# WATCH
# Water Catchment Areas:

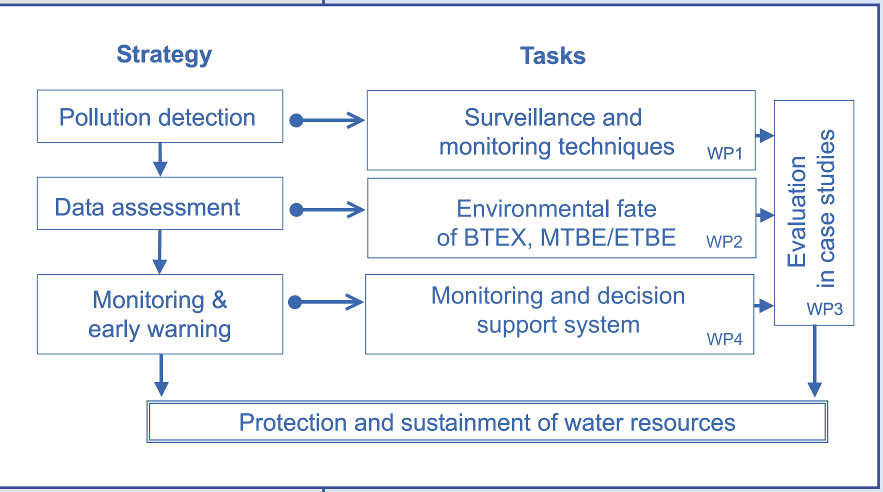
## Tools for Management and Control of Hazardous Compounds

- Objectives
- Results
- Perspectives

# EDITORIAL

In many European regions groundwater is an important resource for drinking water supply. It strongly interacts with the overlaying soils and related surface water systems. As groundwater quality is a parameter that reacts slowly and with some retention to environmental impacts, it needs special attention for sustainable management. This becomes even more important in the light of the European legislation: The water framework directive, the draft groundwater daughter directive and the proposed soil protection act. The water legislation requires e. g. the set up of monitoring programmes and measure plans to keep and bring water resources to a good quantitative and qualitative status.

Beyond this the increasing spreading of anthropogenic compounds, from trace amounts to massive pollutions require advanced detection strategies, an improved understanding of environmental fate and behaviour as well as intelligent strategies to ensure a sustainable management of groundwater resources in terms of monitoring, early warning and decision support.



The WATCH "Water catchment areas: Tools for management and control of hazardous compounds" project approach

As target pollution for this project Methyl tert-butyl ether (MTBE) was selected. MTBE as a fuel oxygenate replaced lead beginning in the 80's but mainly starting in the early 90's. Compared to other fuel constituents and some of the most common groundwater pollutants MTBE is more persistent and can be found in groundwater systems in all concentration ranges from the ng/l level as "trace concentrations" up to the g/l level at "hotspots". In addition MTBE is wide spread in surface waters often up to several 100 ng/l. Being wide spread in aquatic environments poses the risk to ground- and surface water to be affected in their quality status.

WATCH faces these challenges by developing tools for management and control of hazardous compounds in ground-water catchment areas.

The developments of WATCH

- Sub-surface near infrared reflectometer sensor with associated data collection and transmission capabilities for the online remote identification of free-phase hydrocarbons
- Fully automated P&T-GC/MS method for the trace analysis (ng/l-µg/l levels in water, µg/kg in sediments) of MTBE, main degradation products (TBA, TBF) and other oxygenated additives (ETBE, TAME, DIPE)
- A competitive MTBE-enzyme linked immunoassay testkit (ELISA) with a sensitivity of standards down to 0.5-0.05 µg/l, and an application range down to 500-50 µg/l
- An immuno-flow through and a magnetic bead format assay with application ranges < 50 µg/l are under development
- Elaboration of MTBE degradation pathways including inhibiting and stimulating effects
- Integrated management protocol including a conceptual model protocol and a remedial action protocol
- Demonstration of project developments in two case studies help to protect and sustain ground water quantity and quality in Europe.

# NEAR INFRARED FUEL LEAK SENSOR

At the start of WATCH, a prototype fuel leak sensor, developed by Cranfield University, had been developed to the point of 'proof of principle' in identifying insulating oil leakages from sub-surface power distribution cable joint-bays.

The WATCH programme extended this technology via the following objectives:

- To assess device performance as an early warning tool for identification of free-phase hydrocarbons from leaking underground storage tanks (USTs).
- To produce a ruggedised unit amenable to low cost manufacture.
- To assess device performance towards different fuel types, soil types and degrees of matrix saturation.
- To develop cheap compatible systems for on-board data acquisition and transmission.
- To field-test arrays of the sensor in contained environments.
- To assess the sensor as an in-borehole device for monitoring free-phase hydrocarbon contamination of drinking water.
- To evaluate the socio-economic relevance of the fuel leak sensor in the early detection of hydrocarbon fuel releases.

## Description of results

### The Sensor Head

The sensor assembly is housed in a sealed metal tube (70 x 15 mm) incorporating a polycarbonate window (figure 1).

Figure 1: Hydrocarbon sensors and exploded view of sensor head

A reflective hydrocarbon-specific membrane is positioned over this window, which turns translucent on contacting free-phase hydrocarbons. The device may be placed in the interstitial space between double skinned tanks or directly within soil matrices.

A near-infrared (NIR) light-emitting diode and adjacent light-receiving phototransistor are built into the sensor head. The amount of membrane-reflected light received by the phototransistor is continuously monitored as a voltage. On contacting free-phase hydrocarbon, the reflectance of the membrane changes, reducing the amount of incident light upon the phototransistor, culminating in an increase in output voltage (figure 2).

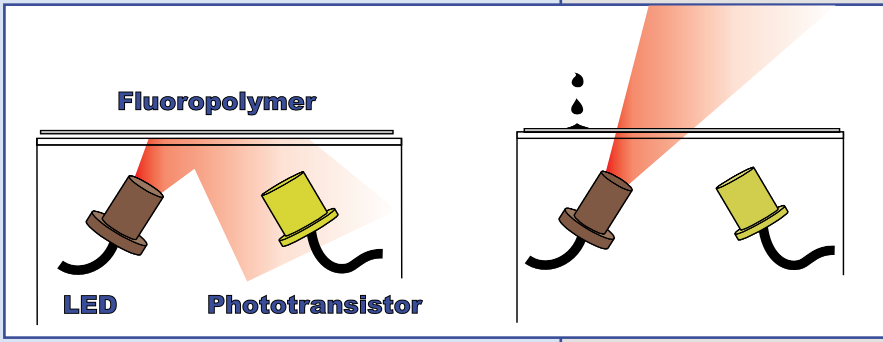


Figure 2: LED signal emission and reflection

The electronic circuitry is mounted on a small printed circuit board which fits inside the sensor assembly. A flying lead connects the sensor to the data acquisition / power supply. The sensor provides two outputs – a digital signal that triggers when the reflected signal drops below a predetermined level, and an analogue voltage that is directly proportional to the reflected IR signal level. Multiple sensors may be linked to create a distributed system for monitoring large scale hydrocarbon repositories. Water and alcohol-based solvents have no effect on membrane reflectivity.

### Data Acquisition and Communication

Up to 8 sensors can be connected to the 'BioDAQ' data acquisition system. The system supplies power to the sensor heads and records sensor outputs. BioDAQ performs on-board data processing, such as detecting alarm conditions and forwards data to other systems via a wired or wireless data link.

The BioDAQ and sensor units consume microAmp currents, thus the system can operate for extended periods on AA batteries. Sophisticated power management features are incorporated, including a 'sleep mode' function to prolong battery life. Signal outputs below the alarm threshold are date stamped and stored in the on-board memory and/or sent to the operator as required. Breach of the alarm threshold triggers communication.

A RS232 serial connection with Labview software allows simple visualisation of transmitted data. Two wireless technologies have so far been implemented: a GSM Cellphone Modem and a Point to Point FM wireless link, with wireless Ethernet link currently under consideration.

## Membrane reversibility and selectivity

Fluorotrans membrane (Pall Corporation Inc.) gave the largest response to all fuel types and was sufficiently rugged for prolonged field usage. The membrane had a rapid 'recovery' with an evaporation/baseline recovery of 3.2 min. Similar tests performed in water after fuel exposure (closer simulation of the real word situation) resulted in longer recovery times (12 min., petrol in water). Slightly elevated baselines were evident after each successive analyte addition, indicating that only limited regeneration was possible. Examination of the response-time profiles indicated that different fuels yielded different signal response profiles. Rates of fuel evaporation/migration were used to distinguish between fuel types.

## Detection of different fuels in a range of soils with varying water saturation

Tests were performed on sand, clay and sand-clay mixtures. Petrol, diesel, central heating oil and MTBE were tested at different contamination levels. The water content varied from dry to 100% saturated. Around 8% w/v fuel in soil is required to trigger a sensor response. Dry soils provided optimal conditions for rapid sensor response, whereas poor responses were observed in 100% saturated homogeneous heavy clay soil.

## Sensor trials:

## Laboratory testing:

Initial laboratory tests were performed using a 9-sensor distributed network within a tank with simulated water flow and UST leakage (figure 3). It was found that:

- The sensors perform optimally under non-saturated conditions
- The sensors were able to identify the direction and rate of free-phase fuel migration
- Sensors were regenerable under certain conditions
- Sensors suitability to field trials was indicated.

Figure 3: Laboratory trials of fuel leak sensors

## Large-scale lysimeter (field) trials

Field-based trials were performed in a 1.0 x 0.8 m lysimeter. The open top allowed natural flow-through of rain water. Trials were performed with sand and soil. A 19 x 16 cm 'UST' complete with leakage point was placed onto a gravel bed within the matrix (figure 4).

Figure 4: Positioning of sensors and leaking UST tank in lysimeter field trials

## NEAR INFRARED FUEL LEAK SENSOR

In a typical trial, 3 sensors were placed close to the base of the leaking vessel, with a further 4 sensors placed at uniform depths below the vessel. The sensors were linked up to the on-site data acquisition unit and sampled hourly over several weeks. The data was stored and relayed to the operator by daily email.

