SESSION 3 B - NATURAL ATTENUATION AND PERSISTENT POLLUTANTS (CONTINUED)

CHAIR: MR. URS ZIEGLER, SWITZERLAND
CO-CHAIR: MR. DIETMAR MÜLLER, AUSTRIA

INTRODUCTORY REMARKS OF THE CHAIRMAN: Mr. Urs Ziegler, Swiss Agency for the Environment

Welcome back again for the last session of today. I hope you have enough energy for two more interesting presentations on Natural Attenuation and, of course, a discussion which will hopefully bring us one step further.

In continuation of the Natural Attenuation discussion, I would like to ask Bob Harris now to tell us something about the development of an approach to Monitored Natural Attenuation in the United Kingdom from a "do-nothing" to a "protocol and practice" approach.

So please, Bob.

Note: This text was prepared by the compilers from Mr. Ziegler's recorded presentation.

DEVELOPING AN APPROACH TO MONITORED NATURAL ATTENUATION (MNA) IN THE UK: FROM DO-NOTHING TO PROTOCOL AND PRACTICE

Speaker: ***Mr. Bob Harris***
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http://www.environment-agency.gov.uk

Background

- Significant problem of groundwater pollution in UK results from 250 years of industrial legacy;
- legislative approach late to develop, so problem dealt with by (pragmatic) default; (e.g. "pump and treat" by water undertakings plus "do-nothing" approach);
- however, with regulatory drivers we must be sure of the underpinning science with respect to both problems and solutions in order to apply risk-based decision making.
- It also makes economic sense to seek low cost solutions….

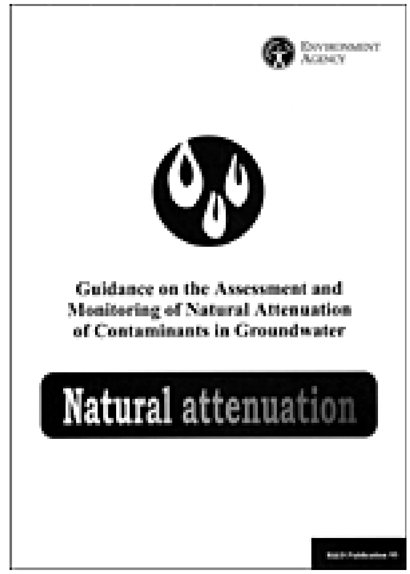
Economic Benefits of Adopting Natural Attenuation for Remediation

- If c. 2000 sites in the UK with groundwater pollution require remediation and if costs of active remediation average £0.5 M/site = £1 billion costs to UK economy;
- if natural attenuation adopted at only 50% of these and if the remedial costs are reduced by c. 75%, then savings amount to: 1000 x £375K = £375 million;
- in reality the savings could/will be much larger since:
  - the majority of polluted sites are potentially amenable;
  - the cost savings are conservative;
  - the largest problem sites will cost much more.

Approach to Accepting MNA as a Remedial Option

- Review case studies in the UK;
- understand other countries' experiences;
- develop and manage focused R&D programme; collaborate with others to increase funds;
- produce guidance related to new regulatory regime in order that staff are able to use site-specific scientific evidence in decision making;
- continue to understand the science and refine the guidance.

Guidance published in 2000 for regulatory staff and others on the screening, demonstration, assessment and implementation of Monitored Natural Attenuation as a remedial option for polluted groundwater.



Natural Attenuation (NA)

"The effect of naturally occurring physical, chemical and biological processes, or any combination of those processes to reduce the load, concentration, flux or toxicity of polluting substances in groundwater. For natural attenuation to be effective as a remedial action, the rate at which those processes occur must be sufficient to prevent polluting substances entering identified receptors and to minimise expansion of pollutant plumes into currently unpolluted groundwater. **Dilution within a receptor, such as in a river or borehole, is not natural attenuation."**

Monitored Natural Attenuation (MNA)

"Monitoring of groundwater to confirm whether NA processes are acting at a sufficient rate to ensure that the wider environment is unaffected and that remedial objectives will be achieved within a reasonable time scale; typically this will be less than one generation or 30 years."

Key Principles

- Applicable to destructive and non-destructive processes
- 1 generation maximum time frame (typically <30 years) for reasons related to:
    - sustainability
    - institutional control
- Minimal expansion of plume into clean aquifer; balance between:
    - protection of water resources
    - allowing NA processes to establish
    - allowance for some plume migration in the demonstration of NA
- Consultation a key feature
- Contingency plan imperative
- Based on Conceptual Model (continually challenged)
- Lines of evidence approach advocated

- Not a 'do-nothing' approach
- Will most often be accepted in association with proactive treatment (treatment trains)
- Onus on problem holder to demonstrate:
  - NA will be effective in protecting receptors and will continue to do so;
  - NA can be monitored;
  - NA achievable in reasonable time frame.
- Data requirements
  - minimum ~ 2 years base monitoring
- Technical, regulatory, practical and financial aspects

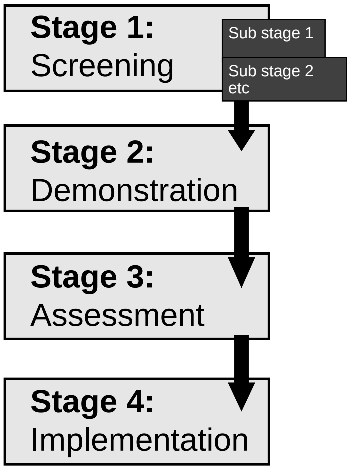
Other Protocols

- STM (1998) → petroleum hydrocarbons
- AFCEE (1995) → petroleum hydrocarbons
- RTDF (1997) → chlorinated solvents
- Sinke (1998) → decision support system
- USDON (1998) → petroleum h/carbons and chlorinated solvents
- Weidemeier (1999) → monitoring

Track Records (mainly North American)

