Mixing Processes in Enhanced and Natural Attenuation

Project No. 835.80.005

Final Report/Eindrapportage

P.A.S. Ham

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Contents

1 GENERAL INFORMATION

This report is constructed in accordance with the NWO guidelines. Numbers in brackets refer to those guidelines.

1.1 Project Title and Number [01,02]

"Mixing Processes in Enhanced and Natural Attenuation", TRIAS Project No. 835.80.005.

1.2 Project Duration [03]

This research project was started on 1st October, 2001. The project lasted for four years, with an additional extension of four months. The project terminated on 31st January, 2006.

1.3 Researchers [04]

PhD student: P.A.S.Ham
Promoter: Prof. S.M. Hassanizadeh
Supervisor: Dr. R.J. Schotting

During the period 1/10/2001 to 31/12/2003, this research was undertaken at:

Delft University of Technology,
Faculty of Civil Engineering & Geosciences,
Section of Hydrology & Ecology,
Stevinweg 1, Delft.

After the relocation of the research group to the University of Utrecht, this research was completed at:

University of Utrecht,
Faculty of Geosciences,
Environmental Hydrogeology Group,
Budapestlaan 4, Utrecht.

The project ended in the publication of a PhD thesis entitled "Dispersion Controlled Natural Attenuation: The role of conservative plume characteristics in modelling reactive mixing processes". This thesis was successfully defended on Monday, May 1st, 2006 at the Academic Building in Utrecht.

2 SCIENTIFIC SUMMARY [05]

The aim of this project was to gain a fundamental understanding into competing mixing processes involved in natural/enhanced attenuation; processes which occur chiefly in the transition zone of a contaminant plume. Analytical and numerical methods, in combination with laboratory and field data, were employed to quantify these mixing processes. In particular, the focus of this work was on transverse dispersion, believed to be the most important mechanism resulting in the mixing of electron acceptors (EA) and electron donors (ED).

A new two-dimensional analytical solution was derived, proving conclusively that transversal dispersion is indeed the most important dispersion mechanism leading to the attenuation of steady-state contaminant plumes where species (e.g. EA and ED) mix and instantaneously react together. This model was extended generically in three-dimensions and also to further include anaerobic core degradation processes, which have been demonstrated to play an important role in some remediation cases. This occurs when core degradation rates are comparable to fringe degradation, which is often the the case when EA availability is limited. It must be noted that although three-dimensional solutions can be formulated, in practice most problems can be considered in two-dimensions.

In another study, a numerical model was developed to access the competing mechanisms of transverse mixing and kinetic-controlled biodegradation where two species react together. The base model consisted of three non-linear governing partial differential equations (PDE), describing EA and ED migration, and moreover microbial growth, in time. These can be reduced to two PDE by the introduction of a new parameter relating concentrations of EA and ED to each other. The PDE describing this variable can be solved using an appropriate "intermediate" analytical solution. In the steady-state, the equations reduce to just one PDE, in terms of one variable, requiring a numerical solution. The new model provides an elegant solution to the problem and agrees excellently with the base model. Furthermore, the new model allows an easy assessment of the effects of interacting dispersion and reaction parameters on plume development. The value of longitudinal dispersivity is paramount to provide an accurate solution, whilst transversal dispersivity and microbial growth control fringe width and the attenuation capacity of contaminant plumes. The combination of these effects can be seen as 'effective' dispersion.

In another study, a model-based interpretation of laboratory scale experimental data was undertaken. It was demonstrated that the classical form of the dispersion coefficient does not hold at the laboratory scale, when plumes of reacting species are considered. Using a new empirical formula combined with derived diffusion coefficients, the laboratory data could be accurately simulated using pure forward modelling techniques.

In the last exercise, the analytical model derived in a previous study was applied to field data for a well documented petroleum hydrocarbon plume. The plume consists of a non-reactive benzene plume and a steady-state, reactive toluene plume. Extracting parameters from data profiles for conservative species, it was possible to accurately predict plume lengths of the reactive hydrocarbon plume.

The results of these studies provide useful modelling tools, particulary in the assessment of studies in monitored natural attenuation.