The results from trial 2 are shown in figure 5. All sensors triggered except sensors 3 (positioned to one side under the leaking UST) and 7 (base of lysimeter, 1m depth). Excavation of the sensors indicated that they had not contacted the fuel. Sensors 1 and 2, closest to the leak point, triggered within 6 h of fuel addition. The signals of all triggered sensors remained high, regardless of weather conditions.

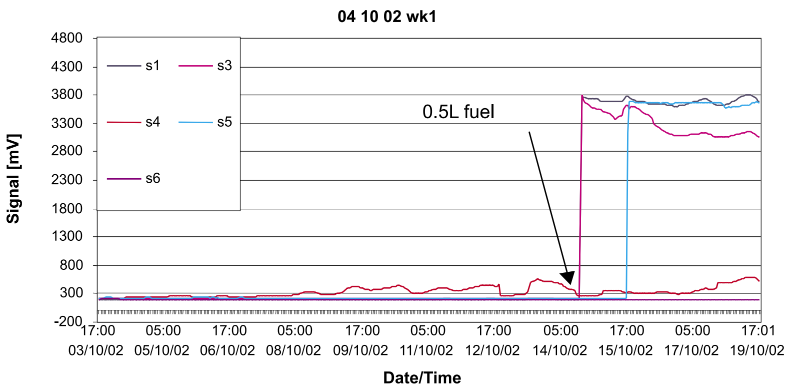


Figure 5: Fuel leak sensor data output from lysimeter trial 2

### Conclusion and Perspectives:

The integrated fuel-leak/immunoassay approach has implications within the European Union Water Framework Directive (WFD), by directly contributing to groundwater protection, essential given that groundwater supplies 65% of all Europe's drinking water. The directive states that monitoring programmes should be operational as a basis for water management by December 2006, an aspiration that is supported by the early warning and monitoring tools developed in WATCH.

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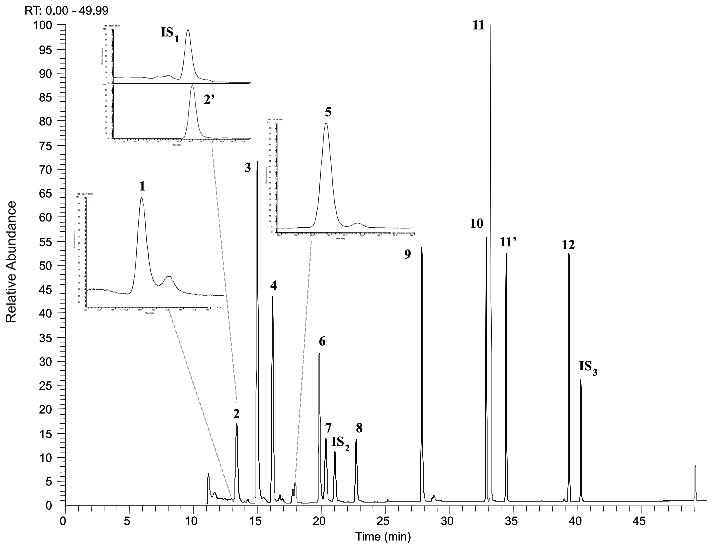
## ANALYSIS OF MTBE AND RELATED COMPOUNDS IN SOIL AND GROUNDWATER

An analytical protocol for sample handling and analysis of methyl tert-butyl ether (MTBE), its main degradation products, tert-butyl alcohol (TBA) and tert-butyl formate (TBF); other gasoline additives, oxygenate dialkyl ethers: ethyl tert-butyl ether (ETBE), tert-amyl methyl ether (TAME) and diisopropyl ether (DIPE); aromatics: benzene, toluene, ethylbenzene and xylenes (BTEX) and other compounds causing odour events in groundwater such as dicyclopentadiene (DCPD) and trichloroethylene (TCE) was achieved by CSIC. Three different methods were developed to analyse target compounds in water, soil and gasoline. Innovative fully automated purge and trap coupled to gas chromatography – mass spectrometry (P&T-GC/MS) was optimised for the simultaneous determination of above mentioned compounds, which permitted to detect concentrations at ng/l (ppt) to µg/l (ppb) in water and µg/kg in sediments. The use of mass spectrometer allows unequivocal identification of the analytes present in environmental samples. Special attention was given to the determination of polar MTBE degradation products, TBA and TBF, since not much data on method performance and environmental levels is given on these compounds in groundwater. The protocol also includes different parameters to guarantee the quality assurance of the analytical methodology.

From the data reported, it is clear that MTBE poses a problem of groundwater contamination and severe monitoring programs at risk sites (potential gasoline point sources) are needed to know the extend of this contamination and start remediation actions. Appropriate tools are thus necessary. The data obtained from these monitoring sites will be useful to know the presence, behaviour of the MTBE contamination plume and its degradation rate under the subsoil conditions. This protocol includes guidelines for transportation of contaminated groundwater and soil samples from different European sites to the central laboratory and the parameters of extraction, identification, and quantification of the pollutants in these samples.

In general, the application of this protocol can allow to monitor and control risk sites or water catchment areas. Contaminated gasoline "hot spots" can be identified with MTBE levels up to US Environmental Protection Agency drinking water advisory limit values (20-40 µg/l) or taking into account stricter measures, as Swiss guideline value for groundwater of 2 µg/l based on precautionary principle, protecting in this way end-users. The presence of TBA (MTBE and ETBE key intermediate) in drinking water merits similar (or even more) consideration than its parent compound due to its complete water solubility and demonstrated toxicity and carcinogenicity in rats and mice. Therefore, the present analytical methodology permits to detect this pollutant from low levels (0.1 µg/l).

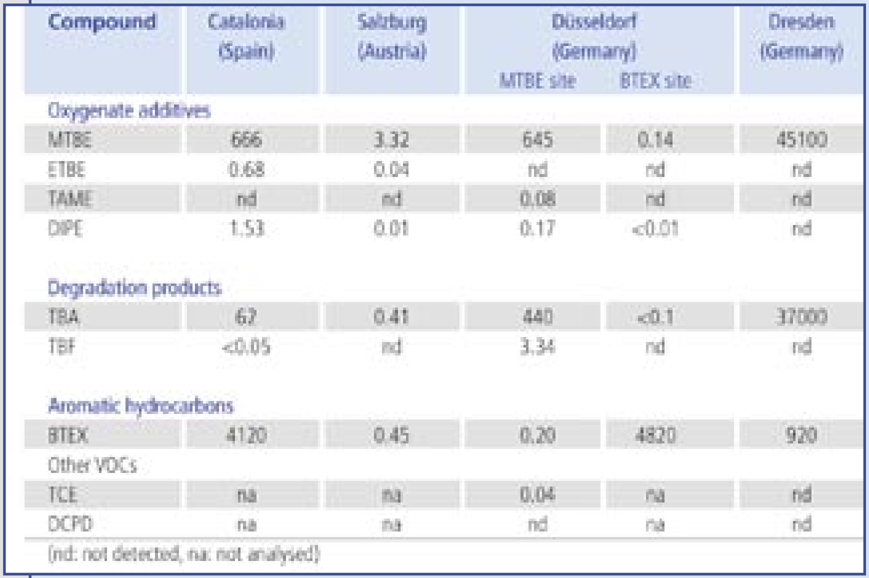
Figure 1: Total ion chromatogram (TIC) in Selected Ion Monitoring (SIM) mode for a 1 µg/L spiked groundwater.



**Compound identification number:**
1= TBA (m/z = 59), 2 = MTBE-d$_3$ (IS1: m/z = 76)+ MTBE (2': m/z = 73), 3 = DIPE, 4= ETBE, 5= TBF (m/z = 59), 6= benzene, 7= TAME, IS$_2$= fluorobenzene, 8= TCE, 9= toluene, 10= ethylbenzene, 11= m+p-xylene, 11'= o-xylene, 12 = DCPD and IS$_3$= 1,2-dichlorobenzene-d$_4$.

In practice, diverse water monitoring campaigns were carried out from 2001 to 2004 in different sites located near gasoline point sources all over Europe: Catalonia (Spain), Salzburg (Austria), Düsseldorf and Dresden (Germany) and Faro (Portugal). The most analysed samples contained MTBE at levels varied between 0.01-670 µg/l. But the highest concentration of MTBE detected in groundwater (45 mg/l) was found under a refinery. Therefore, several "hot spots" were identified in these study sites with levels up to 20-40 µg/l and even some of them also exceeded Danish suggested toxicity level of 350 µgl. In addition, some inter-laboratory comparisons by analysing groundwater samples from these sites were done obtaining similar results among labs. In addition, the analysis of samples from SENSPOL field tested in Koblenz (Germany) permitted the elaboration of a protocol for immunoassay validation to compare the response between developed immunoassay methods (by Cranfield and Diaclone) and GC-MS method (by CSIC).

Of special interest was a two-year monitoring program in a gasoline contaminated site of Düsseldorf (middle-west of Germany) that was carried out to determine the presence, behaviour (horizontal movement and vertical profile) and evolution of the 12 target gasoline additives in a total of 96 samples from 14 groundwater wells. The origin of the contamination was suspected to be a gasoline spill at a gas station. The study of the plume showed that the distribution of the MTBE and TBA in the aquifer forms a similar vertical concentration profile which is influenced by the groundwater flow direction. And as a result of WATCH partners' collaboration, a conceptual model



| Compound | Catalonia (Spain) | Salzburg (Austria) | Düsseldorf (Germany) MTBE site | Düsseldorf (Germany) BTEX site | Dresden (Germany) |
|---|---|---|---|---|---|
| Oxygenate additives | | | | | |
| MTBE | 666 | 3.32 | 645 | 0.14 | 45100 |
| ETBE | 0.68 | 0.04 | nd | nd | nd |
| TAME | nd | nd | 0.08 | nd | nd |
| DIPE | 1.53 | 0.01 | 0.17 | <0.01 | nd |
| Degradation products | | | | | |
| TBA | 62 | 0.41 | 440 | <0.1 | 37000 |
| TBF | <0.05 | nd | 3.34 | nd | nd |
| Aromatic hydrocarbons | | | | | |
| BTEX | 4120 | 0.45 | 0.20 | 4820 | 920 |
| Other VOCs | | | | | |
| TCE | na | na | 0.04 | na | nd |
| DCPD | na | na | nd | na | nd |

(nd: not detected, na: not analysed)

Table 1: Maximum detected levels (in µg/l) of target compounds found in European studied groundwaters.