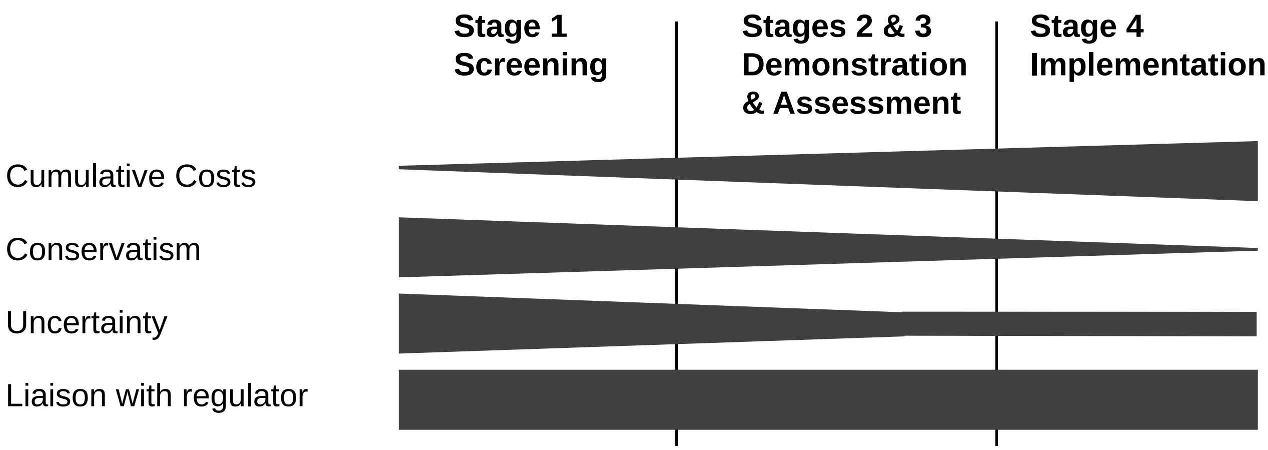
- Petroleum hydrocarbons → good
- Chlorinated solvents → moderate
- Phenols → good
- MTBE → limited
- PAH → limited + high sorption
- Ammonia → limited + sorption/cation exchange
- Heavy metals → high sorption

Framework for Guidance



Stage 1: Screening	Preliminary assessment	**Is NA a viable option?**
Stage 2: Demonstration	Site characterisation	**Is there evidence that NA is occurring <u>now</u>?**
Stage 3: Assessment	Prediction and modeling	**Will MNA meet risk management objectives in the <u>future</u>?**
Stage 4: Implementation	Verification and monitoring	**Does MNA continue to meet objectives in practice?**

The Four Stages



Consultation

- Liaison with stakeholders e.g.
  - regulators, third parties, insurers, financiers….
- Issues include:
  - applicability
  - public perception
  - public confidence (e.g. blight)
  - risk communication
  - accountability

NA and Geological Formations – Applicability

	Non Aquifer	Minor Aquifer	Major Aquifer
Intergranular	Oxford Clay	Sand and gravels	Greensand
Intergranular and Fracture	Mercia Mudstone	Coal Measures	Permo Triassic Sandstone
Fracture	Shales	Millstone Grit	Chalk Carboniferous Limestone

Increasing ease of demonstrating NA is effective

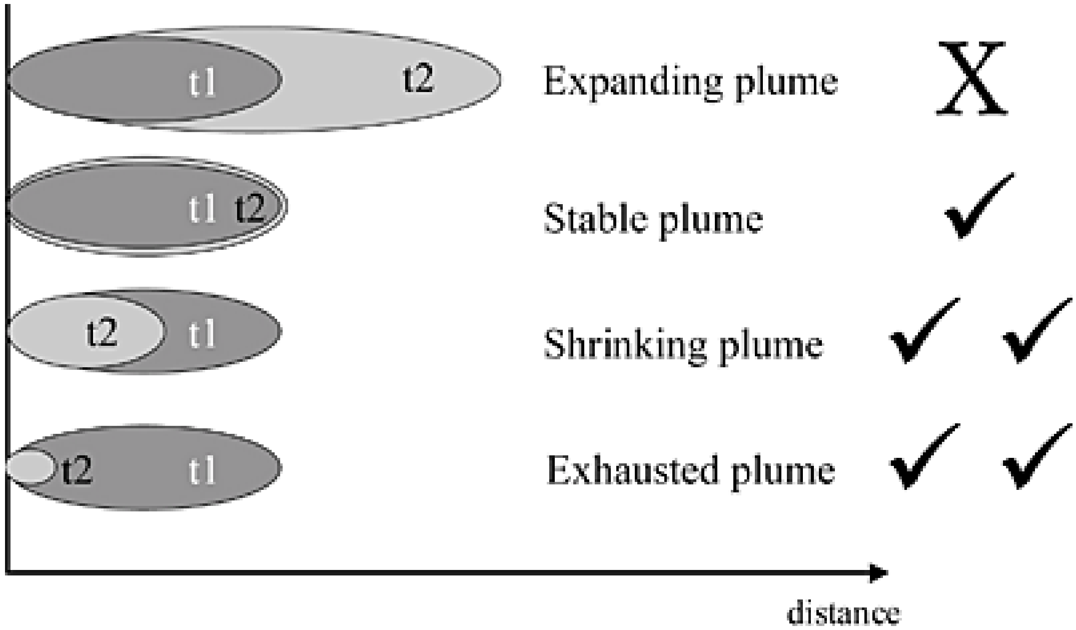
'Operating Windows'

- Based on observations in the field
- Indication that NA will work (all other factors being favorable) e.g.
  - contaminant concentrations (e.g. degradation inhibited at high concentrations)
  - (an)oxic conditions (>0.5 mg/l)
  - pH (optimal pH range 6 to 8.5)
- Research needed?
  - case history plus track record (limited UK examples)
  - more operating windows

Lines of Evidence

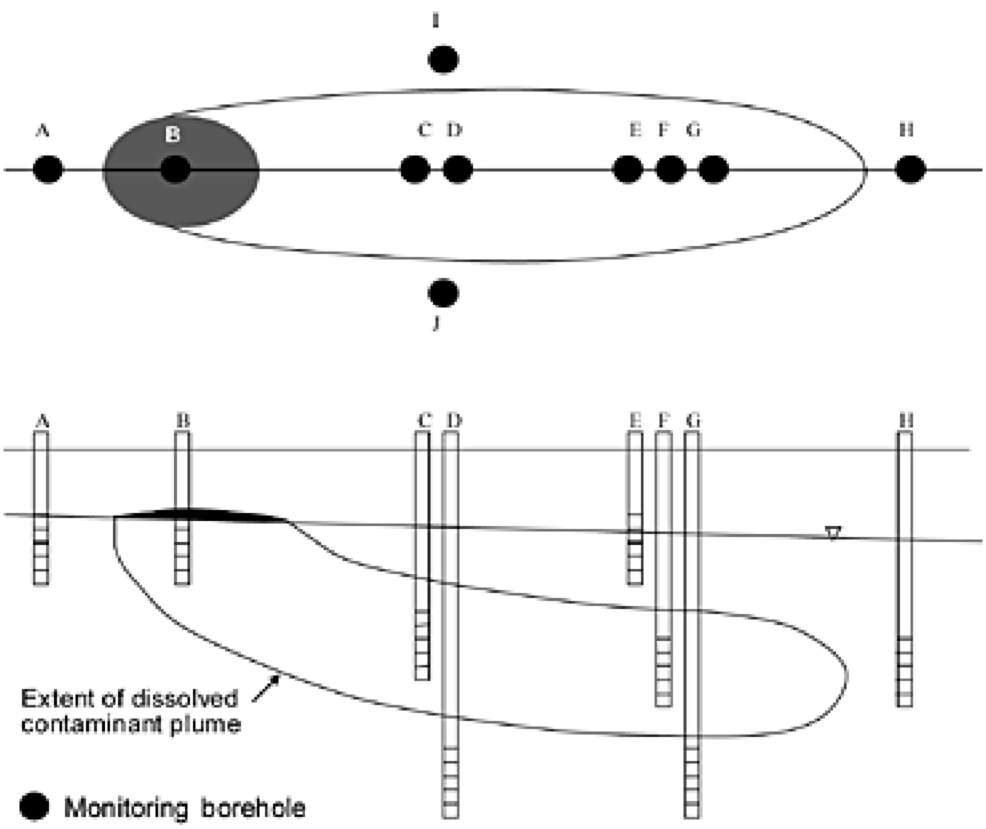
- Underpins demonstration process:
  - documented loss of contaminant mass in the field (such as historic data showing a reduction in contaminant concentrations with time);
  - geochemical and biochemical indicators which demonstrate the natural attenuation process that is resulting in the reduction in contaminant concentration;
  - microbiological data to support the occurrence of biodegradation.

