conducted to screen the materials based on their removal efficiency and environmental compatibility. Column studies were subsequently performed to evaluate the selected materials under dynamic conditions. Breakthrough curves (BTCs) were generated to evaluate the performance of the column materials.

Latest results

The BTCs were generated for both Pb and benzene by plotting their normalized concentrations (C/Co) against the pore volumes (PV) of fluid eluted through the barrier material. A comparison of the BTCs of the different materials (Figure 2) shows that the brown coal-compost mixture in a ratio of 3:1 is the most effective in retarding Pb. In fact, the experimental period was too short for Pb breakthrough to be observed. In the case of benzene, the experiments were performed until the elution of 30 PV. A comparison of the BTCs of the different materials (Figure 3) also shows that brown coal-compost (5:1) is the most effective for benzene removal, as breakthrough only occurred after eluting 20 PV. The difference in the performance of the materials may be ascribed to the mechanisms used in removing the studied contaminants. The estimated retardation factors (R_f) and distribution coefficients (Kd), describing the extent of sorption of the chemicals, are presented in Table 1. Currently, geochemical modelling is being performed to help interpret the results from the column experiments.

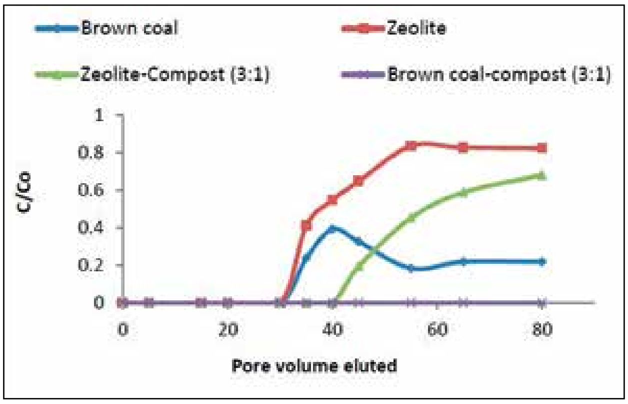


Fig 2 Pb BTCs for the studied materials

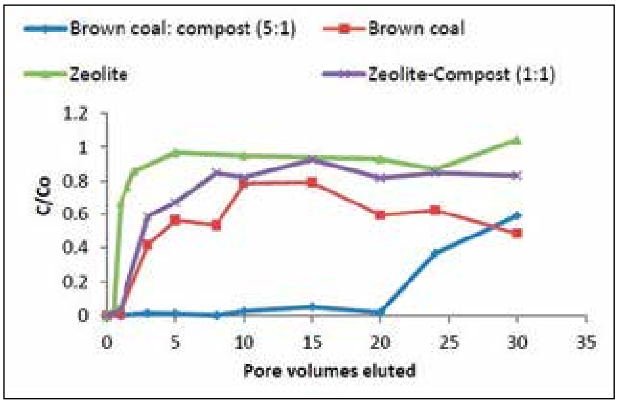


Fig 3 Benzene BTCs for the studied materials

Table1. The retardation factors (Rf) and distribution coefficients (Kd)

Contaminant	Materials	Ratio	Rf (-)	Kd (mL/g)
Lead				
	Brown coal		>80	>19.6
	Brown coal-Compost	3:1	>80	>17.17
	Zeolite		36	9.44
	Zeolite-compost	3:1	56	15.02
Benzene				
	Brown coal		5	1.00
	Brown coal-Compost	5:1	26	6.20
	Zeolite		1.6	0.16
	Zeolite-compost	1:1	3	

The next phase

The next phase of the research involves evaluation of the selected materials in a pilot field-scale experiment. The Tuczepy site in SE Poland has been selected to host this experiment. The site is located on a shallow unconfined Quaternary aquifer. Field investigations were conducted to evaluate the hydrogeological, geochemical, and geotechnical conditions of the site, and to determine the most suitable location for the pilot field-scale PRB installation. The evaluation indicated that the site conditions are favourable for PRB installation at a zone of preferential groundwater flow for interception of the contaminants by the PRB.