Figure 2: Fully automated P&T-GC/MS analytical system: SOLATek 72 Multi-Matrix Vial Autosampler coupled to a Purge and Trap Concentrator Tekmar 3100 (both Tekmar-Dohrmann, USA) and a Trace GC coupled to a Voyager MS (ThermoQuest Finnigan, USA).

for the distribution of MTBE in the aquifer was developed based on the chemical properties of the pollutants, the hydrogeological conditions of the aquifer and the microbial degradation capacity. This is one of the first studies of groundwater contamination of together MTBE and TBA in Europe due to the difficulty of TBA analysis at trace concentrations.

Furthermore, the wide range of application of P&T system to analyse different aqueous matrices (rain, domestic waste, sewer and sea waters) in the vicinity of Faro (Portugal) has permitted to observe fuel additives ubiquity in the aquatic environment and their daily and seasonal variability close to urban centres.

## Conclusions and Perspectives:

An analytical protocol for sample handling and analysis of MTBE, its main degradation products, other oxygenated dialkyl ethers and aromatics present in gasoline, and other compounds causing odour events was achieved by CSIC. This fully automated P&T-GC/MS was optimised and applied to environmental samples for the simultaneous determination of above mentioned compounds, which permitted to detect concentrations at trace levels (ppb) in water and sediments. This protocol is ready for use by other laboratories, water suppliers and public authorities to monitor and control risk sites or water catchment areas.

Figure 3: Sampling at multilevel well on a BTEX contaminated site in Düsseldorf, July 2003.

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# Immunoassay for Field-based Determination of Methyl Tert-Butyl Ether

## Tasks and targets

Concerns over the health and environmental hazards associated with the addition of lead-based compounds into fuels, has led to the use of alternative fuel oxygenate compounds. Methyl tert-butyl ether (MTBE) is the most widely used fuel oxygenate, being found in ~80% of fuels at up to 15% volume. Current studies suggest that MTBE is less toxic than the lead-based additives, although longer term studies are still on-going. However, MTBE exhibits a particularly unpleasant taste and odour, even at trace levels. This factor, coupled to the high solubility and long-term persistence in the environment has resulted in the contamination of drinking water. Whilst many standard methods exist to determine MTBE, these are laboratory based and may suffer long sample turnaround times, during which a pollution incident may escalate. Correspondingly there is a demand for rapid, field-based tests that may be used to screen suspected contaminated sites and provide timely end-user information.

As part of the WATCH programme, an MTBE immunoassay was developed to fulfil this need. Immunoassays make use of the specific binding of target analytes by biological binding proteins called antibodies. The following tasks were undertaken by the WATCH programme to develop an MTBE specific immunoassay:

- Production of a new antibody cell line producing monoclonal antibodies with binding specificity towards MTBE
- Production of immunoreagents for construction of MTBE immunoassays
- Determination of optimum immunoassay format
- Testing of immunoassay with synthetic samples and environmental samples collected from contaminated site
- Evaluation of immunoassay performance
- Examination of immunoassay cross-reactivity towards structurally similar compounds.

## Description of results

### Development of monoclonal antibodies

The usefulness of monoclonal antibodies (mAbs) stems from their specificity of binding, their homogeneity and their ability to be produced in unlimited quantities.

To increase the ability to induce an immune response, MTBE was coupled to bovine serum albumin (BSA), a larger protein molecule called carrier.

Hybridomas were produced by fusing the mouse myeloma cell line X63Ag8.653 and antibody secreting cells isolated from the spleen of MTBE immunised BALB/c mice. The myeloma cells provide the correct genes for continued cell division and the antibody-secreting cells provide the functional immunoglobulin genes.

Hybridoma screening was done by ELISA using coated BSA conjugated MTBE, BSA alone or irrelevant BSA conjugated antigens. Only the hybridomas secreting antibodies which specifically react on BSA conjugated MTBE were selected. After a positive culture supernatant has been identified, the cloning of the antibody-producing cell was performed.

Four stable clones of hybridoma cells were isolated. The mAbs of IgG1 isotype anti MTBE are B-A48, B-B47, B-T31 and B-E40.

### Selection of optimum MTBE Immunoassay format

A wide variety of immunoassays can be used to detect and quantify antigens. There are many variations on the ways in which immunoassays can be performed. Three classes of immunoassays can be generated: (1) the two antibody sandwich assay, (2) the antigen capture assays and (3) the antibody-capture assays.

## Model N°1 :
## the two antibody sandwich immunoassay

The Elisa sandwich immunoassay incorporates the use of two different mAbs, each directed against different epitopes of the antigen needed to be measured. The antigen in the sample or standard binds to the antibody-coated well used as a catcher Ab. The labelled second antibody used as a tracer Ab then forms a "sandwich" (antibody-antigen-antibody). After addition of chromogenic substrate for the enzyme used and then a stop solution, the resulting colour is reported in optical density (OD) units. The intensity of the OD is directly proportional to the concentration of the antigen in the sample. The concentration is calculated on the basis of a standard curve.

## Model N°2:
## the antigen capture immunoassay

The Elisa competitive immunoassay is based on the binding competition between the antigen in the sample and the labelled antigen for the antibody-coated wells. The mAbs are used as catcher antibodies. The intensity of the OD is inversely proportional to the concentration of the antigen in the sample.

## Model N°3:
## the antibody-capture immunoassay

The Elisa competitive immunoassay is based on the binding competition between the antigen in the sample and the coated antigen. The mAbs can be used as tracer antibodies. The intensity of the OD is inversely proportional to the concentration of the antigen in the sample.

Experiments have been done in order to define the optimum MTBE immunoassay format. The following issues were elucidated: (1) the choice to make a competition or a sandwich ELISA assay, (2) the specificity and the sensitivity of the immunoassays.

The ELISA selected was a competitive ELISA using immobilised BSA conjugated MTBE antigens and the tracer mAb B-E40. The major degradation products TBF and TBA are detected by ELISA without significant detection of unrelated components such as toluene and benzene.

## MTBE competitive ELISA:
## Assay Development

A competitive immunoassay for MTBE was developed by partners Diaclone and Cranfield. The competitive immunoassay format exploits the specific binding of the anti-MTBE antibody for the target MTBE analyte. In this particular assay format, a limiting quantity of MTBE-BSA immunogen (essentially an MTBE 'analogue') is immobilised onto a solid phase support, such as a microtitre well wall or magnetic bead (figure 1). During the assay, the end-user supplies sample, containing free MTBE analyte and anti-MTBE antibody (non-limiting), either free or conjugated to a binding protein (streptavidin). The free MTBE antibody will either bind to the free MTBE or immobilised MTBE analogue.

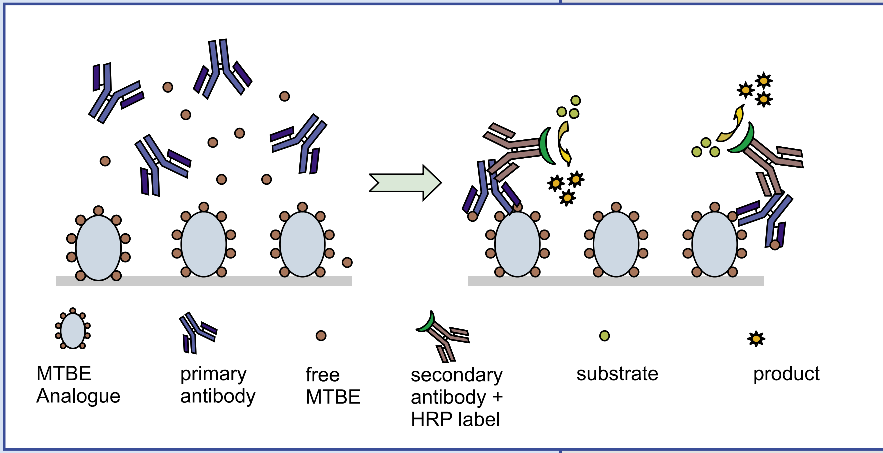

Figure 1: Competitive ELISA immunoassay, with immobilised MTBE analogue. Free MTBE competes with immobilised MTBE for anti-MTBE primary antibody binding sites. Following washing, residual immobilised antibody is determined using secondary antibody with HRP label. Following a further washing step, HRP label activity is determined. The amount of product formed is inversely proportional to the amount of free MTBE present in the original sample.

The binding process is competitive, thus the more free MTBE present, the greater the amount of antibody that will bind to this analyte and hence will be removed from the system on washing the microtitre wells. Conversely, the lower the amount of free analyte, the greater the amount of antibody binding to the analogue immobilised on the solid phase support. The amount of immobilised anti-MTBE antibody is determined by addition of tracer material, in this case the enzyme horseradish peroxidase (HRP), either linked to biotin (which has binding affinity for streptavidin) or a 'secondary' antibody having affinity for the 'primary' anti-MTBE antibody (grown in mouse and hence having binding affinity to the mouse-raised anti-MTBE antibody). Enzyme activity is determined by addition of enzyme substrate that produces a colour in the presence of enzyme that may be recorded using a simple portable photometer.

The overall process is simple to perform, requiring only the sequential addition of assay reagents followed by incubation and washing steps. The procedure can be completed in ~2h and allows multiple sample throughputs. The simplicity of the process allows kit usage in field-based locations without recourse to centralised laboratories. The assay is often referred to as an Enzyme-Linked ImmunoSorbent Assay (ELISA).