Plume Behaviour – Evidence



Based on Weideneuer *et al*, 1999.

Design for Monitoring



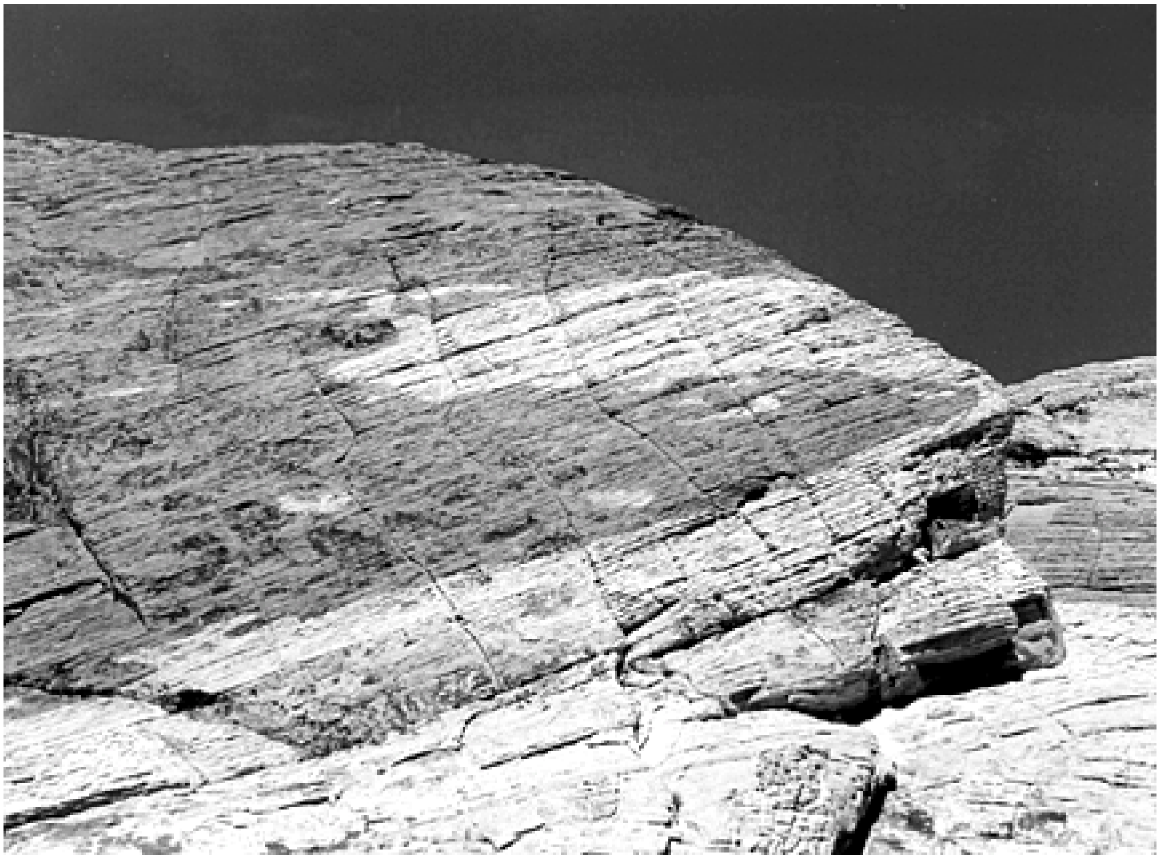
- Background (A)
- Source (B)
- Plume (C-G)
- Migration (H-J)
- Design considers
  - receptor location
  - travel times
  - stratigraphy & hydrogeology
  - **No minimum number**

Messages

- No quick fix - NA is a complex four-stage process.
- Time period for Stages 1-3 will probably exceed two years.
- Limited expansion of the plume is permissible.
- Highly site-specific.
- Requires large amounts of time series data.
- Technical expertise regularly updated by new findings is crucial to MNA application.
- Contingency plan is necessary with financial provision.
- May be one element of a wider risk management strategy, e.g. treatment trains.
- Application may be limited by ability to adequately characterise and predict behaviour of contaminants.

Have to remember the LITHOLOGY in the Conceptual Model.

Have to remember the MINERALOGY in the Conceptual Model,



... and the third dimension.

NATURAL ATTENUATION IN DENMARK

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Outline

- Background information
  - Groundwater/drinking water
  - Point sources
- Terminology
- Guidelines on Remediation of Contaminated Sites
  - Risk assessment in relation to groundwater protection
  - Biodegradation or degradation under natural conditions
- Experience gained in two cases
- Conclusive remarks

Drinking Water Based on Uncontaminated Groundwater

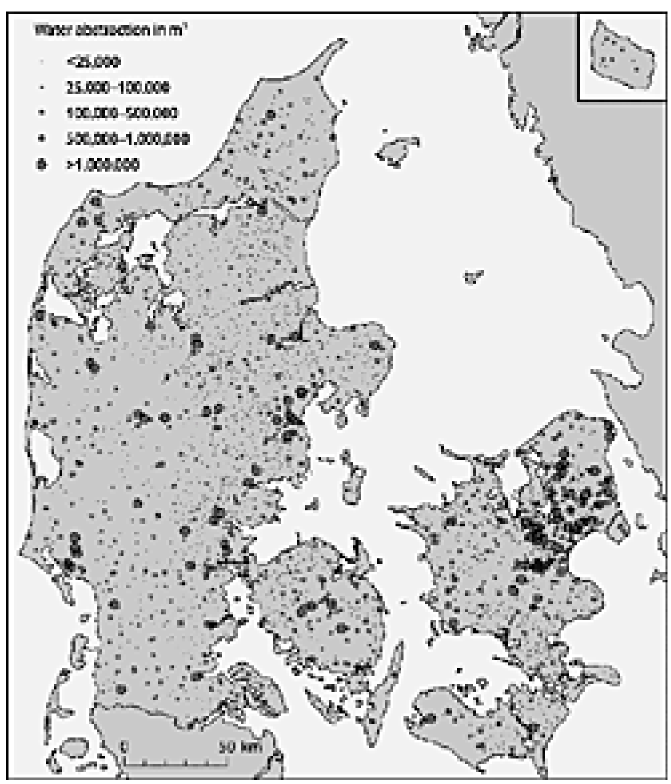
- More than 98% of all drinking water is based on groundwater
- No advanced treatment (GAC, ozone etc.)
- Only aeration and sand filtration