Oksana Voloshchenko (UFZ, Germany)

Oksana graduated with an MSc in Biochemistry from Dnipropetrovs'k National University by Oles' Gonchar, Ukraine. During her studies she also trained in the Department of Enzyme Chemistry and Biochemistry at the Palladin Institute of Biochemistry of the NAS in Ukraine. Her diploma thesis focused on "Nanoliposomes preparation with surface lipids of plants". She subsequently worked as a teacher of human anatomy in Dnipropetrovs'k State Medical academy, Ukraine, for two years.

In 2011, she joined the ADVOCATE team, pursuing her PhD in “Microbial nitrogen transformation in horizontal subsurface flow constructed wetlands for the treatment of contaminated groundwater” and has spent the past three years working within Work Package 5 on developing in *situ* treatment strategies for mixed contaminants.

Introduction

The main goal of Work Package 5 is developing *in situ* treatment strategies for mixed contaminants. Oksana’s research focuses on ammonium (NH_4^+), a major pollutant in groundwater. Ammonium, due to its toxicity to fish and because it causes eutrophication of lakes and wetlands, is a serious environmental problem. The Council of the European Union set a recommended level of 0.05 mg/L and a maximum level of 0.5 mg/L of NH_4^+.

Fig. 1: Megasite Leuna

Oksana is investigating how this compound is removed by constructed wetlands (CWs). CWs are widely used in wastewater and groundwater treatment due to their low energy requirements and easy operation. Due to the mosaic of aerobic and anaerobic zones within the root zone of the plants, contaminants in CWs can be eliminated by a various aerobic and anaerobic processes..

However, the quantification of these processes can be difficult due to the complexity of the wetland systems. Some of the pathways for NH_4^+ removal are total nitrification with further denitrification and partial nitrification coupled with anaerobic ammonium oxidation (ANAMMOX). The importance of ANAMMOX in the N-cycle in CWs is still unclear, as well as the correlation of this process with other N-transformations. Therefore, the aim of this work is to study the role of the ANAMMOX process in man-made wetland ecosystems to obtain a more complete picture of the ongoing processes as part of the N-cycle.

Fig.2: The pilot scale plant in Leuna (courtesy of M. Kaestner)

Technology description

The pilot-scale plant is located in Leuna, Germany, and operated from 2007 to 2013 (Fig. 1). As Leuna has been a location for chemical industry since the beginning of the last century, a range of contaminants has been released into groundwater through accidental spills, improper handling, and damage from heavy bombing during World War II. Consequently, the contamination is complex, and the main pollutants are petroleum hydrocarbons (BTEX), methyl tert-butyl ether (MTBE), and NH_4^+.

Whilst various types of CWs are present in Leuna (Fig. 2), the following types of CWs were chosen for the investigations: (i) planted horizontal subsurface flow constructed wetland (HSSF)-CW[(1)], (ii) unplanted HSSF CW, and, (iii) floating plant root mat (FPRM). The HSSF CW was planted with common reed (*Phragmites australis*) and filled with gravel. A floating plant root mat was only supported by the densely woven root bed and was operated at a water depth of 30 cm. Inflow water was supplied from a nearby groundwater well. The hydraulic loading rate was fixed to 7 L h^{-1}. During the period of investigation, the concentration of the groundwater contaminant was ca. 19 mg NH_4^+-N L^{-1}. Sampling was done from June 2012-June 2013 at biweekly intervals except for the winter season, when contaminant removal was negligible. Samples were taken from inflow, outflow and along the flow path at different distances from the inlet and depths.