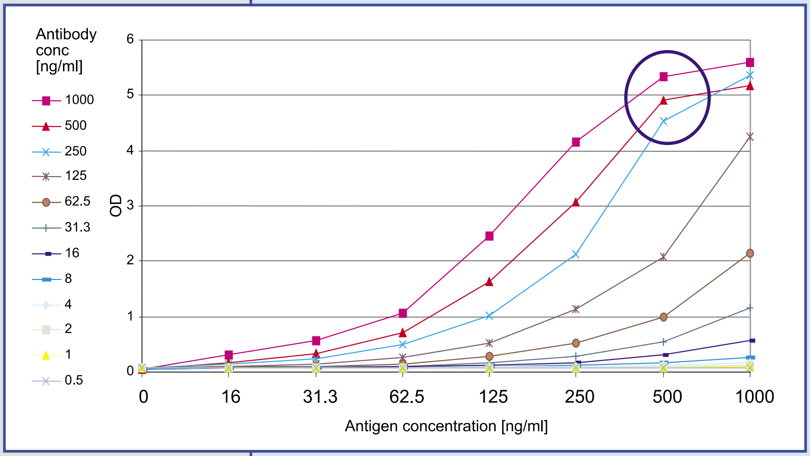

Figure 2: Checkerboard titration used to determine the optimum loading of coating antigen and primary antibody.

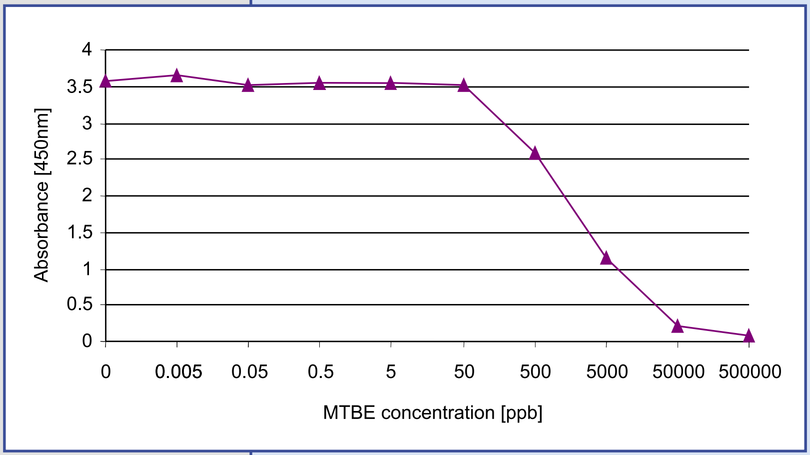

Figure 3: MTBE competitive ELISA calibration curve constructed with MTBE standards diluted in buffer. An assay calibration range of 50-5000 ppb (ng $l^{-1}$) is evident.

## ELISA secondary antibody linked to HRP

Optimal concentrations of both Ag and Ab (biotinylated and native) were determined by checkerboard assay. The optimal concentrations of coated antigen conjugate and biotinylated and native Ab were all found to be 500 ng/ml (figure 2). Full details of the protocol may be found elsewhere[1].

## Microtitre plate MTBE ELISA performance: synthetic samples

The ELISA protocol was first developed using buffer solutions spiked with various quantities of MTBE. The classic sigmoidal response curves (absorbance versus analyte concentration), characteristic of competitive ELISAs were observed (figure 3).

## Real samples testing programme

The following samples have been tested:

- Samples from SENSPOL Koblenz technical meeting
- Samples supplied by partner TUD to Diaclone and Cranfield University
- Groundwater samples supplied to Cranfield by Salzburg AG

SENSPOL, Koblenz: DECHEMA, Diaclone and Cranfield were given the opportunity to test the MTBE immunoassay under 'blind' conditions at the SENSPOL Technical Meeting on Problems related to Diffuse Pollution Sources[1]. A summary of the results is given in figure 4. A greater variation in response is evident using the MTBE ELISA, but the overall trends indicated by the ELISA with respect to MTBE levels are comparable with those values obtained by GC-MS.

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[1] Huntley, S., Track, T., Setford, S., Vermot-Desroches, C., Bourdin, L., Wijdenes, J. and Rosell Linares, M. On-site application of the novel Methyl tert- butyl ether (MTBE) Enzyme Linked Immunosorbent Assay. SENSPOL Technical Meeting on Problems related to Diffuse Pollution Sources: Characterisation of Sediment, Dredged Material and Groundwater, 28-31 October 2003, Bundesanstalt für Gewässerkunde (BFG), Koblenz, Germany.

Samples from TUD: Samples from an MTBE contaminated site were supplied from TUD, with samples also being analysed by GC. Both MTBE and TBA (tert-butyl alcohol) were present in the samples. Higher concentration values (typically ~100% higher) were reported by ELISA with all samples being in the range 5-50 ppm. The observed increase in OD values was possibly due to cross-reactivity from other structurally related compounds, such as TBA, in the sample test solutions.

## Alternative assay formats

### Magnetic bead format

In order to simplify the MTBE immunoassay for use in the field, the immobilisation of the MTBE analogue to micro-scale magnetic beads has been attempted. Preliminary results (figure 5) indicate that a superior limit of detection is possible using this assay format.

### Enzyme-Linked Immunosorbent Flow Assay (ELIFA)

Automation of the assay using a flow-through approach, in which key assay components are pre-immobilised to a membrane, was also examined in order to further simplify the assay format. The principle of the approach has been proven, but further assay refinement is required to reduce the incidence of non-specific binding of enzyme label to the solid phase support.

Figure 6: Immunoassay and colour development during laboratory testing

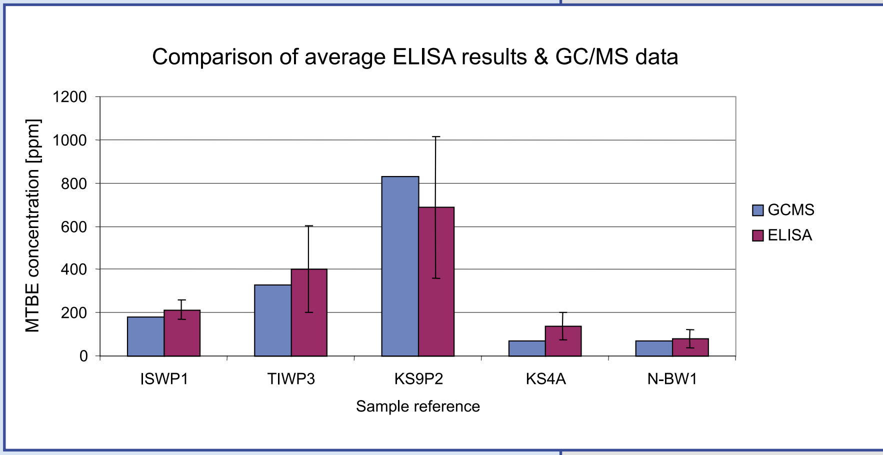

Figure 4: ELISA results versus GC-MS results for spiked MTBE samples provided 'blind' during the SENSPOL Koblenz technical meeting.

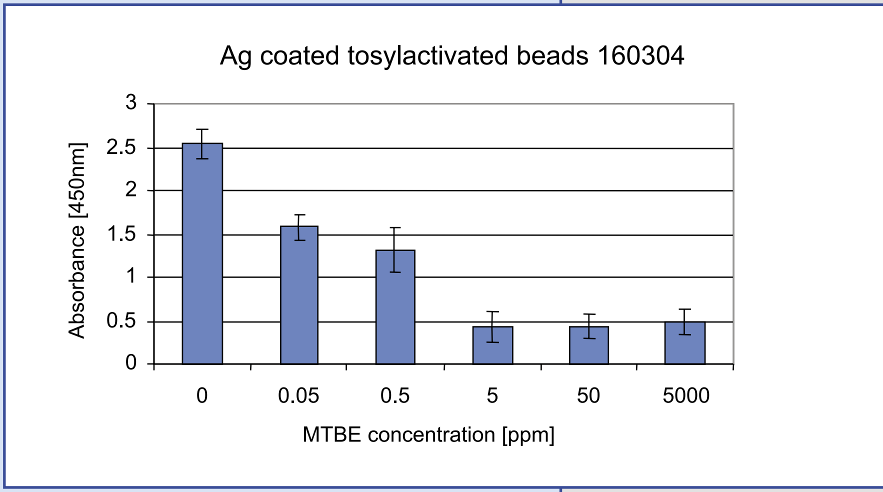

Figure 5: MTBE immunoassay with antigen coated onto tosylactivated magnetic beads. The immunoassay, when in the magnetic bead format, can identify lower levels of MTBE contamination (<50ppb) compared to >50ppb in the microtitre plate format.

## IMMUNOASSAY FOR FIELD-BASED DETERMINATION OF METHYL TERT-BUTYL ETHER

### Conclusion and Perspectives:

For the first time, a simple immunoassay has been developed for the field-based determination of the fuel oxygenate MTBE. A large-scale development programme was required to obtain antibodies of the desired binding specificity due to the small size of MTBE. Promising monoclonal antibody cell lines were produced and tested before selection of the final desired clone and assay development. When working with contaminated groundwater samples, the assay range is 50-5000 ppb MTBE and thus can be used to assess site pollution without the need for costly and time-consuming central laboratory analysis. Certain other structurally related compounds can also be determined using this assay, including TAME and ETBE and the MTBE breakdown products, TBA and TBF. The assay is not designed as a replacement for GC analysis. It is essentially semi-quantitative, but has uses for the rapid decentralised assessment of a site where an MTBE contamination is believed to have occurred and where rapid information to allow near-instantaneous on the spot decision making to be made with respect to pollution incident control and management.

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## ELUCIDATION OF STIMULATING AND INHIBITING EFFECTS ON BIODEGRADATION

Work in the WATCH project focused on early detection and risk assessment decisions of environmental pollutions in drinking water catchment areas, especially those which use groundwater as water source.

For project related research the choice was on a very mobile hazardous compound, the gasoline additive methyl tert-butyl ether (MTBE). Gasoline contains MTBE as an antiknock compound / octane booster which replaced the very toxic lead compounds like tetra-ethyl lead. The extent of MTBE`s usage in EU-countries is around 3 Mio tons a year.