Larger Waterworks

- 600 million m^3 groundwater/yr.
- 3,000 waterworks supplying > 10 houses (units)
- Responsible for 90% of all distributed drinking water

Smaller Waterworks and Wells

- 700 waterworks supplying < 10 houses (units)
- 91,000 private wells
- 1,250 wells for industrial purposes



Contaminated Sites - Point Sources

- Point sources e.g. petrol stations, dry cleaning facilities, landfill sites
- 8,000 registered and mapped sites 31.12.2000
- 30,000 - 40,000 sites are suspected to be contaminated and have to be assessed
- Around 14,000 are anticipated contaminated

NA/Intrinsic Bioremediation(IB)/Bio-/degradation – Terminology

- NA, IB, biodegradation or degradation - not a remediation technique or method
  - Compare to pump and treat, air sparging, etc.
  - No active measures are carried out in order to enhance removal or to decrease further spreading of contaminants.

Monitored NA – Terminology

- Monitoring technique or methodology
- Design of network for observations/monitoring wells, screen interval, etc.
- Sampling and choice of parameters for analysis
- Analysis methods

Monitoring is a technique or may involve several techniques

Where to Take Account of Bio-/degradation?

- In the risk assessment
  - If degradation is sufficient, no remedial action is needed.
- Intent to separate processes:
  - dilution due to dispersion: a mass neutral process, and
  - degradation: a mass decreasing process.

Guidelines on Remediation of Contaminated Sites

- Comprises a description on how to handle a contaminated site.
- Where to retrieve information on land use/activities.
- Design of survey, samples and analyses.
- <u>Risk assessment regarding soil, indoor air and groundwater</u>
- Quality criteria for soil, air and groundwater
- Description of remedial actions and techniques

Principles in Groundwater Risk Assessment

- Predicting groundwater concentration using simple equations
- Several assumptions:
  - isotropic/homogeneous aquifer
  - only dissolved contaminants
  - continuous leaching
  - pseudo-steady state
- Definition of a groundwater risk
  - If the predicted concentration exceeds groundwater criterion

Stepwise Risk Assessment

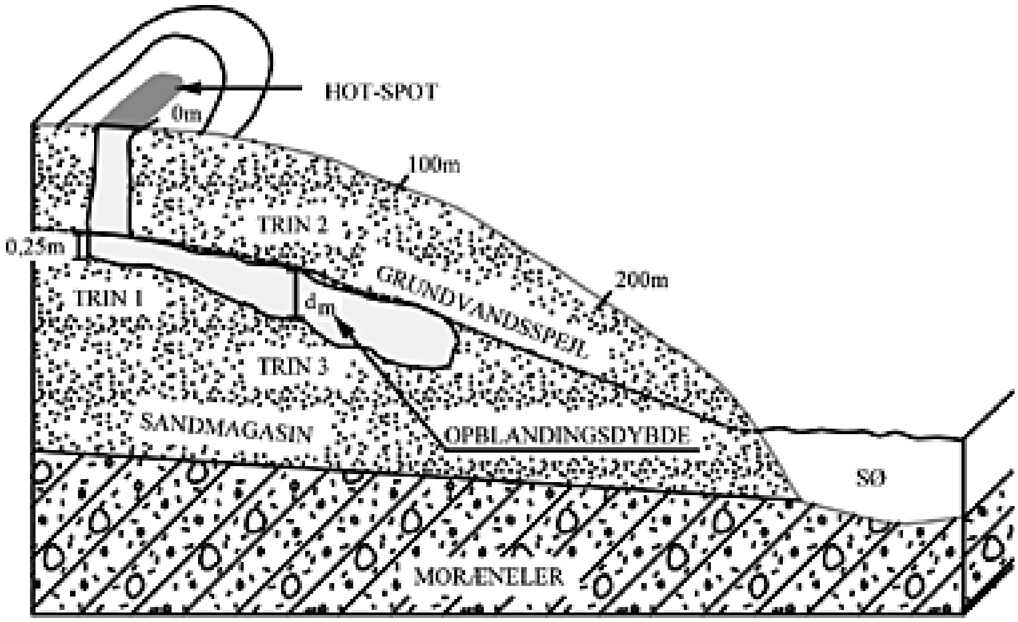
- Step 1: Near-source mixing model
  - mixing in the first 0.25 m of the aquifer
- Step 2: Down gradient mixing model
  - mixing at a distance equal to 1 year groundwater flow, maximum 100 m down gradient
  - increased mixing zone due to vertical dispersion of the plume. Standard parameters suggest a mixing zone of 1.8 m

Step 3: Down Gradient Mixing Model With Degradation

- Only applicable if contaminants have reached the aquifer.
- Only applicable if groundwater geochemistry indicates condition in favour of degrading the observed contaminants.
- Based on first order degradation constants from the literature. Time available for degradation is equal to the retardation due to sorption.
- Requires subsequent documentation (monitoring) and determination of the site-specific degradation constant.