3 SAMENVATTING [06]

Natuurlijke afname (NA = Natural Attenuation) en gestimuleerde natuurlijke afname (ENA = Enhanced Natural Attenuation) kunnen een belangrijke rol spelen bij het saneren van bodem- en grondwaterverontreinigingen. Onder verontreinigde locaties, zoals bijvoorbeeld afvalstortplaatsen en Industrieterreinen, is veelal sprake van een mobiele verontreinigingspluim, bestaande uit in het grondwater opgeloste stoffen. De beweging wordt veroorzaakt door de stroming van het grondwater. Een samenspel van natuurlijke fysische, chemische en biologische processen bepaalt het lange-termijngedrag van zo'n pluim: afhankelijk van een complex van factoren kan de pluim groeien, krimpen of niet meer in omvang veranderen (de stationaire toestand). Deze laatste twee mogelijkheden kunnen betekenen dat van kostbare en ingrijpende saneringsmethoden, zoals afgraven en geohydrologische isolatie, afgezien kan worden. In deze gevallen reduceren natuurlijke processen de milieurisico's of nemen deze zelfs helemaal weg (zoals bij een krimpende verontreiniginspluim het geval is). Met name in de overgangszone aan de rand van de verontreinigingspluim vinden de relevante NA processen plaats. Mengprocessen als diffusie en mechanische dispersie spelen een cruciale rol. Ten eerste zijn deze processen verantwoordelijk voor het ontstaan van de diffusieve/dispersieve mengzone. Ten tweede zorgt deze menging voor contact tussen het locale geochemisch reactieve en biologisch actieve natuurlijke milieu. Dit laatste vormt een belangrijke randvoorwaarde voor de effectiviteit van NA. Grondig fundamenteel inzicht in de relatie tussen NA-processen en dispersieve menging is dus zeer belangrijk.

Dit onderzoek geeft inzicht op methodes voor de beoordeling van de potentie van NA in voorkomende verontreinigingsgevallen, waarbij sprake is van een verontreinigingspluim. Met name, gaat dit onderzoek over de identificatie van de relevante mengprocessen door gebruik te maken van analytische en numerieke methodes. Het blijkt dat transversale dispersie als mengmechanisme het meest belankrijk proces is, vooral voor het bepalen van de lengte van 'steady-state' pluimen. Bovendien leidt de interactie tussen transversale verspreiding en biologische afbraak tot het ontstaan van effectieve dispersie waarden.

Een van de analytische modellen die ontwikkeld werdt maakt het mogelijk uit een beperkt aantal parameters de lengte van een verontreinigingspluim en de concentratie van de verontreiniging in het grondwater te berekenen. Bovendien is te voorspellen of de pluim zonder interventie zal uitzetten of juist inkrimpen. Deze formule is geldig voor elke grondsoort en voor elke vervuiling die biologisch moeilijk afbreekbaar is. De benodigde parameters zijn de porositeit van de grond, de grondwatersnelheid, de concentraties van de vervuiling en de mate waarin de vervuiling zich loodrecht op de grondwaterrichting verspreidt. Hiermee is het model zeer geschikt om in te schatten of bodemsanering nodig is. Bijvoorbeeld werdt het model getest op een verontreinigde locatie in Perth, Western Australia, waar de oplossingen bleken goed overeen te komen met de werkelijke lengte van de pluim.

De resultaten van dit onderzoek maken het mogelijk dus om efficiënt, maar wel voorlopige, voorspellingen te doen t.a.v. de effectiviteit van NA als verantwoord saneringsalternatief.

4 PRESENTATIONS, PUBLICATIONS & APPLICATIONS

4.1 Conference Proceedings and Presentations [08]

1. Ham, P. A. S., and R. J. Schotting. Two-dimensional aquifer bioremediation: a (semi-) analytical approach. Proceedings Computational Methods in Water Resources, Delft, The Netherlands, 2002, Vol.1, 835-842.

2. Ham, P. A. S. Analysis of two-dimensional aquifer bioremediation. Proceedings 1st National Scientific Symposium Bodem Diep, Zeist, The Netherlands, 2002, 1-5.

3. Ham, P. A. S., and R. J. Schotting. A reactive solute transport model for the determination of plume lengths. Geophysical Research Abstracts, Volume 5, EAE03-A-10626, Nice, France, 2003.

4. Ham, P. A. S. Dispersive mixing: A reactive solute transport model for the determination of plume lengths. Proceedings 2nd National Scientific Symposium Bodem Diep, Zeist, The Netherlands, 2003, 7-10.

5. Ham, P.A.S., R.J. Schotting, and H. Prommer. Predicting plume development of reactive solutes using an analytical transport model. American Geophysical Union, H11D-0890, San Francisco, CA, Dec 2003.

6. Prommer, H., P.A.S. Ham and R. J. Schotting. Numerical modelling of plumes controlled by transverse dispersion. American Geophysical Union, H11D-0889, San Francisco, CA, Dec 2003.

7. Ham, P.A.S., R.J. Schotting, and C. Berentsen. Biodegradation and transverse mixing: Controlling processes in aquifer remediation. American Geophysical Union, H51F-0435, San Francisco, CA, Dec 2005.