A lot of environmental data show the gasoline additive MTBE as a substance, which has the potential to seriously endanger the quality of groundwater reservoirs in subsurface sediments. Its toxicity is not comparable with the replaced lead compounds, but its sensorial properties make it so problematical. Humans can taste and smell MTBE in water at very small concentrations in a parts per billion range (sensorial threshold value approx. 10 µg/l).

Unfortunately also its physical data, such as high water solubility (up to 60 g/l) and the HENRY-constant (50 – dimensionless form, $\text{CMTBE}_{\text{water}}$ / $\text{CMTBE}_{\text{air}}$, at 20 °C)

Table 1: Exemplary physical data of MTBE in comparison to other volatile organic pollutants.

| | Water solubility [mg/l –20°C] | Boiling point [°C] | Vapour pressure [mbar – 20°C] | Henry-Constant $C_{aq.}$ / $C_{gas.}$ at 20 °C (relation of concentration in water phase to gas phase) [-dimensionless-] |
|---|---|---|---|---|
| MTBE | 42.000 | 55 | 268 | 50 |
| Benzene | 1.750 | 80 | 101 | 4,4 |
| Toluene | 510 | 110 | 29 | 3,7 |
| Ethylbenzene | 140 | 136 | 9,5 | 2,8 |
| Xylols | 200 | 140 | 6,7 | 3 - 4,6 |

predetermine an enrichment of MTBE in groundwater. The effect is intensified by the low adsorption affinity of MTBE in the soil matrix. A further negative aspect is, that the ether linkage and tertiary carbon structure make MTBE relatively recalcitrant to microbial degradation and let fear an accumulation of this compound in the aquatic environment.

Available knowledge on the behaviour of MTBE in groundwater was still very weak. Detailed investigations were necessary to estimate the real risk of moving MTBE plumes in the groundwater. Validation of the recalcitrant and persistent character of MTBE should help in clarifying the expectable extent of natural attenuation of these hazardous compound in groundwater systems.

## Project Tasks:

- Development of a specific, sensitive and reproducible laboratory procedure for MTBE/BTEX quantification
- Characterization of MTBE degradation capacities under groundwater conditions
- Identification of favourable electron acceptors on biodegradation

## Laboratory procedure

A first step was the development of a specific, sensitive and reproducible laboratory procedure for MTBE/BTEX quantification via gas chromatographic analysis. With the used GC/FID-system (6890, Hewlett-Packard) coupled with an automatic headspace sampler (HS40XL, Perkin-Elmer) it is possible to determine these compounds in the environment. The detection limits are 4.0 µg/l (MTBE), 5.0 µg/l (ETBE) and 1.0 µg/l (each BTEX compound). For routine analyses this equipment is sufficient. For recurrent periodical identification it is also possible to use a GC/MS system.

## Soil and groundwater sampling

In order to estimate how natural processes affect MTBE biodegradation and retardation in laboratory experiments, sediment samples had to be obtained from the groundwater zone. Those natural groundwater sediments are expected to contain a sufficient amount of autochthonous bacteria. Retardation effects can be investigated best in original soil samples. Due to the local variation of indigenous microorganisms, significant investigations of natur-ally occurring biodegradation entail using sediment samples from sites with different hydrogeological and geochemical conditions. Therefore soil samples were taken from different sites in eastern Germany, some of which are contaminated by MTBE and BTEX. Additional sediment samples were collected from a project model site in Düsseldorf, western Germany.

## Biological degradation experiments

Comprehensive laboratory experiments on biological degradation were performed under groundwater similarly conditions. They availed to estimate the capacity of natural occurring processes on MTBE degradation in groundwater with respect to favourable electron acceptors (biochemical reaction partners of the organic pollutants, e. g. oxygen, nitrate, iron-III, sulphate). An important aim was to identify electron acceptors that will support MTBE mineralisation.

Degradation experiments were performed with aquifer sediment-samples collected from 13 different sites. Investigations concentrated on the search for effective electron acceptors and on the possible formation of MTBE metabolites. The experiments were established under six different conditions promoting aerobic degradation, denitrification, sulphate reduction, Fe(III) reduction, Mn(IV) reduction and methanogenesis. In additional experiments, the MTBE degradation behaviour of groundwater samples collected in a contaminated aquifer at a refinery site was studied under aerobic and sulphate reducing conditions.

## Aerobic Degradation:

It was clearly apparent that oxygen is the preferred electron acceptor for MTBE biodegradation. Several aerobic (oxygen containing) experimental microcosms showed a significant decrease in MTBE concentrations, even after multiple readdition of MTBE. The sediments of all these microcosms came from sites which had been contaminated by MTBE. Sediments from completely unpolluted sites were unable to biodegrade MTBE in a time scale of 10 months.

Groundwater samples collected in a contaminated aquifer near a second refinery site showed efficient MTBE degradation capacities. The groundwater of these wells had a MTBE contamination of 45 mg/l and no BTEX content. Initial MTBE concentrations of 13 mg/l in the batch experiments (after dilution with aerobic media) could be degraded completely within 2 months. Readded MTBE (up to 80 mg/l) was completely consumed in less than 2 weeks.

## Anaerobic Degradation?

Under anaerobic (oxygen free) conditions no significant MTBE degradation was observed, in spite of the successful achived anaerobic milieu and ongoing electron acceptor decrease in most microcosms. Only some experiments under iron and sulphate reducing conditions seemed to show a MTBE degrading capacity with very low reaction velocities.

## Which other factors affect the MTBE degradation?

Additional experiments showed the inhibiting effects of BTEX (benzene, toluene, ethyl benzene, xylenes) contaminations on MTBE biodegradation. BTEX are typical gasoline contents and range up to 50 Volume-% in gasolines. They are expected as co-contaminants of MTBE in many gasoline spill and leakage incidents.

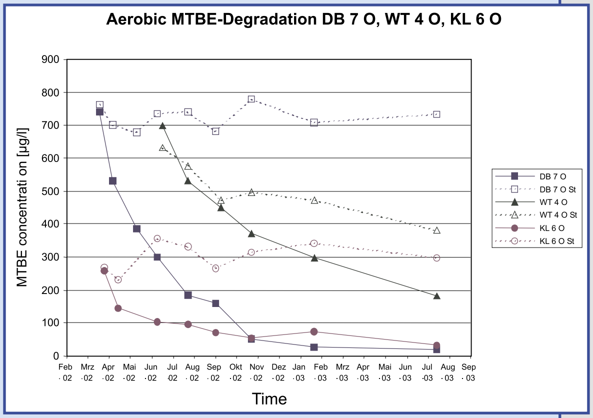

Figure 1: Degradation of MTBE in 3 aerobic microcosms (with aquifer sediment) over 16 months (St = sterile control)

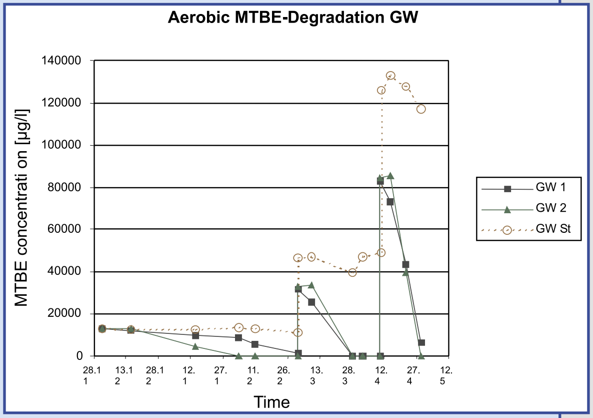

Figure 2: Refinery groundwater experiments GW 1, GW 2 (parallel control) and GW St (sterile control)

BTEX, in comparison to MTBE, are more favoured and more rapidly used substrates for the investigated groundwater sediment bacteria. The "inhibition" appears as an effect of substrate preference causing consecutive degradation of BTEX and MTBE. Also, the postulated MTBE-metabolite TBA was degraded faster by the bacteria culture than MTBE; this observation could explain why TBA does not accumulate during MTBE biodegradation in the experiments.

# ELUCIDATION OF STIMULATING AND INHIBITING EFFECTS ON BIODEGRADATION

Clarity was sought on a cometabolic MTBE degradation during a consumption of other organic Carbon sources. We tested the effect of the known, well degradable, co-substrates sodium acetate, sodium succinate and methanol on biodegradations velocity of MTBE. Often several environmental pollutants which are not effectively useful as the sole C-source can vanish during a cometabolic degradation of microorganisms, which degrade other available primary substrates. The effect can be explained by an unspecific activity of enzymes, which are produced in the metabolism of the primary substrates.

But all these amendments, except methanol, decelerated the degradation of MTBE significantly compared to the batch test without any addition of other C-sources. A real enzymatic co-metabolism was not observed.

## Conclusions and Perspectives:

Experimental results of the WATCH project Work package 2 confirmed the recalcitrant and persistent character of MTBE under groundwater conditions. An efficient natural attenuation of this hazardous compound can not be expected on each site.

As demonstrated in literature and observed in our own experiments, a biodegradation can reduce MTBE pollutions significantly only under the presence of oxygen (aerobic conditions). Our experiments provided further evidence of a non-ubiquitous distribution of an aerobic degradation potential. A presence of a potential MTBE degradation was only found in aerobic microcosms with sediments from MTBE contaminated sites.

MTBE represents a serious threat for groundwater bodies and regarding the European Framework Directive on Water, MTBE should be a cause of alarm as a typical contaminant that accompanies production, distribution and sale of petrol products. A main demand is to include this compound in standard measuring and monitoring programs as well as risk assessments related to drinking and groundwater questions. It is necessary to include MTBE threshold values in European Drinking water regulations. Chemical Research should concentrate on the search for an alternative antiknock fuel additive.