Groundwater criteria

Parameter	**Groundwater criterion, μg/L**
Benzene	1
Toluene	5
Ethylbenzene + xylenes	5
Total hydrocarbons (mineral oil)	9
MTBE	5 (2-5)
Chlorinated solvents (PCE + TCE + DCE)	1
Vinyl Chloride (VC)	0,3



Trin 1: Opblanding i magasinets øverste 0,25m

Trin 2: Med dispersion i mættet zone

Trin 3: Med dispersion, sorption og nedbrydning i mættet zone

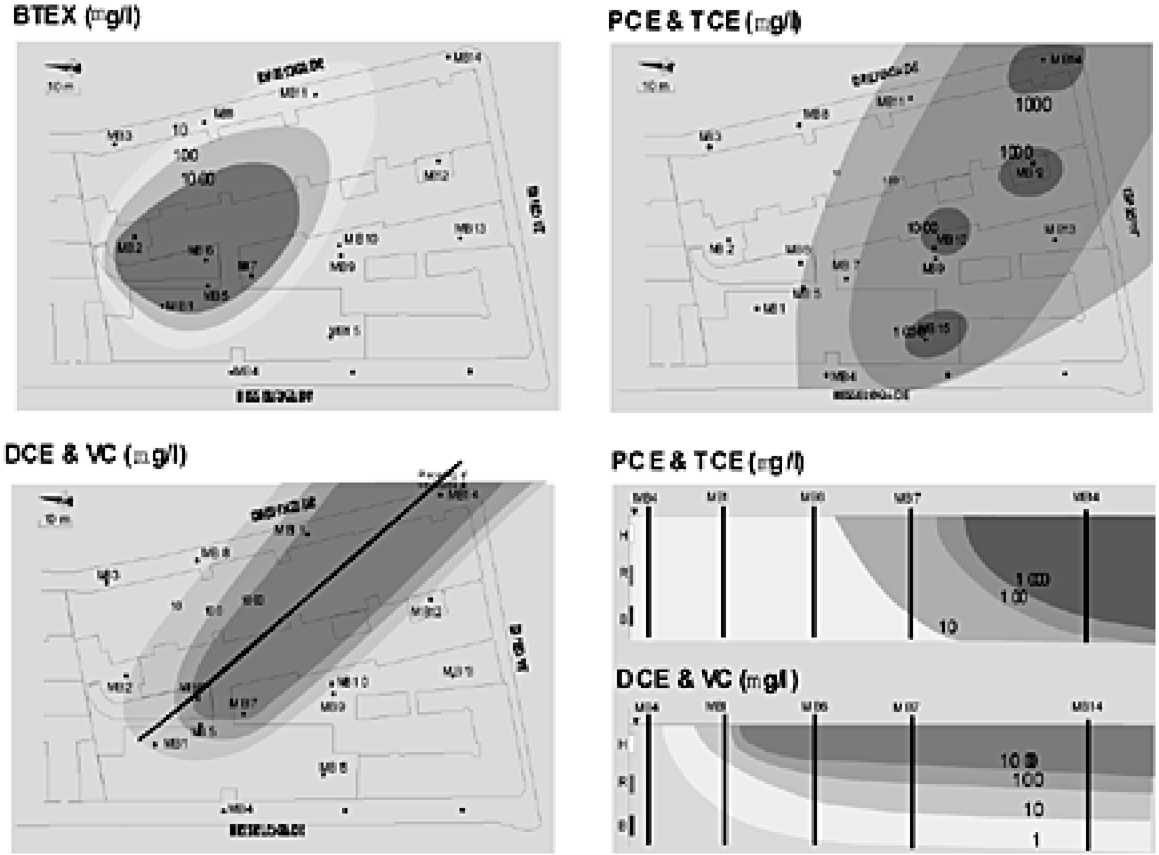
Case 1 ”DREJØGADE”

- Land use and contaminants
  - Former industrial dry cleaning facility
  - Contaminants: mineral spirits (BTEX,THC) and chlorinated solvents (PCE, TCE, DCE and VC)
  - Present land use: housing/flats

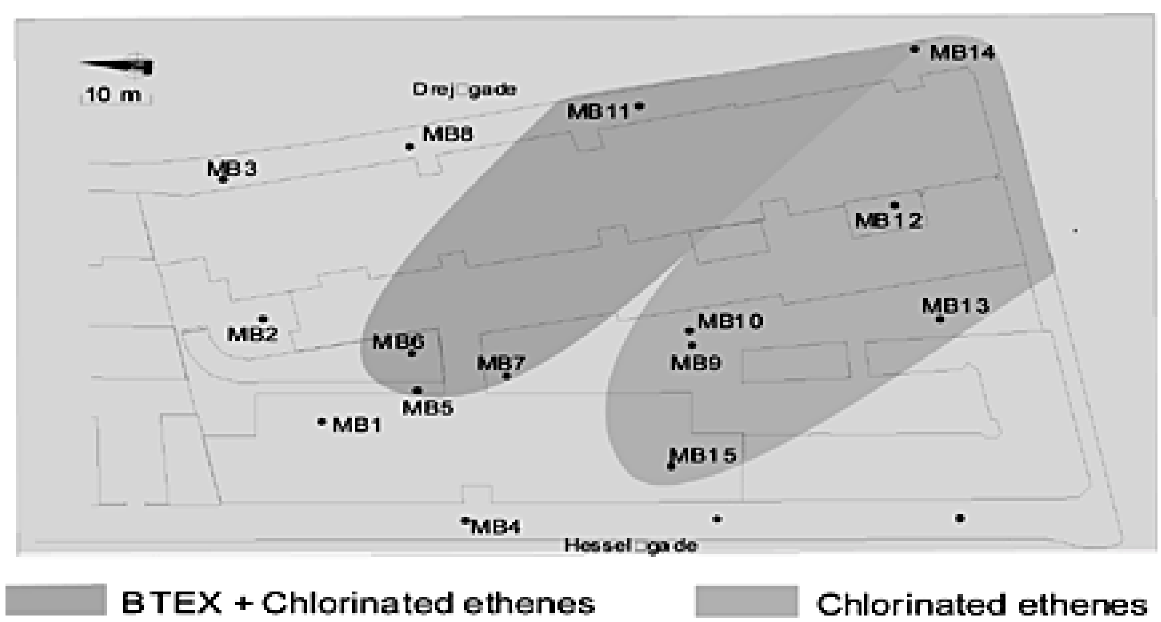
  ➡ Note that indoor air is at risk.

- Geology
  - Limestone is covered by fine sand having a thickness of 18 m.
  - The unsaturated zone is 8.5 m.
  - The plume is located in the sand aquifer.

