

## RETENTION AND DEGRADATION PROCESSES TO REDUCE CONTAMINATIONS IN GROUNDWATER AND SOIL (KORA)

JOCHEN MICHELS & CHRISTOPHER FREY

(\*) KORA Management office - DECHEMA e.V.;Theodor-Heuss-Allee 25 D-60486 Frankfurt/Main, Germany - e-mail: michels@dechema.de

### ABSTRACT

The overall goal of KORA (supported by the Federal Ministry of Education and Research, BMBF) is to investigate natural attenuation (NA) processes for consideration in contaminated land management.

The funding priority is focused on the results of international research, especially from the U.S.A. The research contains investigations of biological, (hydro-) geological and chemical processes in soil and groundwater under different environmental conditions and delivers insight into legal issues and acceptance of official bodies and the general public.

### INTRODUCTION

Germany has a long history of industrial activity and its legacy is evident within the groundwater environment, where a range of pollutants is found, particularly in urban areas.

The number of (suspected) contaminated sites in Germany totalled up to 300.000 cases. The threat of contamination hazards for men and nature originating out of those locations is inherent. The budget and tools for a long-term and technical reclamation of these contaminated sites are limited.

#### *Reasons for investigating NA-processes*

In recent years it has become obvious how important knowledge of natural attenuation processes is with regard to the risk-management of contaminated sites. There are good reasons why these processes should be investigated more in detail:

- more and more contaminated sites have been identified in Germany. Moreover, due to the use of new methods of site investigation, the expansion of known contaminated sites has had to be scaled up.
- national and international experience has shown that often conventional remediation technologies merely shift the problem (e.g. "dig and dump") or are not effective within reasonable timeframes (e.g. "pump and treat"). However, the expenses of implementing these technologies often bears no relation to the actual value of the site.
- new investigations have come up with evidence that intrinsic

degradation and retention processes at a site are more effective than artificial processes induced by technical remediation measures. So natural attenuation is becoming increasingly accepted as a viable, cost-effective option for managing the risk posed by contaminated groundwater in certain situations.

The funding priority KORA derives its objectives and its legitimation from these areas of experience. Naturally occurring degradation and retention processes in the subsurface are able to slow down the propagation of contaminants in soil and groundwater. In the plume they can, under favorable conditions, lead to a reduction of contaminant concentrations. The processes are first summarized by the US EPA under the term "natural attenuation". The long-term monitoring of intrinsic processes ("monitored natural attenuation" - MNA) is the US EPA's prerequisite for the acceptance of natural attenuation as (part of) a remediation strategy. The transition from natural attenuation to active remediation measures is smooth, the US EPA defines the borderline for the exclusion of human intervention. Measures which are suitable for supporting intrinsic processes and enforcing their efficiency are known as "enhanced natural attenuation".

#### *Acceptance situation in Germany*

The acceptance of a groundwater plume as a reaction space conflicts with existing water legislation in Germany. The long periods involved, which can span many decades, give rise to questions regarding the guarantee of responsibility over several generations.

On suggestion of the *Commission on Contaminated Sites* (ALA) an ad-hoc-subcommittee has been established by *The German National/Federal States Committee on Soil Protection* (LABO) to prove the opportunity to consider natural attenuation processes in contaminated land management. Recently, a federal position paper was published, which provides (i) definitions of the terms NA, MNA, and ENA, (ii) discussion of legislative questions in relation to the integration of NA into contaminated land management (iii) Prerequisites for

using a MNA-concept and (iv) a recommendation for an application strategy. The position paper is limited for the consideration of NA in the saturated zone and provides conclusions for groundwater damages caused by contaminated land.

For the application of an MNA-concept some questions should be addressed: Which processes are responsible for intrinsic retardation and degradation? How can they be detected and evaluated by predictions based on mathematical models? The Evaluation of NA-processes refers to risk assessment, the necessity for remediation and the possibility of integrating them into active remediation measures.

**TASKS AND GENERAL PROJECT AIMS**

The task of the KORA funding priority is the exploration of intrinsically working natural retention and degradation processes in the subsoil on sites of different industrial branches, each with their own typical contaminants. KORA is aimed at developing technical and legal instruments which will facilitate the evaluation and customised use of these processes in the risk assessment and remediation of contaminated soils and groundwater.