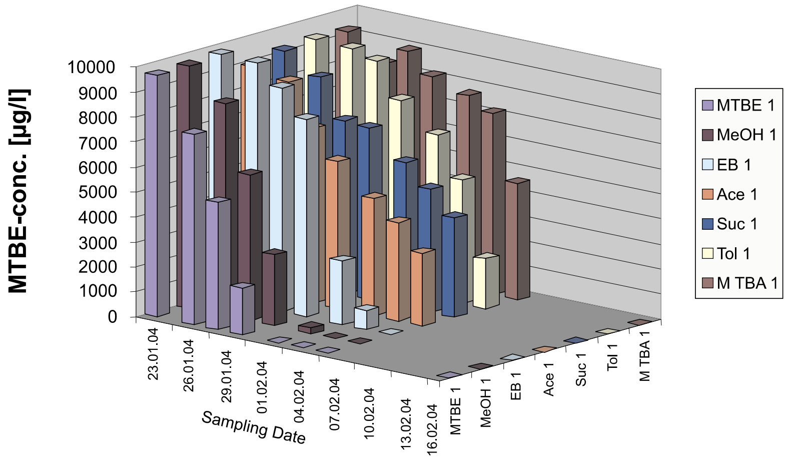

Figure 3: Decrease of MTBE concentration in experimental vessels with different amendments besides the spiked MTBE (MeOH = methanol, Ace = Na-acetate, Suc = Na-succinate, M TBA = TBA, EB = Ethylbenzene, Tol = Toluene, MTBE = no other amendments )

Data about the consecutive degradation of BTEX and MTBE due to the preference of the BTEX compounds by microorganisms cause us to assume that a biodegradation of MTBE is not very probable if BTEX are present in the MTBE contaminated groundwater plume. It is one reason for the significantly longer plumes of MTBE than BTEX plumes in the field, which have been reported by several authors.

This fact and the properties of MTBE, which are listed above have a great weight for real cases of remediation planning at contaminated sites. Natural attenuation strategies for treatment of MTBE should only be implemented under a verified availability of oxygen and the absence of other well degradable organic hydrocarbons including co-contaminants such as BTEX.

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In WP3 Stadtwerke Düsseldorf AG and Salzburg AG provided to the project partners model sites for the testing of the developed early warning tools. In Düsseldorf two sites were identified. At one site the aquifer is contaminated with MTBE and at the other site, a former gasworks area, BTEX contaminations can be detected. The chosen model sites were described in various monitoring campaigns. Some additional monitoring points were installed on the sites.

A conceptual model to support the transport modelling was set up for the MTBE site. The site assessment of the BTEX site was completed with a long term test of an Aqua Monitor (DHI). A measurement protocol for contamination occurring in water catchment areas was developed as an integrated management system in collaboration with Dr. Hitsch from Salzburg AG.

As a water supplier in Europe the Stadtwerke Düsseldorf AG is aware that it is dependent on raw water of good quality to ensure the production of pure drinking water. Furthermore good raw water quality helps to run the water treatment facilities more cost effective so that water suppliers are able to provide customers with drinking water for a reasonable price. That is why the Stadtwerke Düsseldorf AG had a great interest in collaborating in the WATCH-project and has taken over the role of an end user in this project.

## Objectives:

- Description of the sites, collection of data for the concentrations of the contaminants and elucidation of the degradation processes for the development of reliable and effective sensors.
- Support of the conceptual model, early warning and management system set up.
- Developing of an integrated management system for water suppliers to protect their raw water resources from contamination.

## MTBE site

On a site located in the east of Düsseldorf a MTBE contamination was detected in the late 1990`s. An emergency well was found to have a strong smell of MTBE during a sampling in August 1999. At the MTBE site detailed monitoring and site description was possible due to a great number of monitoring wells that have been installed by the environmental authorities because of a former contamination with pesticides. Data about geology, hydraulic conditions, concentrations of MTBE and its suspected degradation products TBA and TBF, chemical parameters and historic site data was collected to understand the behaviour of MTBE in the aquifer.

Nine sampling campaigns were carried out between 11/2001 and 11/2003 to characterize the site and understand the movement of the MTBE plume. The samples were analysed by CSIC for MTBE, TBA and TBF. The results showed in November 2001 high concentrations of MTBE downstream of a petrol station. The results from the following sampling campaigns showed a decreasing concentration of MTBE in the monitoring well 10688 which is situated close to the suspected source in direction of the groundwater flow. This was an evidence for a plume movement with the groundwater flow. In May 2002 soil from the plume area was sampled and send to Jens Fahl of TU Dresden to serve as an inocculum in the MTBE biodegradation assays. In the suspected plume centre no monitoring points were available. So an additional monitoring well (15197) and two multilevel wells (15086-15091 and 15191-15196) were constructed in November 2002. A monitoring campaign was carried out just after the installation of the new wells. All three monitoring wells were located in the plume centre. The highest concentration of MTBE could be detected in the multi-level wells in a depth of 11 m below ground (645 µg/l respectively 414 µg/l). This was evidence for a hori-zontal zoning of MTBE and TBA in the aquifer. Addi-tional sampling campaigns were carried out in order to gather further information about this horizontal zoning and to track the plume movement over the time. The results from the sampling campaigns in 11/2002, 03/2003, 06/2003, 08/2003 and 11/2003 showed that the plume centre (MTBE exceeding 100 µg/l) has moved to the South-West and that the plume has extended to the West (figure 1).

In June 2003 the chemical parameters sulphate, sulphide, nitrate, nitrite, ammonia and chloride were analysed beside the field parameters (pH, oxygen, conductivity and temperature) to support knowledge

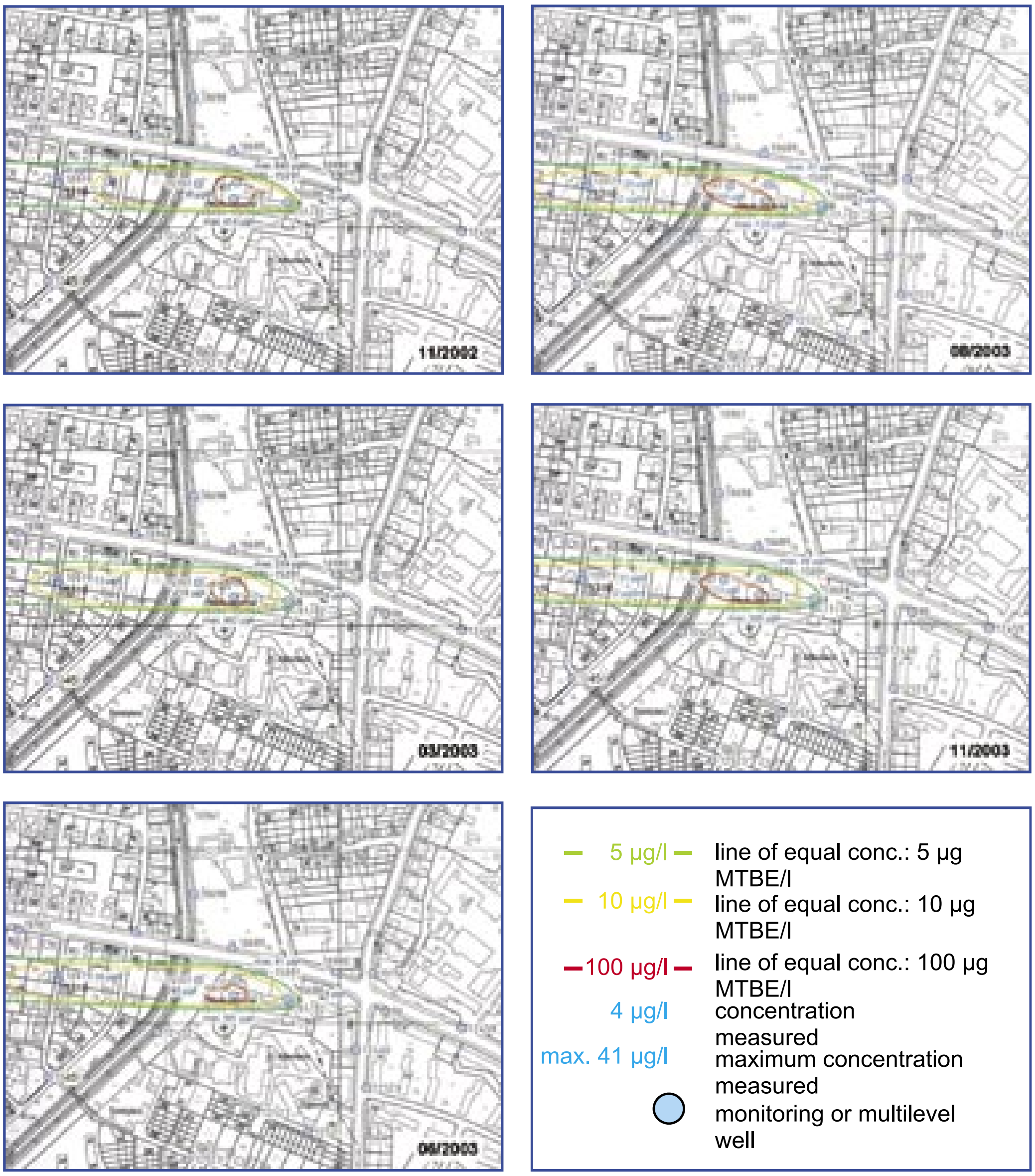

Figure 1: Movement of the MTBE-plume between Nov. 2002 and Nov. 2003.

about potential electron acceptors for biological MTBE degradation. The groundwater had nitrate and nitrite concentrations mostly below the detection limits of the methods used. Ammonia was found in concentrations up to 17.2 mg/l as the groundwater on this site is influenced by the effluent of a former rubbish dump located in the East of the MTBE site. All results showed that the groundwater in this area is of poor condition. Aerobic MTBE degradation can therefore not be expected in this area.

Water samples from MTBE site were send to Diaclone and Cranfield University. Here the developed MTBE immunoassays were tested in the natural crude waters to elucidate the matrix effects of ions and other contaminants present in the groundwater.

All information about geology, hydraulic conditions, concentration of MTBE and TBA, chemical parameters and historic site data was put together into a conceptual model for the transport of MTBE in the aquifer (figure 2).