4.2 Peer Reviewed Publications [09]

1. Ham, P.A.S., R.J. Schotting, H. Prommer, G.B. Davis. Effects of hydrodynamic dispersion on plumes undergoing an instantaneous bimolecular reaction. Adv. Water Res. 27(8):803-813, Aug 2004.

2. Ham, P.A.S., H. Prommer, A.H. Olsson, R.J. Schotting, and P. Grathwohl. Predictive modelling of dispersion controlled reactive plumes at the laboratory scale. Article accepted for publication in Journal of Contaminant Hydrology.

3. Gutierrez-Neri, M, P.A.S. Ham, R.J. Schotting, and D.N. Lerner. Analytical modelling of fringe and core biodegradation in groundwater plumes. Article submitted to Ground Water.

4. Ham, P.A.S., R.J. Schotting, and C. Berentsen. Numerical models for enhanced remediation controlled by dispersion and microbial kinetics. Article in preparation for submission to Advances in Water Resources.

5. Ham, P.A.S., M. Gutierrez-Neri, and H. Prommer. Three-dimensional Modelling of a Petroleum Hydrocarbon Contaminated Field Site in Western Australia. Article in preparation for submission to Environmental Forensics.

6. Ham, P.A.S. Dispersion controlled natural attenuation: Modelling techniques to access aquifer remediation. PhD Thesis, 2006.

4.3 Applications [10]

The analytical model presented in the paper by Ham *et al.* (2004) has been incorporated into a modelling tool called "CORONA SCREEN". Details can be found in:

1. Lerner, D.N., Bjerg, P., Datel, J., Gargini, A., Gratwohl, O., Hollinger, C., Morgan, P., Ptak, T., Schotting, R., Slenders, H., Thornton, S.F., 2005. CORONA - Confidence in forecasting of natural attenuation as a risk-based groundwater remediation strategy, Final report of the EU research project EVK1-2001-00087. University of Sheffield, UK. 26 pages. Available from http://www.shef.ac.uk/corona.

Furthermore, the same analytical model has been applied to field data collected from a hydrocarbon polluted site located in Perth, Western Australia. As a result of this, two environmental forensics agencies in the USA are planning on applying this technique to problems of environmental litigation. A number of engineering companies throughout the world have also expressed an interest in this model in the analysis of natural attenuation processes.

The numerical modelling work carried out has also resulted in two 'reaction modules' being developed for the code PHT3D. The first module enables an instantaneous reaction between two mixing solutes to be modelled. The second extends this model with a first order term, which can be used to model anaerobic core degradation along with aerobic reactions occurring at the plume fringe. Both modules and related publications are available from the PHT3D website: http://www.pht3d.org.

5 RESEARCH IMPACT & RELEVANCE [07,15]

This research has been mainly orientated to a fundamental understanding of mixing processes in the context of natural attenuation (NA). Only through such research can a better scientific understanding be developed. However, it is also of importance that these new developments be employed in practice where possible. The relevance of this project therefore, is that new insights into aquifer remediation have been translated into applicable engineering tools.

5.1 Original Research Objectives [11a]

The main objective of this project was to elucidate the role and impact of dispersive/diffusive mixing processes in relation to natural attenuation of contaminants. In particular, the project focused at the prediction of the fate of contaminant plumes as occur under, e.g., waste disposal sites and abandoned industrial areas. This subject is a typical example of a practical problem, induced by the growing environmental awareness in society, but lacking a thorough fundamental understanding. It is well known that mixing processes play a key role in the effectiveness of NA-processes. The diffusive/dispersive mixing zone of the contaminant plume is a typical example of a reactive interface: in this zone, the NA-processes occur, determining a plume's fate.

It is fair to say that this objective has been largely achieved. Fundamental processes of, in particular, transverse mixing and biodegradation have been identified and quantified through the use of analytical and numerical techniques. It has been demonstrated that transversal dispersivity is the single most important parameter in determining the fate of steady-state groundwater plumes. Moreover, the interplay between dispersion and biodegradation leads to 'effective' dispersion parameters, which is of particular interest when degradation is controlled by reaction kinetics.

Through numerical modelling exercises, this study shows effects of diffusion play only a role when either groundwater velocities are very low, or alternatively, where transversal dispersivity is small. The latter is generally only apparent in well controlled laboratory experiments, where dispersivities are generally in the order of fractions of millimeters. At the field-scale, dispersivities are more commonly in the order of centimeters, since spatial heterogeneity and transient plume effects result in measured or 'apparent' values.

Instead of developing a new numerical code, an existing numerical code (PHT3D) has been used and, where necessary, adapted in order to verify the the analytical models developed in this project. Reaction modules expressing instantaneous and kinetic reaction processes were constructed to compare numerical results against those obtained using the analytical expressions.