The samples were analysed for pH, temperature, redox potential, inorganic ions (NH_4^+, NO_2^-, NO_3^-), dissolved gases (N_2O, CH_4), organic compounds (MTBE, BTEX), stable isotope ($^{15}N/^{14}N$ and $^{18}O/^{16}O$) composition of NH_4^+ and NO_3^- and microbiological determinands, which included DNA extraction, DNA cloning, sequencing, PCR, Q-PCR, pyrosequencing, fluorescence in-situ hybridization (FISH), and confocal laser scanning microscopy

Latest results

Throughout the sampling period, the CWs have shown stable removal efficiencies for ammonium (Fig. 3, 4, 5). Planted HSSF CW averaged 77% removal, unplanted HSSF CW 41% and FPRM 62%. There was a strong seasonal dependency especially for the planted HSSF CW, with maximum removal in summer (100 %) and minimum in spring (68 %). The loads of the planted HSSF CW decreased most significantly at 20 cm depth, which can be explained by the high root density in this zone. Likewise, at 40 cm, below root depth, there was the smallest difference between inflow and loads. Considering that there were no seasonal and depth tendencies in unplanted HSSF CW, we assume that the partial decrease in load in this system results from microbial assimilation.

To examine the microbiological structure of biofilms in CWs, the planted HSSF CW was chosen as it has shown the best results for NH_4^+ removal efficiency. DNA was extracted from the biofilms attached to roots and gravel for molecular analysis of total bacteria, ANAMMOX and ammonia oxidizers. The highest number of total bacteria was found at 20 cm depth, as well as anaerobic NH_4^+ and aerobic ammonia oxidizers (Fig. 6). These results agree well with the pattern of NH_4^+ removal, where the highest removal efficiency was also achieved at 20 cm. The data prove that roots of plants with rhizospheres are necessary for efficient growth of aerobic as well as anaerobic bacteria and thus, the occurrence of both NH_4^+ removal pathways.

Conclusion

Constructed wetlands overall show a good performance for bioremediation of NH_4^+-contaminated groundwater. In summer, 100 % of NH_4^+ removal was reached. However, the removal efficiency is strongly seasonal, which has to be considered in the up-scaling of these systems to full scale contaminated groundwater treatment. Also, understanding the biological and chemical processes occurring within the system is necessary for further technological improvement, as various factors influence processes in the nitrogen cycle. The present work connects removal efficiency of the CWs with the ongoing processes and therefore demonstrates how important it is to take these into consideration when designing a CW facility.

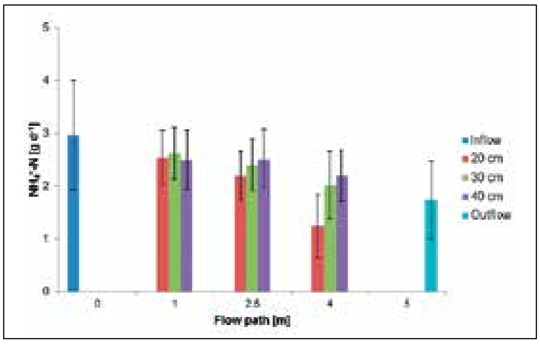


Fig. 3: Average loads of NH_4^+-N in unplanted horizontal subsurface flow constructed wetland

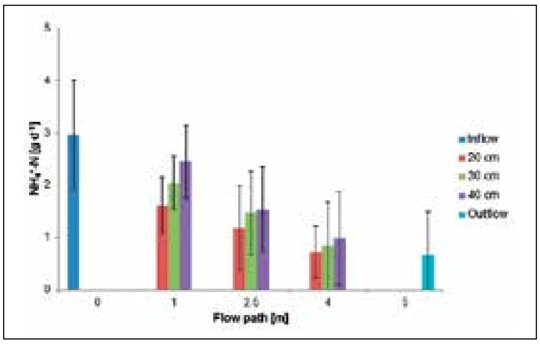


Fig. 4: Average loads of NH_4^+-N in planted horizontal subsurface flow constructed wetland