All data give evidence that the MTBE derives from a single spell point source. Considering the whole plume extension and assuming the MTBE to be equally distributed over the aquifer with 15 µg/l, then a whole freight of 0.54 kg MTBE would have reached the underground. This equals about 6 l of petrol with a content of 10% MTBE. Regarding this result it becomes evident that even minor spills of petrol may have a large impact on the condition of the groundwater not only in urban areas.

## BTEX site

A former gasification site owned by the Stadtwerke Düsseldorf AG served as a model site for BTEX. Heavy pollution of the aquifer and soil caused by decades of gas production and destructions in the Second World War was detected in the early 1990s. A site monitoring programme was started in 1992 and the remediation started in 1995. Excavation of the most contaminated soil and the use of a bioreactor system helped to control the BTEX plume within five years (figure 3).

On the BTEX site a monitoring campaign was conducted in February 2002 to provide WP1 with reliable data for the development of the sensors. The samples have been analysed by CSIC in Barcelona. The BTEX concentrations in the ground-water samples ranged from <10 µg/l to> 4000 µg/l. The dominant fraction in the centre of the plume is re-presented by Toluene, in samples further downstream Benzene is the most dominating substance.

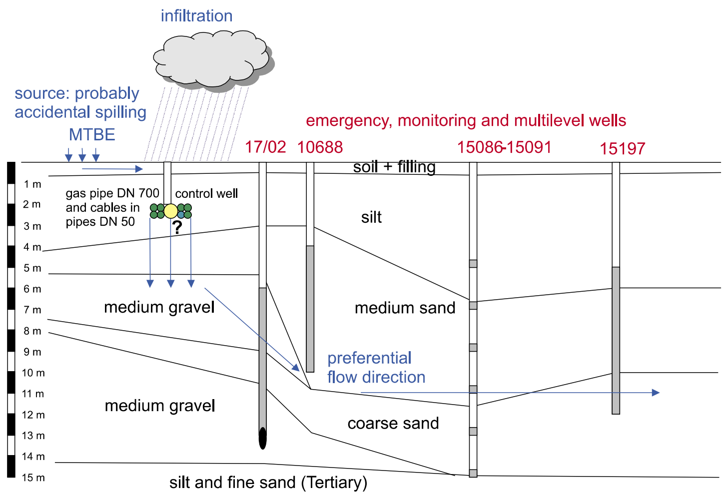

Figure 2: Conceptual model for the flow path of MTBE under the model site in Düsseldorf. The different monitoring wells are given in red. The filters of the wells are marked in grey. In emergency well 17/02 there is a motor pump installed in the depth of 13,50 m.

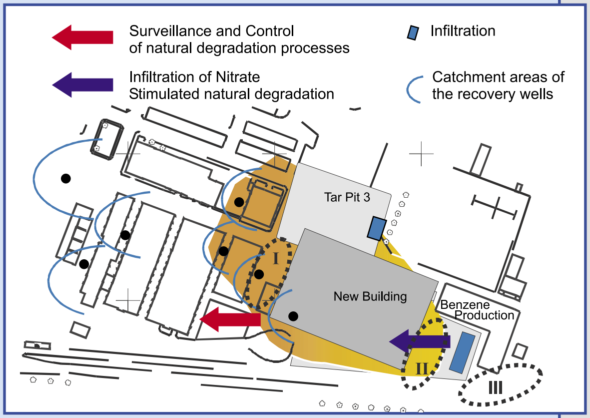

Figure 3: Situation on the BTEX site in the year 2000, the planned infiltration of nitrate has now been taken into terms. The remediation wells in the area of the new building have been shut down in May 2003.

The BTEX site is very well described due to the continuous remediation and monitoring programme. Information about geology, hydrology, concentrations of PAK- and BTEX-compounds, chemical parameters and treatment results was collected over years.

An Aqua Monitor system for of measuring aromatic compounds provided by DHI was installed and tested on the BTEX site in July 2002 and was run with water from the highest contaminated remediation well in continuous flow. The system worked well with high concentrations of PAK and BTEX (up to 2500 µg/l) despite of the heavy biofilm which grew in the measuring cell. In May 2003 the three highest contaminated remediation wells were switched off due to the start of a enhanced natural attenuation remediation programme. So the Aqua Monitor was run in a long term experiment with water from another remediation well which is located in the downstream of the plume centre. The data from the Aqua Monitor were successfully reported every day via cell phone to DHI in Denmark. Here the data were then transferred to a DIMS database to which access was possible via internet.

In summer 2003 water samples from BTEX site were send to Cranfield University to test matrix effects in the water analysis with the improved BTEX immunoassays.

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The aim of WP 4 was to develop a protocol for the management of groundwater resources at water catchment scale. The protocol provides a decision support tool for water suppliers, regulatory agencies/authorities and/or their advisors for the quantification and reduction of risk related to the water resource for the catchment area.

By implementing an intelligent early warning- and management system counter-measures against pollution of drinking water resources can be initiated earlier, cheaper and more effective thereby minimising the need for high cost water treatment at drinking water plants. The development of the protocol for water management will increase the awareness of the water suppliers with respect to possible measures to be taken to protect the safe abstraction of clean water. The dynamic refinement and adaptation of monitoring will support economic efficiency. The definition of strategies for implementation of such a decision support tool requires an advanced understanding of the water cycle within the area of interest.

The user is guided through the seven steps that are required for the basic set up of an early warning and management support tool:

- Initial delineation of water catchment area
- Conceptual model for catchment area
- Interpretation/understanding of conceptual model/water cycle within catchment area
- Identification of risk within catchment area
- Analysis of risks within catchment area
- Optimisation of monitoring for identification of potential pollution of drinking water
- Contingency plans for protecting water supply

The protocol allows the end user to fill this basic framework with case specific information and to identify in detail additional work that is needed. Figure 1 gives an overview on this stepwise and iterative approach.

## From the delineation of the catchment area to a conceptual understanding of the water cycle

The delineation of the groundwater catchment is required for all further activities and it is the basic step of setting up a conceptual understanding of the groundwater system, the conceptual hydrogeological model (CM). The conceptual model provides a reliable basis for the integration of more complex soil-water-sediments systems and for the definition of critical control points, it is a prerequisite for the identification, evaluation, control and management of multicomponent systems. It allows a more reliable application of numerical models to evaluate risk scenarios and management options. Thus it is the basis for reliable decisions in groundwater and integrated catchment area management.

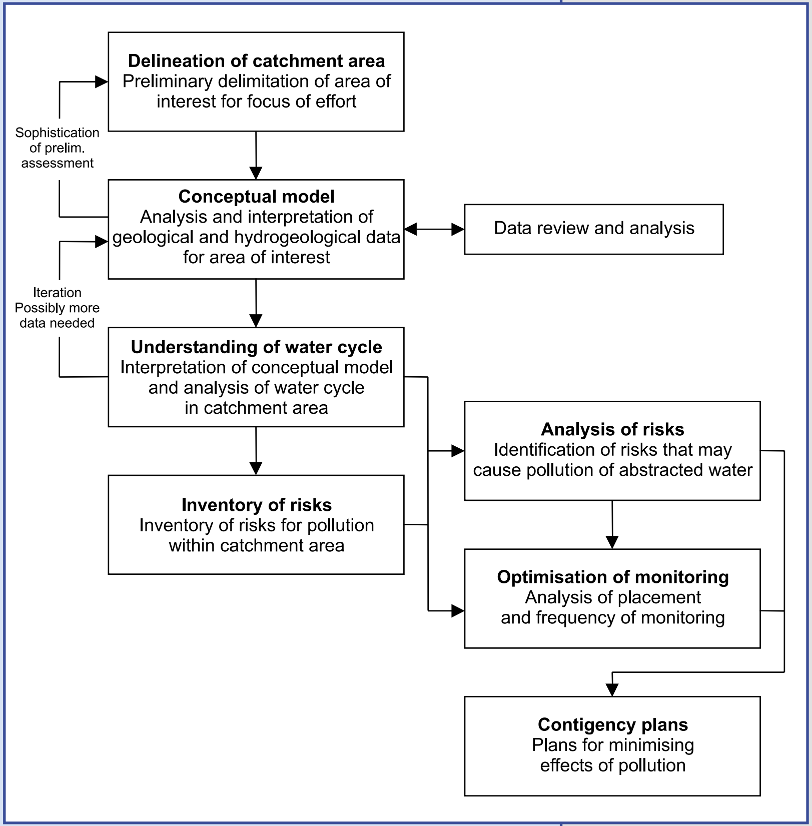

Figure 1: Basic set up of the early warning and management support tool

To support the CM set-up at the case study an online monitoring system was set-up to estimate groundsurface water interactions. The data were received automatically from the AquaMonitor data loggers and the data were placed in a data base system called Dynamic Integrated Monitoring System (DIMS). The monitoring data were available in real time via internet (figure 2).

By integrating the conceptual system understanding in a numerical model system an improved, reliable understanding of the water cycle was derived.

Figure 2: Real time availability of monitoring data in the internet

## Inventory of risks

In practice there is a manifold land use in groundwater catchment areas, that could pose a potential risk to the aquifer (figure 3). The inventory of potential risks for this example shows that these are e.g. main roads, motorways, industry, smaller trade and commerce facilities (e. g. CHC spill form a former dry cleaning in the early 80's), housing (approx. 1000 heating oil storage tanks with more then 3 million litres storage capacity), shooting stand, surface water pollution. The case study for the implementation of an early warning/management system was the Salzburg water supply area consisting of two well fields, St. Leonard (east) and Glanegg (west) with an excellent groundwater quality that needs no pre-treatment for drinking water purposes. These outstanding resources require a sustainable monitoring and managment.

## From analysis of risks to contingency planning

The general procedure to come from the analysis of risks to contingency planning is a four step approach (figure 4). The estimation of risk sensitive areas requires a combination of surface use scenarios with a description and prognosis of groundwater quality and quantity relevant processes. This enables an assessment of existing and planning of future monitoring strategies in terms of:

- What are representative monitoring points for risk sensitive areas?
- What parameters have to be measured and what is there usual operation window?
- When does monitoring has to start in which distance from risk sensitive areas and potential receptors?
- What is the optimised frequency to survey the spreading of pollution?