For this purpose, the projects of KORA will be carried out in different ways at currently 24 contaminated sites. It would not be possible to meet these common goals without a continuous discussion among the members of KORA and with external experts, authorities, and end users. Regular workshops and status meetings will provide for the communication that is essential for interdisciplinary cooperation; they will also ensure that a concrete result will be obtained at the end of the funding period even from the tax payer's point of view: a firm basis for the use of natural attenuation processes in the assessment of hazards and in the treatment of contaminated sites.

**DESIGN OF KORA**

*Thematik Networks in general*

The over 60 projects of this R&D-funding priority are investigating a wide range of sites using different methods. KORA is separated in eight Thematic Networks (TN) with different fields of research. The first six Thematic Networks are analysing effects of natural attenuation in direct dependence of certain industrial contaminations. TN 7 develops software for modelling and problem-related forecasting and TN 8 contains the parts legal aspects, acceptance and economic assessment. The following chart is to give a general survey of the R&D-funding.

*TN°1 Refineries, fuel tanks, fuel/mineral oil*

The Thematic Network 1 deals with the contaminants classed as petroleum hydrocarbons (including BTEX), which are considered to be relatively easily biodegradable. The major focus therefore is on the quantitative assessment and

TN1	Refineries, fuel tanks, fuel/mineral oil (contaminants: TPH, BTEX, MTBE)
TN2	Gas works, coking plants, coal tar processing (PAH, BTEX, coal tar, heterocyclics)
TN3	Chemical industries, metal processing (chlorinated solvents)
TN4	Landfills, abandoned waste disposal sites (household waste, chemical waste, ammonia)
TN5	Former ammunition works (nitroaromatics)
TN6	Mining and sediments (acidic water, heavy metals, DDT, HCH)
TN7	Prognosis, modelling
TN8	Evaluation, legal issues, acceptance by official bodies and the public

Tab. 1 - Survey of Thematic Networks

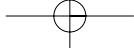
problem prediction at large sites (e.g. refineries, fuel tank farms, airports), together with problematic compounds such as MTBE and decisions whether to undertake NAPL removal in the source area. The main taskline of the TN1 within KORA is the development of a sector guideline, in which both the scientific literature as well as practical experiences gained from the industrial projects of the TN1 will be included.

The general objectives are:

- development of efficient investigation strategies and reduction of any remaining investigation uncertainties;
- (Environmental) conditions for the degradation of TPH, BTEX and MTBE in soil and groundwater;
- degradation rates and limitations;
- usefulness and reliability of indicators/ parameters for the degradation behaviour;
- reliability of modelling of the plume behaviour;
- (long-term-) monitoring;
- boundary conditions for the economically and ecologically meaningful application of MNA;
- cost-efficiency;
- consideration of NA within the active remediation of contaminated soil and groundwater;
- quality management.

P 1.1	METLEN (Methyl-tertiary-butyl-ether (MTBE) - Leuna as reference test site for the implementation of the enhanced natural attenuation-approach(site: Refinery Leuna)
P 1.2	Natural Attenuation and Enhanced Natural Attenuation at typical hydrocarbon contaminated sites (sites: Tank farms Brand and Niedergörsdorf)
P 1.3	Natural attenuation of a complex contaminant mixture in a karstified groundwater aquifer (site: Mineral oil factory Eppele)
P 1.4	Development of an enhanced in-situ bioremediation technology in an aquifer polluted with hydrocarbons (site: former tank farm Berlin Spandau)
P 1.5	Development on an NA and ENA-supported remediation strategy and the conception of an on-site pilot plant on a typical site with spacious TPH and BTEX contamination (site: Refinery PCK Schwedt)

Tab. 2 - Projects of TN 1



RETENTION AND DEGRADATION PROCESSES TO REDUCE CONTAMINATIONS IN GROUNDWATER AND SOIL (KORA)