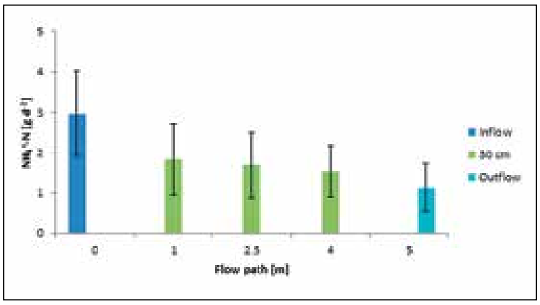


Fig. 5: Average loads of NH_4^+-N in floating plant root mat

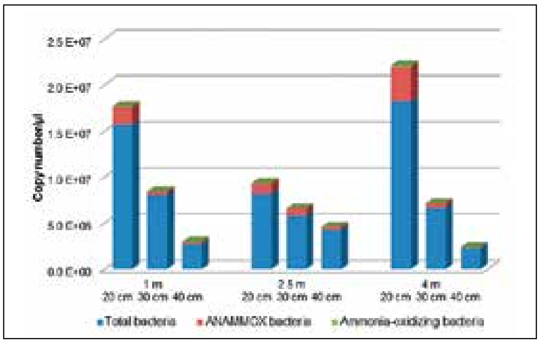
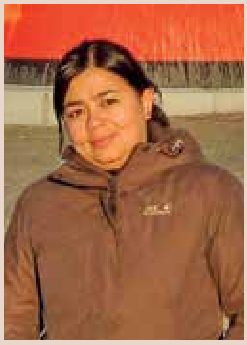


Fig. 6: Copy number of different clusters of bacteria in dependence on depth and distance from inflow in planted HSSF CW

Johana Grajales (AGH, Poland)



Johana Grajales has a BSc in Environmental Sciences from the Technological University of Pereira (Colombia) and an MSc in Hydro Science and Engineering from the Dresden University of Technology (Germany). During her undergraduate studies, Johana worked as a research assistant in the water and sanitation research group in Colombia. After finishing her MSc she worked at the Saxon State Agency of Environment, Agriculture and Geology in Dresden in a project assessing natural attenuation at hydrocarbon-contaminated sites. In 2011, she joined the ADVOCATE team and Work Package 4, pursuing her PhD in "In-situ remediation of contaminated sites using permeable reactive multi barriers (PRmB) systems" in close cooperation with Franklin and Oksana, project partners from Poland (Hydrogeotechnika Sp. Z o.o) and Germany (UFZ) respectively.

Introduction

The focus of this research is to identify the most effective strategy for in-situ sustainable remediation of groundwater contaminated with chlorinated solvents, using permeable reactive barriers (PRB). Laboratory studies were performed to select the most effective reactive material for the design of the PRB. The results are being tested in a field installation and modelling tools will be used to validate conceptual models of contaminant migration and evaluate the performance of the PRB system.

Technology description

Permeable reactive barrier systems are in-situ passive remediation technologies that consist of placing a cell of reactive material perpendicular to the groundwater flow to intercept and treat the contaminant plume. The contaminants are treated by physical, chemical or biological processes such as: oxidation, reduction, biodegradation, sorption and precipitation. The success of this technology, however, depends on the effectiveness of the reactive materials used, the specific design of the installation and the hydraulic performance of the barrier, both of which can be investigated in the laboratory (batch and column studies) and in the field.

Research methodology

Laboratory batch and column studies were performed to select the appropriate reactive material to be placed in the barrier. Batch tests included four reactive materials and four material combinations (i.e. compost, brown coal, zeolite, diatomaceous earth, compost + brown coal, compost + mulch, compost + zeolite, diatomaceous earth + mulch). Zero valent iron (ZVI) was used as a 'control' for its proven ability to effectively remove trichloroethene (TCE) (i.e. the ability of the tested materials to remove TCE was compared to that of ZVI). Table 1 presents some properties of the evaluated reactive materials. TCE removal efficiency for each material was determined by comparison of these experiments with the respective controls. Following the batch tests, the two top performing reactive materials were selected for testing in column experiments. The column experiment set up is shown in Figure 1.