Based on such a monitoring programme the potential impact on water supply facilities can be estimated:

- When is a pollution to be expected to occur in an extraction well?
- What is the expected maximum concentration at the target of protection?
- What is the timeframe available for contingency planning and counter measures?

The availability of answers to all these questions, provided by potential pollution scenarios, allows the set-up and design of groundwater catchment area specific measure plans to protect groundwater resources (figure 5).

In the Salzburg case study the following results were obtained by risk analysis for the catchment area of the two waterworks investigated.

For the Glanegg well field, the flow pattern analysis showed that the source of the water for the abstraction water was run off from the north side of the Untersberg chalk massif, with a very short travel time to the wells (~3 months). The short travel times in this system meant that it would not be practically possible to design an early warning system for this well field.

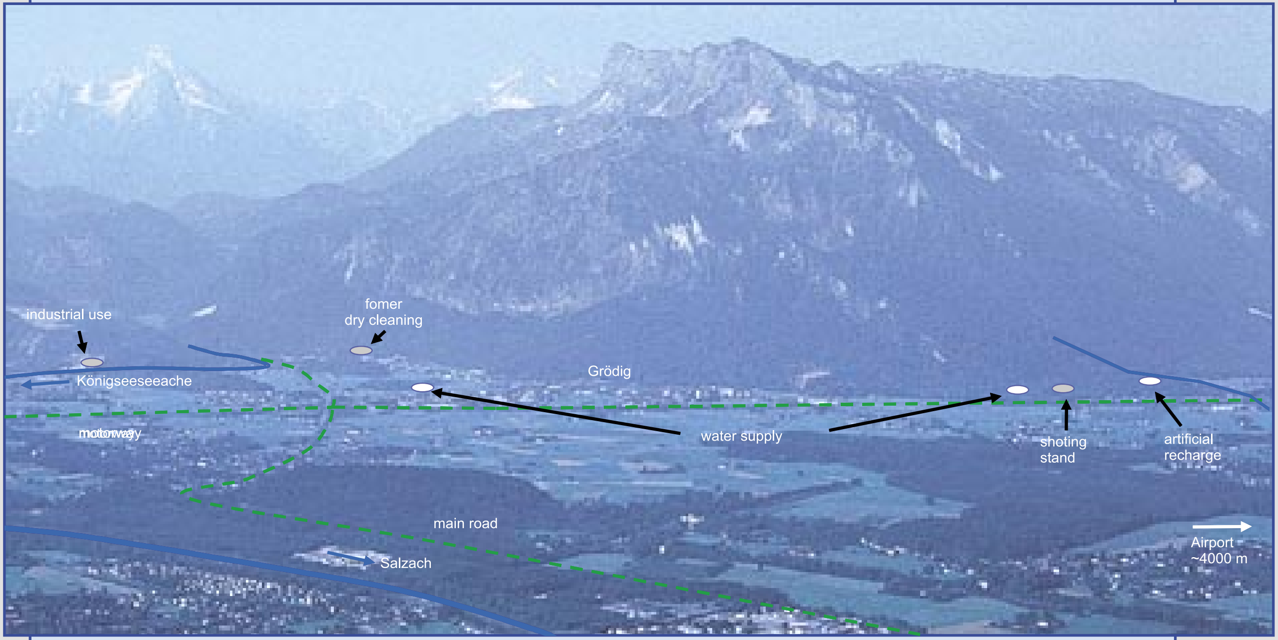

Figure 3: Multiple land use within a groundwater body (view to south-west)

On the other hand the short residence time also meant that the system was flushed out regularly, and therefore there was little threat of the need for of a long-term shut down of the well field.

For the St. Leonard well field, the capture zones were well defined and the analysis of the possibility of minimising the impact of potential contaminations was evaluated by a number of scenarios using the calibrated flow and particle-tracking model. The conclusion was that an effective control strategy would be to identify the capture zone for the roadway intersection as the most sensitive scenario and the install a line of closely spaced defensive hydraulic control wells. Furthermore, the line of wells located downstream of the roadway in the main part of the capture zone could be used for regular early warning monitoring. Such monitoring would give a two to four month warning window depending on the frequency of the monitoring. On the west side of the caputure zone, an existing monitoring well could be used to monitor the arrival of contaminants travelling in the narrow plume coming around the top of the bedrock outcrop.

## Conclusions

The protocol developed is of value to water suppliers, regulatory agencies/authorities and/or their advisors for the quantification and reduction of risk related to the water resource for the catchment area. Anthropogenic trace compounds like MTBE that are meanwhile wide spread in the environment are an good example for the importance of a reliable groundwater management system with that also keeps an eye on the integration of related environmental compartments. It allows those who are responsible for groundwater bodies and catchment areas to optimise to set-up new and effective management strategies for their water resources as well as to improve and optimise existing approaches for a sustainable use of groundwater resources. By setting up an integrated understanding of the complex interactions of processes within a groundwater body and by providing an interface for interactions with soil sediments and surface water it is the basis for socio-ecological and economical sound management planning.

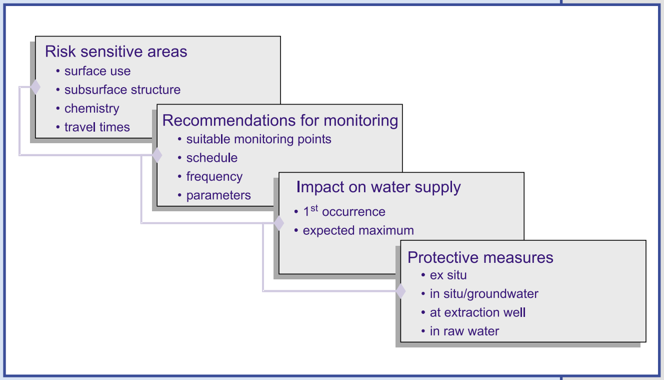

Figure 4: Preparation of contingency plans

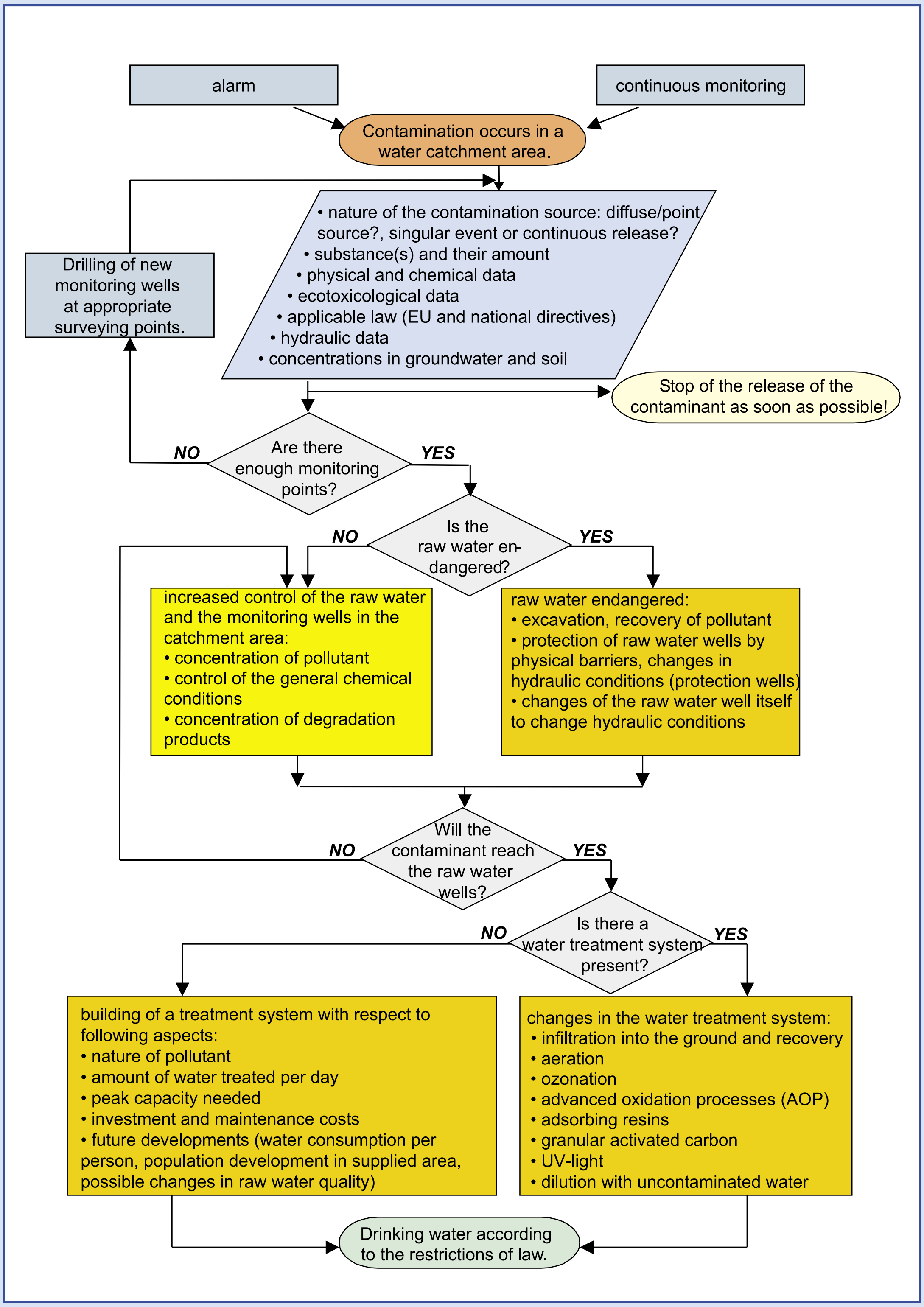

Figure 5: Measure plans – decision tree for contingency planing if pollution occurs in water catchment areas.

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