Mapped Plumes



Two Plume Types



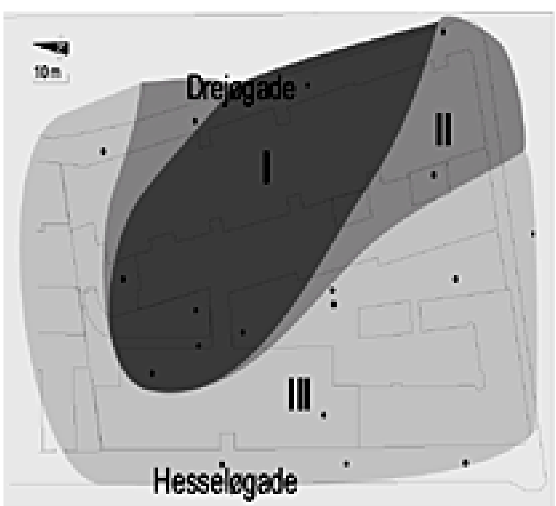
Redox Sensitive Species

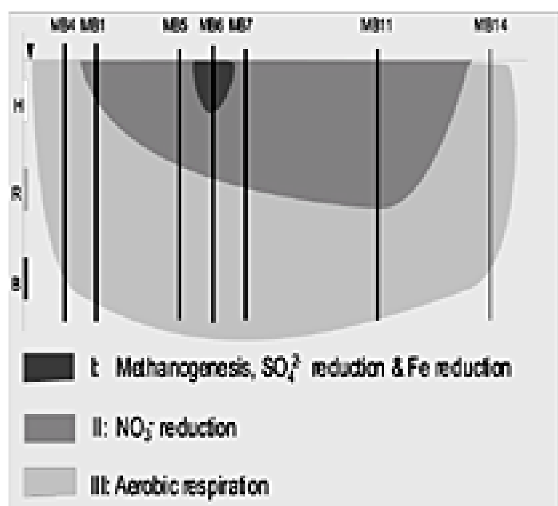
- Organic matter in the groundwater is degraded through reduction of electron acceptors.
- Example: $C_6H_5CH_3 + 4{,}5SO_4^{2-} + 3H_2O \rightarrow 2{,}25H_2S + 2{,}25HS^- + 7HCO^{3-} + 0{,}25H^+$
- Method:
  - consumption of electron acceptors (O_2, NO_3^-, SO_4^{2-})
  - occurrence of intermediates (N_2O)
  - production of reduced species (Fe^{2+}, Mn^{2+}, H_2S, CH_4)

Site-Specific Criteria for Redox Level Assessment

	Aerobic respiration	Nitrate reduction	Iron reduction	Sulfate reducion	Methano-genesis
Oxygen	> 1 mg/l	< 1 mg/l	< 1 mg/l	< 1 mg/l	< 1 mg/l
Nitrate			> 30 mg/l	> 30 mg/l	> 30 mg/l
Dinitrogen oxide		yes			
Iron	< 1 mg/l	< 1 mg/l			
Manganese	< 0,5 mg/l	< 0,5 mg/l			
Sulfate					
Sulfide	0	0	0	yes	
Methane	< 1 mg/l	< 1 mg/l	< 1 mg/l	< 1 mg/l	< 1 mg/l

Horizontal and Vertical Redox Zonation





Effect of Biodegradation

- **BTEX+Chl. ethenes plume:**
  - 99,5% PCE degradation
- **Chlorinated ethenes plume:**
  - 5% PCE degradation
  - Reductive dechlorination requires strongly reduced conditions, i.e. the presence of a carbon source.

Is there a risk?

Parameter, BTEX + Chl. ethenes	Gw-criterion, µg/l	Conc. 60m (MB11) downstream, µg/l	Exceeding factor
Benzene	1	48.4	**48**
Toluene	5	4.4	<1
Ethylbenzene + xylenes	5	<0.1	<<1
Total hydrocarbons (mineral oil)	9	530	**>50**
Chlorinated solvents (PCE+TCE+DCE)	1	PCE: 38 TCE : 14 DCE: 157	**>200**
Vinyl Chloride (VC)	0.3	VC: 82	**>270**

Is there a risk?

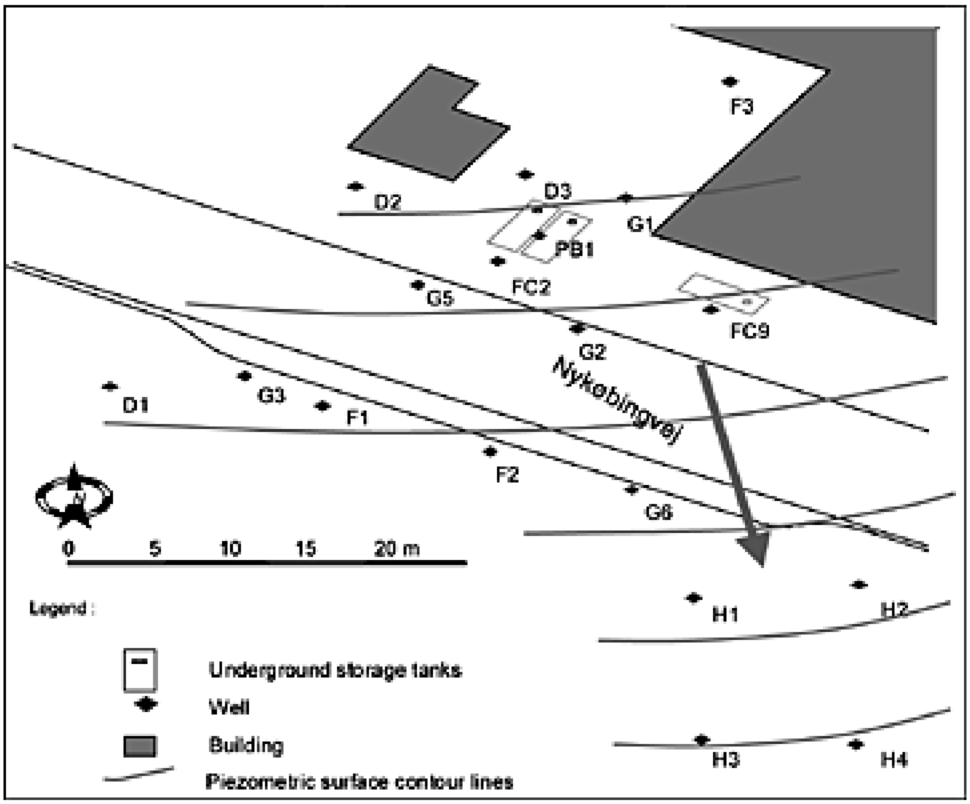
Parameter, Chl. ethenes	Gw-criterion, µg/l	Conc. 60m (MB14) downstream, µg/l	Exceeding factor
Benzene	1	3.5	**>3**
Toluene	5	<0.1	<1
Ethylbenzene + xylenes	5	<0.1	<1
Total hydrocarbons (mineral oil)	9	490	**>50**
Chlorinated solvents (PCE+TCE+DCE)	1	PCE: 1400 TCE : 180 DCE: 1337	**>2900**
Vinyl Chloride (VC)	0.3	VC: 1200	**4000**

CASE 2 ”RADSTED”