Table 1. Properties of reactive materials used in experiments

Materials	pH		Bulk density,	Water content (%)	Total organic
	H_2O	1M KCl	ρb (g/cm^3)		carbon content (%)
Compost	8.05	7.39	0.69	44.4	34.88
Zeolite	7.13	5.49	0.8	5.2	5.2
Brown coal	4.91	4.56	1.13	16.2	64
Mulch	4.86	4.68	0.28	11.29	80.1
Diatomaceous earth	5.18	5.0	1.2	55.8	33.9

Results

Results from batch tests show that the four selected reactive materials have removal efficiencies higher than that of ZVI (80%); brown coal, however, was the material which had 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. 1). The TCE removal efficiency for the compost-brown coal mixture (1:1) was 78%, while the other combinations had removal efficiencies lower than 50% (Fig. 2).

Fig. 1: Column experiment set up

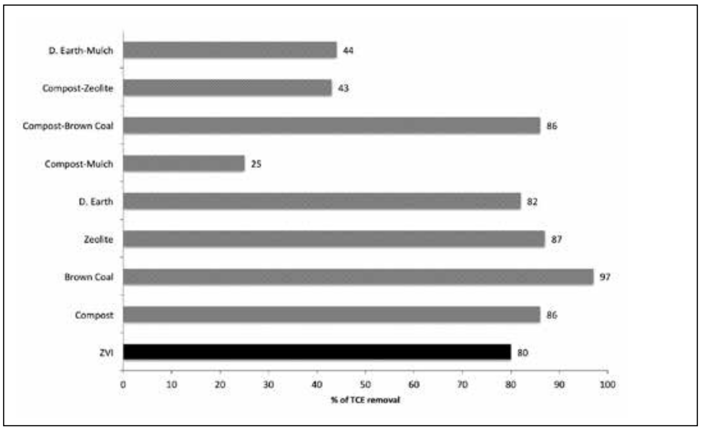


Fig.2: TCE removal efficiency for the evaluated reactive materials

The top performing material was brown coal. Compost and zeolite also exhibited a good performance. However, when zeolite was combined with compost, the removal efficiency dropped considerably. From the results above, brown coal, compost and the brown coal-compost mixture were the materials selected for column experiments.

Results from column tests (Fig. 3) show 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.

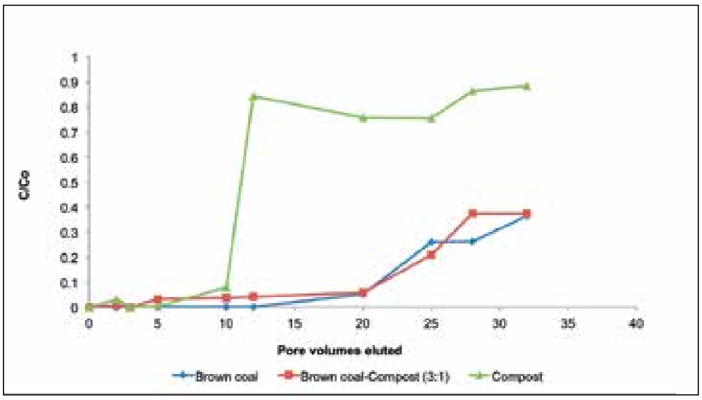


Fig. 3: TCE breakthrough curves for brown coal, compost and brown coal-compost

Current and next stage of the research

Currently a field installation of the technology (Fig. 4) using the two selected reactive materials (compost and brown coal) is being evaluated. When this stage is completed, modelling studies will be used to interpret the results in a full-scale PRB.

Fig. 4: Field demonstration of the PRB with the selected reactive materials

The Advocate team gathered in Switzerland for a workshop, preparing and supporting our Fellows in their decision-making regarding career paths. We discussed CVs and job applications; and invited academic and business partners to talk about their positions, personal and professional experiences and the ways to excel in their field of expertise.

You can find our full list of partners on our project website (**www.theadvocateproject.eu**). If you would like any further information please contact Gabriella Kakonyi at g.kakonyi@sheffield.ac.uk.

Contact information for lead scientists at organisations hosting Research Fellows within the ADVOCATE Marie Curie Initial Training Network

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We are also pleased to have a number of associated partner organisations from different commercial and industrial sectors of the contaminated land and groundwater management field within the network, who are helping us with training and technical assistance. You will find details of these partners and their contribution to the network on our website.