TN<sup>2</sup> Gas works, coking plants, coal tar processing

The Thematic Network 2 mainly deals with sites contaminated with coal tar and tar oil. Polyaromatic hydrocarbons (PAH) are predominant on these sites. In addition monoaromatic compounds, heterocyclic polyaromatic compounds (NSO-PAH), phenols and mineral oil hydrocarbons are reported to exist as co-contaminants. The key questions to be answered during the course of the research activities of TN 2 are summarized below:

- under which environmental conditions are coal tar oils degraded in the aquifer?
- what are the geological, geophysical, geochemical and biological requirements for the degradation of those compounds and how can this be determined?
- how to characterise the conditions which enable enhanced degradations?
- how can information be obtained to predict the fate of the contamination and how can the timeframe of natural attenuation processes be determined?
- can the gained experiences be transferred to other sites?

TN 2 contains four sites with very different conditions (gas work (2), coking plant (1), wood preservation plant (1)). Each of them is characterised by a particular pollutant consortium with specific environmental conditions. In addition to the site specific projects, three projects are concerned with questions of general importance addressing the identification and quantification of heterocyclic aromatic compounds and similar products, their ecological and toxicological impact as well as the development of standardised microcosm techniques.

P 2.1	Heterocyclic aromatic hydrocarbons and other pollutants typical for creosote in groundwater - Assessment of substance properties and occurrence with regard to the potential of natural attenuation
P 2.2	Monitoring and assessment of stimulated and non-stimulated natural attenuation in a BTEX- and PAH-contaminated aquifer (site: Gas work Düsseldorf Flöngern)
P 2.3	Development and testing of an exemplarily monitoring program with respect to NA strategies for a BTEX/PAH contaminated plume at a former coking plant site (site: Coking plant Castrop-Rauxel)
P 2.4	Enhanced Natural Attenuation for the in-situ biodegradation of heterocyclic hydrocarbons in groundwater (site: Gas work Stuttgart Gaisburg)
P 2.5	Assessment and prediction of natural attenuation processes by means of a process related analysis at a tar oil contaminated site in Saxony (site: Wood preservation plant Wülknitz)
P 2.6	Identification and quantification of toxicological relevant metabolites of PAH, hetero cyclic PAH and substituted PAH at contaminated sites and their behaviour in the aquifer
P 2.7	Development of standardized microcosm techniques for the assessment of natural attenuation in PAH contaminated aquifers

Tab. 3 - Projects of TN 2

TN<sup>3</sup> Chemical industries, metal processing

Within Thematic Network 3 the potential of natural attenuation processes for remediation of sites contaminated with chlorinated solvents will be identified and assessed.

Chlorinated solvent plumes are characterised by rather long extensions, and intrinsic degradation processes are rather complex and so far not entirely understood. Exploration strategies in combination with hydrogeochemical and microbiological investigation are tested and optimised by means of six reference sites, which are represented by the projects.

Results of site investigations and additional knowledge deriving from literature studies will be summarised within a sector guideline. This guideline is intended to serve as a decision- support tool to apply MNA at chlorinated solvent sites.

Apart from a practical demonstration of MNA at the reference sites, the following scientific topics are investigated:

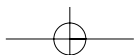
- practicability and significance of hydrogeological /hydrochemical and microbiological methods to demonstrate natural attenuation processes;
- formulation of suitable combinations of parameters and methods to assess MNA and describe site conditions;
- direct evidence of NA processes and quantification of NA;
- which organisms are responsible for degradation of chlorinated solvents, what are the functional correlations between present organisms and occurring NA processes?;
- regional, temporal and financial range of long-term monitoring;
- transferability of laboratory measurements to field conditions;
- potentials of model approaches to compensate data uncertainties and missing data;
- imitations of MNA regarding chlorinated solvent sites.