5.2 Non-Scientific Objectives [11b]

The aim of this project was to elucidate the role of mixing processes and to develop a method that enables decision makers to judge whether a specific site can be remediated by NA (or enhanced NA), or not. Through the development of analytical and numerical models, which can predict plume fate where either instantaneous or kinetic-controlled reactions occur, this project has provided a suite of tools which can be used by experts or consulting engineers. Although the techniques developed use simplifying assumptions and cannot capture the subsurface intricacies of a particular site, the models give first estimates, for example, the maximum extent to which a plume will develop. This can be instantly translated into an answer to whether or not natural attenuation is occurring at a particular site. These simple models are invaluable to engineers because it enables them to decide on an appropriate course of environmental remediation and if further, more detailed, modelling is required.

5.3 Networking [11c,18]

The project description originally intended for international collaboration with a number of partners. Through the involvement with the EU (5th Framework) project "CORONA", collaboration was established (chiefly) between the Groundwater Protection and Remediation Group, University of Sheffield; Centre for Applied Geosciences, University of Tuebingen; and Land and Water Division, CSIRO (Australia). This has lead directly to three joint publications. Furthermore, the analytical method (Ham *et al.*, 2004) developed within this project has been incorporated into the engineering tool “CORONA SCREEN” (see publications).

There were no specific network links created between similar TRIAS projects. The closest connection is perhaps to the project “Multiphase flow and enhanced biodegradation of dense non-aqueous phase liquids”. Although no definite collaboration occurred, it is possible that some of the methods used in this project are of interest there, particulary in the application of PHT3D, which can easily handle multi-phase flow problems.

6 RESULTS

6.1 Application of Results [12,13,19]

In this project, analytical and numerical models have been developed in order to access cases where natural attenuation of contaminants occur. These models give fundamental insight into relevant dispersion processes which occur when species mix and react together.

Although the original intention of this project was to develop a numerical model, instead more emphasis has been placed on understanding processes themselves. Analytical modelling results have been implemented into (i) the existing numerical model PHT3D, through the development of “add-on” modules, and (ii) an engineering tool “CORONA SCREEN”. Furthermore, the analytical and numerical model development within this project can be used as independent models and applied to site-specific examples. A number of engineering companies worldwide are intending to adopt the analytical models developed in this project for their own applications.

6.2 Shortfalls [16]

The major shortfalls of the analytical/numerical modelling with this project lie within the basic assumptions which have been made. For example, the results from this project are only applicable to homogeneous media. The numerical tools developed to validate the analytical solutions can be extended to incorporate subsurface heterogeneities, but the solutions themselves cannot. In many cases this limits the use of the solutions to providing first estimates as to whether natural attenuation is a feasible remediation strategy, however there maybe some cases when the assumptions are valid, for instance, for the validation of laboratory scale experiments. Despite these shortfalls, if the solutions developed within this project indicate that natural attenuation is feasible at a particular site, then the results should act as a pre-cursor to more detailed modelling studies which incorporate more of the site complexity. Such tools are or particular interest to engineers.

6.3 Dissemination of Results [20]

Results have been disseminated through the following channels:

1. Publications in journals. There are four/five journal publications intended for this research, which will have a largely scientific audience, and are the most important means of disseminating results in the long term.

2. Presentations at conferences and meetings. Over the four years of research, a large network has been built up, as a result of presenting work at conferences and meeting scientists and consultants active in similar research. This has lead to results/modelling techniques being applied in a number of projects.

3. Projects. Involvement in the CORONA project has meant that the analytical methods developed have been incorporated into the engineering tool ‘CORONA SCREEN’. This disseminates the principles to the wider engineering community.

4. Working Visits. Two extended trips to Australia has resulted in a strong collaboration with researchers at CSIRO, the exchange of knowledge and joint publications.

5. Thesis. Of course, the thesis itself presents all the results and principles behind the work completed and the results of this project. This may form the basis for any follow-on research.

6.4 Further Research [14,17]

Further research into this subject area should investigate the following questions:

1. To what extent do transient effects, particulary the effects of strong seasonal variations, affect the remediation of groundwater plumes and values of transversal dispersivity? The Eden Hill field-site provides extensive data which can be analysed.

2. Can the effects observed at the laboratory scale, which indicate that transversal dispersivity is dependent on flow velocity, be proved theoretically?

3. How can results/conclusions obtained from laboratory studies be translated to the field scale?

The first question is of particular interest, and some research is already being carried out by other researchers. This is because seasonal variations can cause enhanced mixing between reactive species, but actual transversal dispersivity values can remain small. In the case of Eden Hill, this may also form part of the answer to the last question.

FUTURE [21]

Following the completion of research, P.A.S. Ham has returned to England to establish and run a small property renovating company. Whilst he has no ambitions to return to scientific research, he intends to enter industry in the future.