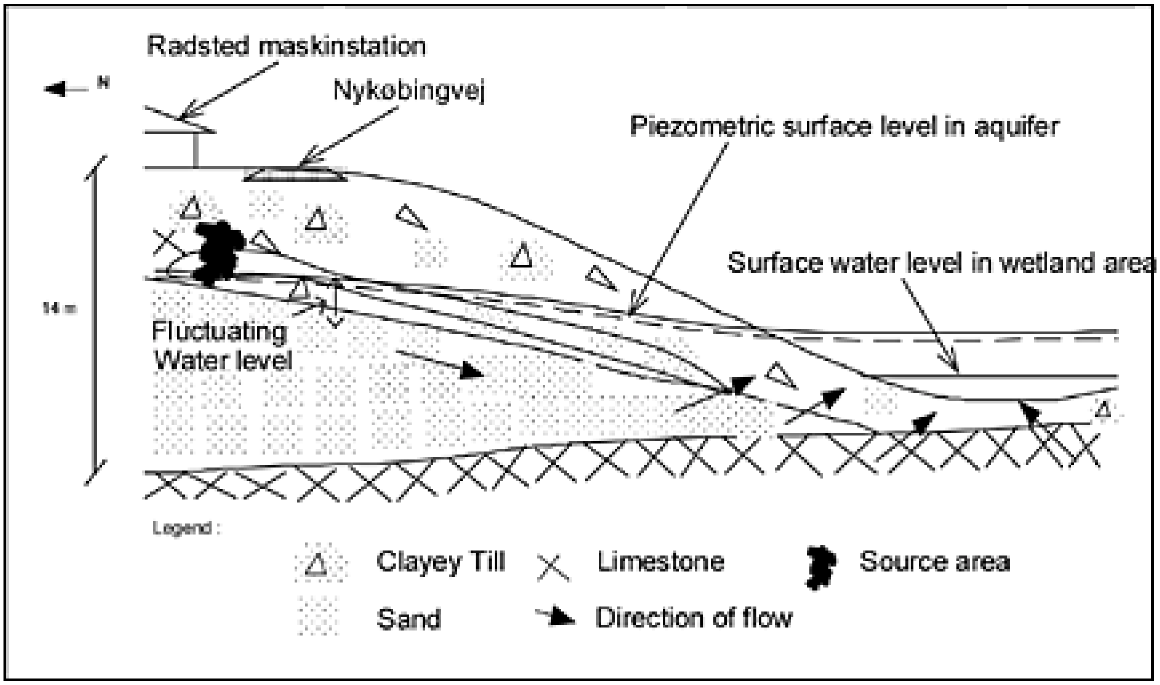
Land Use and Contaminants

- Former petrol station, closed in 1975
- Contaminants: mineral spirits (BTEX,THC)
- Source removal in 1996
- Residual contamination in unsaturated zone c. 25-50 kg, mainly BTEX compounds