P 3.1	Regional differentiated and innovative monitoring of CHC contaminated groundwater within a structured unconsolidated aquifer (site: Chemical industrial site Kertess-Chemie, Hannover)
P 3.2	Indication of microbial degradation of volatile chlorinated hydrocarbons at a highly polluted site (site: Tank farm WGT airport Perleberg)
P 3.3	Investigation of natural attenuation at a VCH-contaminated site (site: Metal processing site Karlsruhe-Killisdorf)
P 3.4	Site characterization, development of a method for prognosis and monitoring of natural attenuation at a model site (site: Industrial site Düsseldorf-Lierenfeld/Oberbilk)
P 3.5	Field-scale quantification of the potential of NA in deep large-scale aquifers (site: dry cleaners in Rosengarten Ehestorf)
P 3.6	Field study on the natural degradation and retention of chlorinated hydrocarbons (site: industrial site, Frankenthal)

Tab. 4 - Projects of TN 3

TN<sup>4</sup> Landfills, abandoned waste disposal sites

The research topics of the Thematic Network 4 are investigations of monitored and enhanced natural attenuation processes of polluted soil and groundwater beneath landfills and abandoned waste disposal sites. The research will focus on the conditions under which natural attenuation occurs and on reliable methods for measurement, evaluation and control of these processes.



At present the TN 4 comprises four different investigation sites, which are regarded as case studies. In addition, a project of the Federal Ministry of Education and Research is associated. All these locations have in common that there is an existing or expected soil and groundwater pollution originating from landfills.

The specific situation at the case site Berlin-Kladow/Gatow is characterised by different dump sites and their impacts on groundwater. The plume of contaminated groundwater at that area may spread further down-stream. On the other hand, at the landfill site Deponie Monte Scherbelino in Frankfurt/Main the groundwater pollution is under control by sheet piling. Therefore, research focuses on the polluted groundwater outside of the sheet piling. At the site Deponie Weiden West the spreading of polluted groundwater beneath the landfill is prevented by a vertical drainage. To eliminate the non-tolerable groundwater pollution microbiologically mediated oxic degradation processes will be stimulated by air or oxygen gas injected into the subsurface. The site Spüldeponie Großkayna is a subaquatic landfill within a residual lake formed in an closed open caste mine. The objective of this project is to investigate the natural attenuation processes in the lake and the infiltration of the polluted lake-water into.

P 4.1	Detection of natural attenuation processes at abandoned waste disposal sites with special regard to different landfills in Berlin-Kladow/Gatow
P 4.2	Enhanced natural attenuation processes in the aeration and groundwater zone below a closed landfill site (site: landfill Weiden/West)
P 4.3	Model based analysis and prediction of natural attenuation in landfill leachate plumes (site: Landfill "Monte Scherbelino", Frankfurt)
P 4.4	Natural attenuation of contaminants Emerging from a subaquatic Landfill (site: Subaquatic Landfill Großkayna)

Tab. 5 - Projects of TN 4

*TN°5 Former munitions works*

A fundamental goal of the Thematic Network 5 is the identification and evaluation of the natural retention and attenuation processes of compounds typical for explosives as well as the development and standardisation for the necessary technical equipment and methodology. Field investigations will be carried out.

The test results will benefit the evaluation and remediation of over 72 munitions refuse sites and over 400 explosive disposal locations in Germany and will be compiled in a practice-oriented sector guideline. This should be used to help in decision making during detailed risk assessment, define handling instructions, as the foundation for remedial measures to be performed as well as for progress control in the aftercare phase.

For the conception of the sector guideline the following four major tasks emerge, which overlap all projects in this

Thematic Network:

- quantification of the transformation and prognosis of the transport of explosives and their metabolites in the soil and the groundwater (emphasis on polar nitroaromatic compounds)
- advancement and validating of standardised analysis procedures for explosives and polar nitroaromatics in the soil and the groundwater
- transfer of the results gained in laboratory and on the small scale to site conditions
- evaluation of natural attenuation potentials determined from the aforementioned questions (1-3) and work on the guidelines.

P 5.1	Use of natural attenuation processes in TNT contaminated upper soils (site: TNT-factory Clausthal-Zellerfeld)
P 5.2	Prognosis and monitoring of natural attenuation of nitroaromatic compounds in a karstified aquifer (site: TNT-factory Stadtallendorf)
P 5.3	Examination of natural attenuation in explosives contaminated aquifers with respect to environmental conditions (site: TNT-factory Torgau Elsnig)
P 5.4	Investigation of soil and groundwater on polar nitroaromatics and related compounds - quality control
P 5.5	Investigation of biological and chemical processes in soils and groundwater under different environmental conditions
P 5.6	Dendrotolerance against compounds typical of explosives in contaminated soils and fate of [14C]-trinitrotoluene und [14C]-RDX in coniferous wood)

Tab. 6 - Projects of TN 5

*TN°6 Mining and sediments*

The final goal will be the production of a sector guideline for the Thematic Network 6 in which natural attenuation processes for both anthropogenic brown coal spoil heaps and industrially polluted river sediments will be explained. This sector guideline will note the definitive results and will contain procedural instructions for the target groups identified as: The bodies responsible for the polluted areas, regulatory authorities, and engineering companies. A methodology will be sketched out to evaluate the progress of natural attenuation processes in brown coal wastes and contaminated river sediments and to characterise the temporal behaviour of the pollutant retention as well as its time scale.

P 6.1	Methods of determination, assessment and forecasting for the intrinsic/temporarily enhanced pollutant retention in contaminated sediments (site: floodplain area Spittelwasser)
P 6.2	The importance of reductive processes in changes to groundwater constitution in brown coal spoil heaps (site: brown coal spoil heaps Jeßnitz)

Tab. 7 - Projects of TN 6

*TN°7 Prognosis, modelling*

The Thematic Network 7 is a cross-sectional network organised by the KORA funding priority. The specific role

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given to TN 7 following this classification lies in solving cross-sectional tasks, such as evaluation, prognosis, modelling and process control. The results presented in TN 7 are essential for the success of the investigations, because the use of ENA/NA processes during risk evaluation and within the framework of remediation requires a reliable, model-supported prognosis.

The emphasis of the work in the coordination project will be focused on the production of a chapter of the recommendation handbook to be compiled by the KORA Management. Questions involve tuning of the model-supported, process explanatory epignose with the current process monitoring and model-supported prognosis at the centre of interest. Thus the foundations for durable prognosis models will be created.

Currently, TN 7 includes three projects. The main item of the joint project 7.1 is the development of an information and simulation system for the computer based evaluation of exploration strategies, redevelopment, and monitoring. The second project 7.2 in TN 7 investigates the time variability of groundwater flow conditions influencing the spatial development of plumes. In 7.3 an efficient tool for the numerical simulation of reactive transport of contaminants in the unsaturated zone will be developed.

P 7.1	Virtual Aquifer (VA) - Computer supported evaluation of investigation-, remediation- and monitoring-strategies regarding the natural attenuation and enhanced natural attenuation potential of contaminated soils and groundwater
P 7.2	Temporal variability of groundwater flow conditions in relation to the quantification of natural attenuation processes on contaminated sites
P 7.3	Modelling of the reactive transport of contaminants in the (un)saturated zone for the prognosis of natural attenuation

Tab. 8 - Projects of TN 7

*TN°8 Evaluation, legal issues, acceptance by official bodies and the general public*

The elaboration of scientifically, socially, ecologically and legally established procedures is essential when considering NA in terms of hazard review, preparation, execution and evaluation of the success of measures to reduce the hazard to the environment and public health.

While Thematic Networks 1-7 are primarily concerned with scientific investigation, technical matters and organisational methodology, Thematic Network 8 concentrates mainly on solving economic, legal, social and ecological questions.

A fundamental objective of Thematic Network 8 is to use established scientific principles together with the concerted investigations undertaken by the participating organisations to compile the handbook of recommendation.

To respond to the following and further question arising during the completion of the funding priority the coordinator

of Thematic Network 8 maintains close cooperation within TN 8 and also with the coordinators of the other Thematic Networks (1-7) and the KORA Management.

The following questions are of particular relevance:

- under what circumstances will a legally binding implementation of NA processes in the decontamination process be possible? Which explanation and line of argument is necessary?
- how can prognoses of the subsurface involving long time observation periods be expanded into risk assessment or remedial investigation or rehabilitation objectives/ remedial actions?
- how can the social acceptance of NA be appraised (citizens' participation and transparency of decision making)? Which factors influence social acceptance?
- which possibilities of regulation and inclusion of NA-processes in rehabilitation practice do exist?
- how can MNA- and ENA processes be economically and ecologically evaluated especially considering the long term monitoring required?