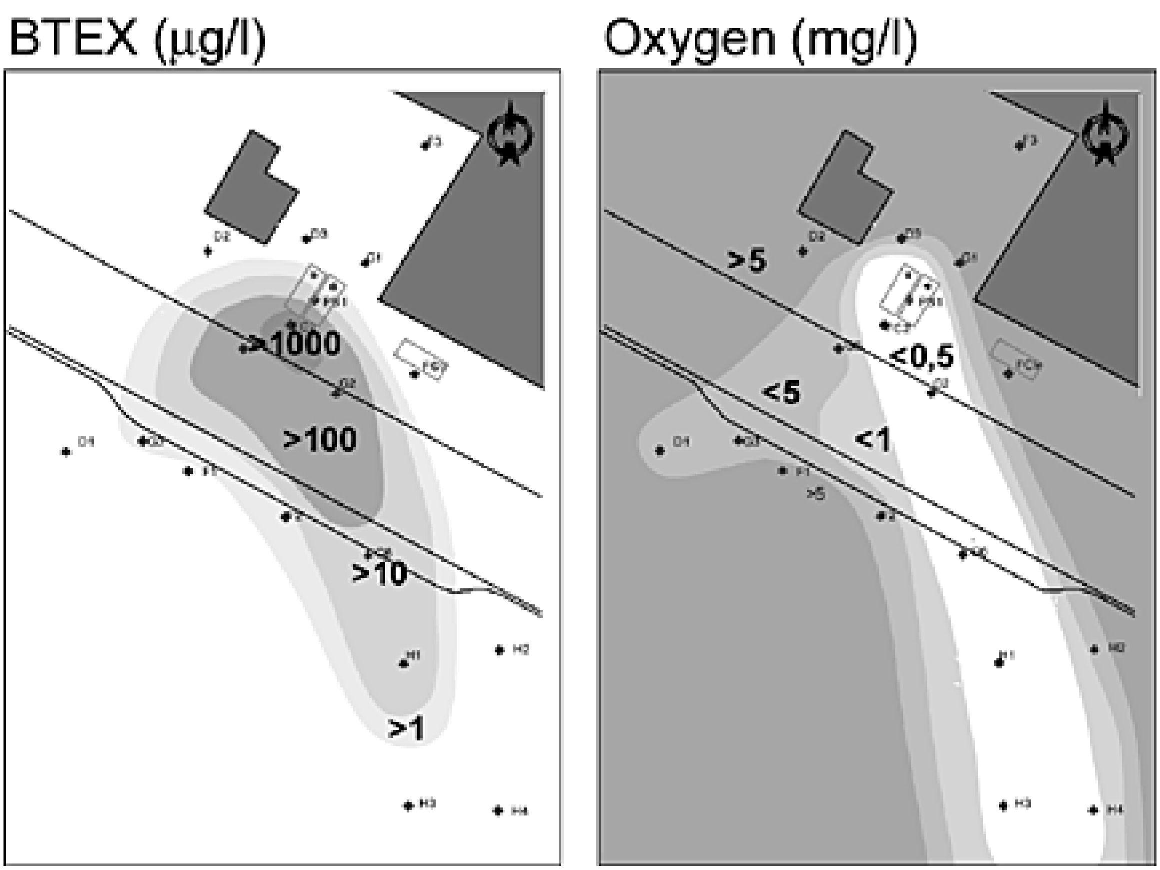
Groundwater Flow Direction



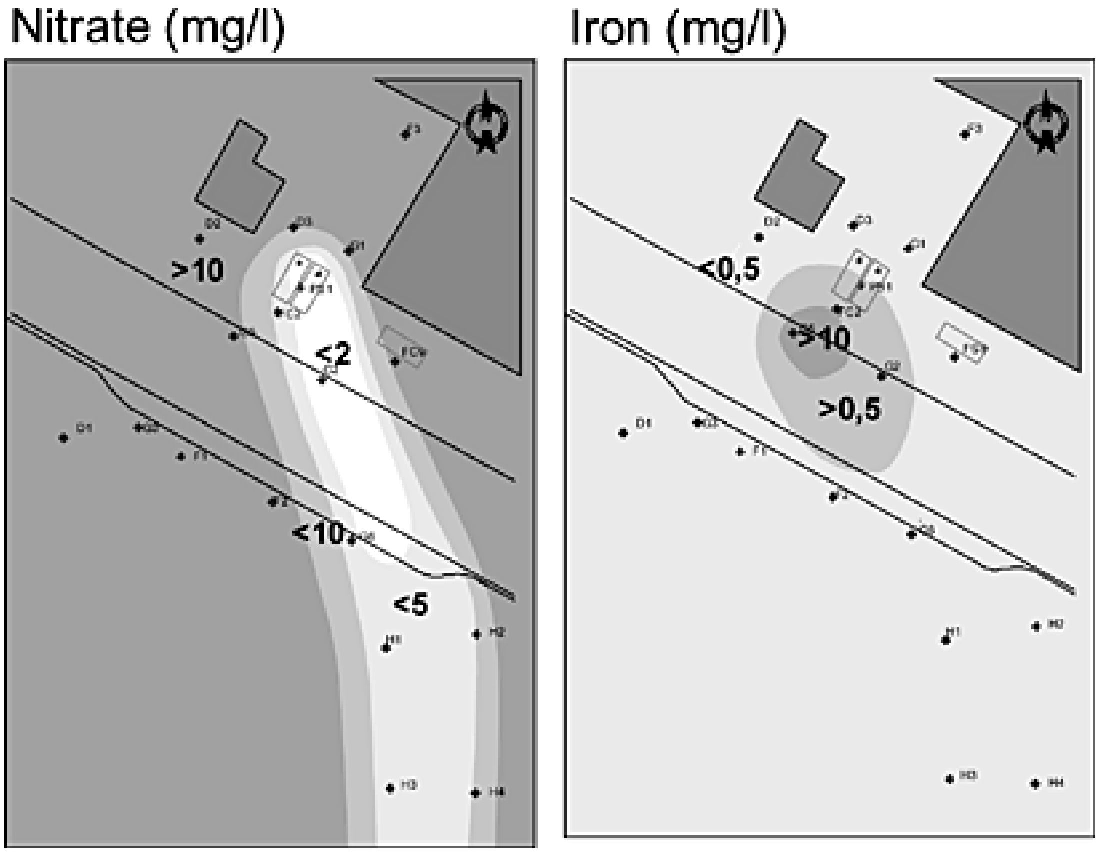
Geology, Cross-Section



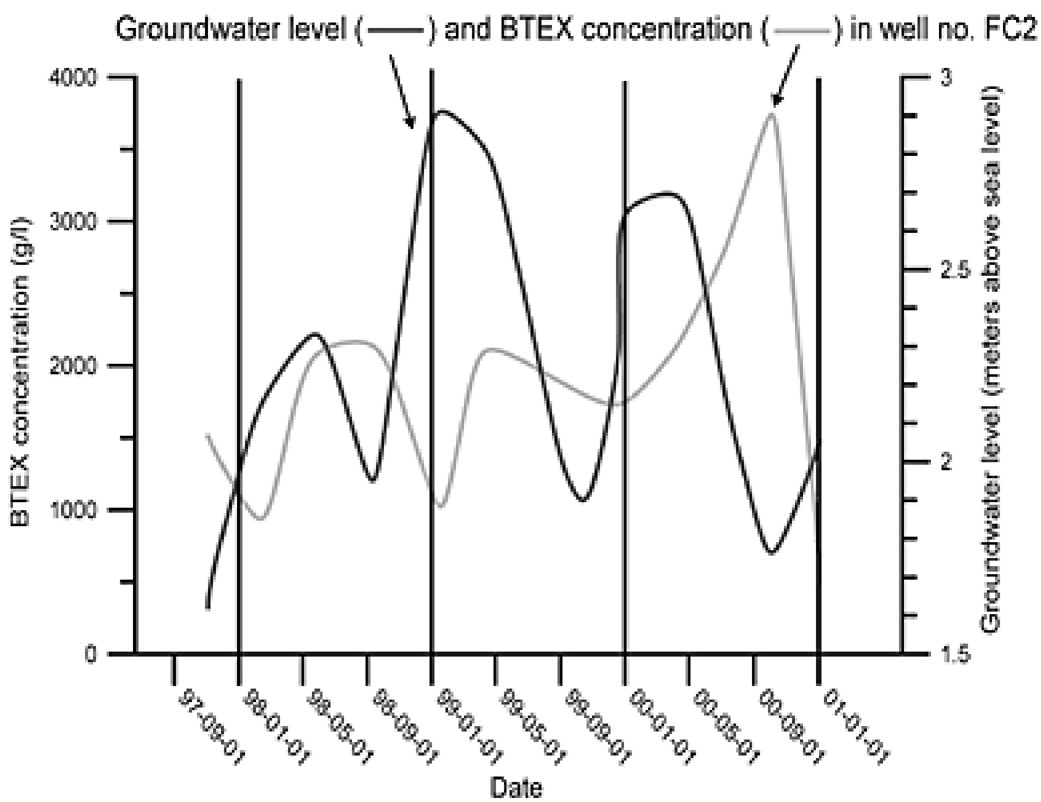
Mapped Plume - BTEX and O_2



Mapped Plume - NO_3^- and Fe(II)



Groundwater level and BTEX concentration



Monitoring from 1997 to 2001

- See Slidepak

Is There a Risk?

- Interpretation of data is difficult
  - Heterogeneous geology
  - Variation in groundwater level and flow direction
  - Variation in redox parameters
  - Influence of two mixed water types
  - Natural geochemical reaction e.g. nitrate reduction due to pyrite oxidation,
    $FeS2 + 14/5NO3- + 4/10H2O \Rightarrow Fe2+ + 2SO42- + 4/5OH- + 14/10N2$
  - H1Ø and H2Ø indicate a risk.
  - Are location wells and screen intervals correct?
  - THC conc. 70-80 µg/l at 45m downstream
  - High detection limit

Conclusive Remarks

- Abstraction wells are located in all parts of DK.
- Drinking water is based on pure groundwater that only needs simple treatment before distribution to consumers.
- In the coming years around 30,000 sites have to be assessed in order to decide if they pose a threat to the groundwater.
- Bio-/degradation is not seen as a remedial technique but is taken into account in the risk assessment.
- Conducting monitoring is one technique or involve several techniques.
- Interpretation of redox zones can be difficult due to variations in hydrogeology and natural processes changing groundwater geochemistry.
- High rates of degradation were not sufficient to avoid a groundwater risk.

Acknowledgements and references

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  - Christian Mossing, Hedeselskabet
    E-mail:hedeselskabet@hedeselskabet.dk (Radsted)

- **Selected references:**

  - Naturlig nedbrydning af olie og chlorerede opløsningsmidler i grundvandet på Drejøgade 3-5, Miljøprojekt nr. 544 2000.
    Web site: http://www.mst.dk
  - C.E. Riis et al. 2000. Redox Characterization for Natural Attenuation of Chlorinated Ethenes and BTEX. 2. Int. Conf. on Remediation of Chlorinated and Recalcitrant Compounds.