P 8.1	Development and prototypic proving of an integrative conception for risk communication at NA-/ENA-remedial actions for contaminated sites
P 8.2	Techno-economical and environmental assessment and optimisation of monitored and enhanced Natural Attenuation for contaminated soil and groundwater remediation
P 8.3	Examination of the legal conditions for the utilization of intrinsic retention and degradation processes in remediation tasks

Tab. 9 - Projects of TN 8

*Cross-section topics*

The project members of the eight thematic networks will form working groups on cross-section topics, which will rank higher than the thematic networks. The cross-section topics will be discussed, for instance, in special workshops. The aim of the workshops is to determine certain procedures for general use within KORA. These procedures will be collated and added to the handbook of recommendations. At present the following cross-sections are considered to be necessary:

1. sampling, investigation, monitoring;
2. microbiology, isotopes;
3. geology, investigation;
4. transport, modelling;
5. legal aspects.

*Steering Committee*

The Steering Committee is a body, whose members are nominated by the Federal Ministry of Education and Research to support the execution of the funding priority. These members include renowned experts from the Federal and State

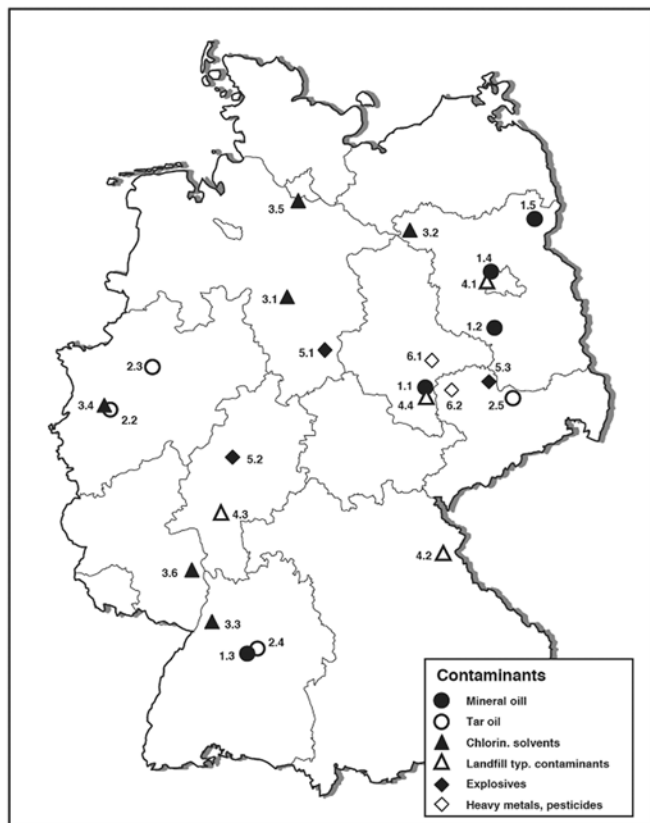


Fig. 1 - The project site of KORA

Ministries, regional associations, regulatory authorities, and professional and trade organisations. The main functions of the Steering Committee are:

- to pass on impulses from the practical end users to the researchers
- to monitor the success of cross section projects and thematic networks
- to ensure that the R&D results reach the end users and their practical operations quickly.

Thus the members of the Steering Committee exercise an important control function over the funding activity. It is the responsibility of the members of the Steering Committee, assisted by the KORA Management and the coordinators, to put forward recommendations for possible necessary legislative measures arising from R&D results of the funding priority.

#### *The KORA Management*

The KORA Management is assigned to actively supporting all participants in the funding priority. They should promote the collaboration of the individual thematic networks to present a joint recommendation handbook and compile this using the knowledge and experience gained in the funding priority.

Furthermore, the general public is kept informed about the results of the funding priority through appropriate public relations work.

#### **RUNTIME AND MONEY**

The German funding priority KORA of the BMBF started in late summer 2002. The runtime is limited until end of 2007.

The funding exceeds  $\square$  20 million of the total expenditures of  $\square$  25 million and will be provided by the Federal Ministry of Education and Research.