GASSYS: Direct in-situ and passive gas sampling
from unsaturated soil and from groundwater

by

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Outline of presentation

- **Design of system and sampling methodology**
  - Basic subsurface sampling methods for gases
  - Basics of GASSYS design
  - Sampling of gas with GASSYS
  - Range of gases sampled thus far with GASSYS
- **Case histories**
  - Langenfeld waste disposal site [methane]
  - Terrania [hydrogen]
  - Schwarze Pumpe [BTEX, methane, H_2S]
  - Düsseldorf/Hilden CHC remediation
    [CHC, VC, ethene, ethane, CO_2, hydrogen]
- **Conclusions**
- **Outlook**

Basic Sampling Methods 1

Active sampling

- by pumping soil-air from boreholes into plastic bags or glass containers

Disadvantages

- gas flows preferentially in higher permeable systems
- gas is not representative for the sampling point
- gas may also be collected preferentially due to differences in partial pressure for different gases
- sampling cannot be repeated under identical conditions (changes of ambient air pressure etc.)
- Gas in groundwater cannot be sampled in a representative manner

Basic Sampling Methods 2

Passive sampling

A: Adsorption samplers

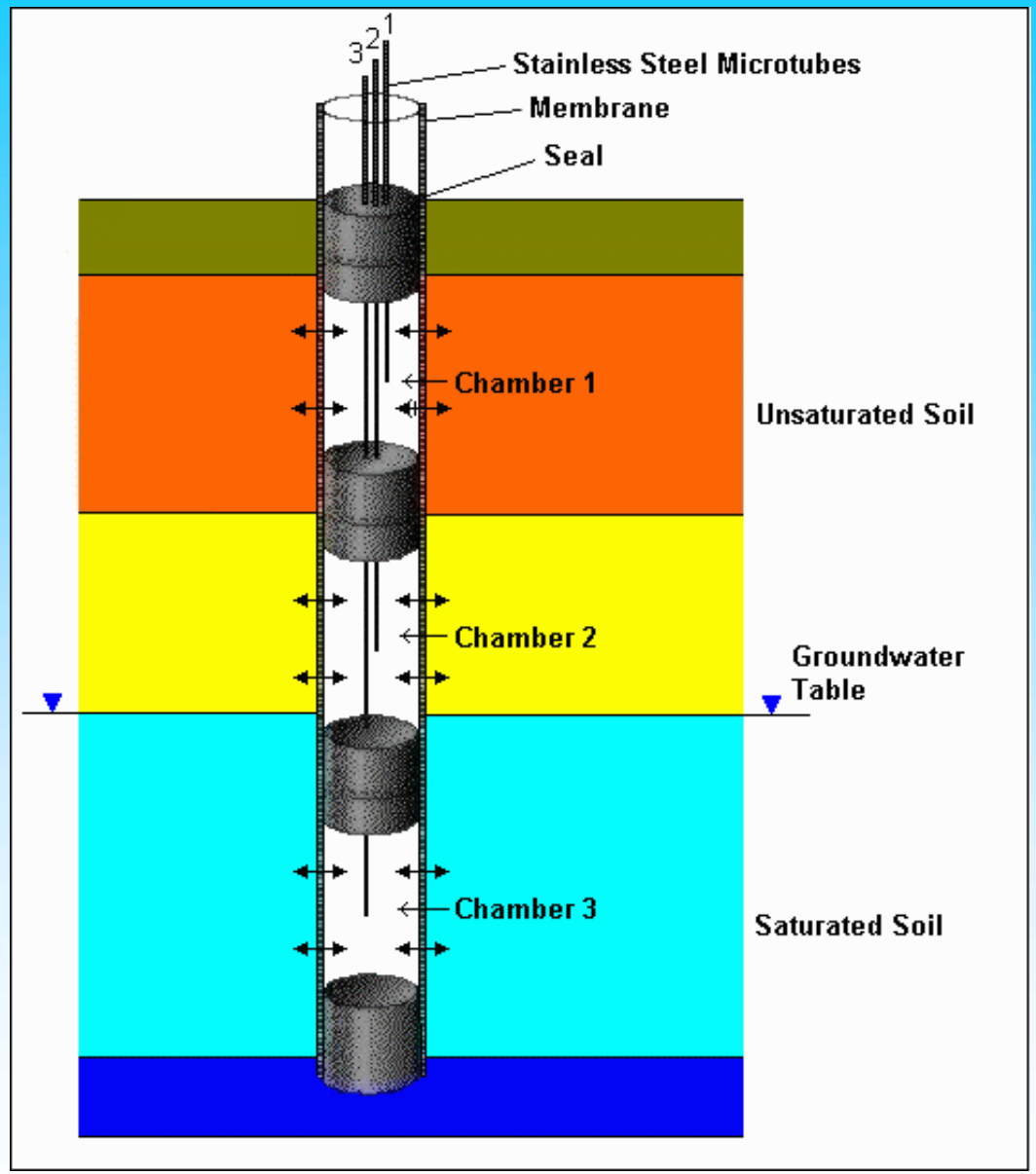
- collect soil gas on adsorbing surfaces such as activated coal
- determine only relative gas concentrations as no direct gas sample is taken
- indicate only a relative degree of contamination

B: Diffusion samplers

- Collect gas samples of actual soil air or gas dissolved in groundwater by diffusion into chambers which are then evacuated for analysis

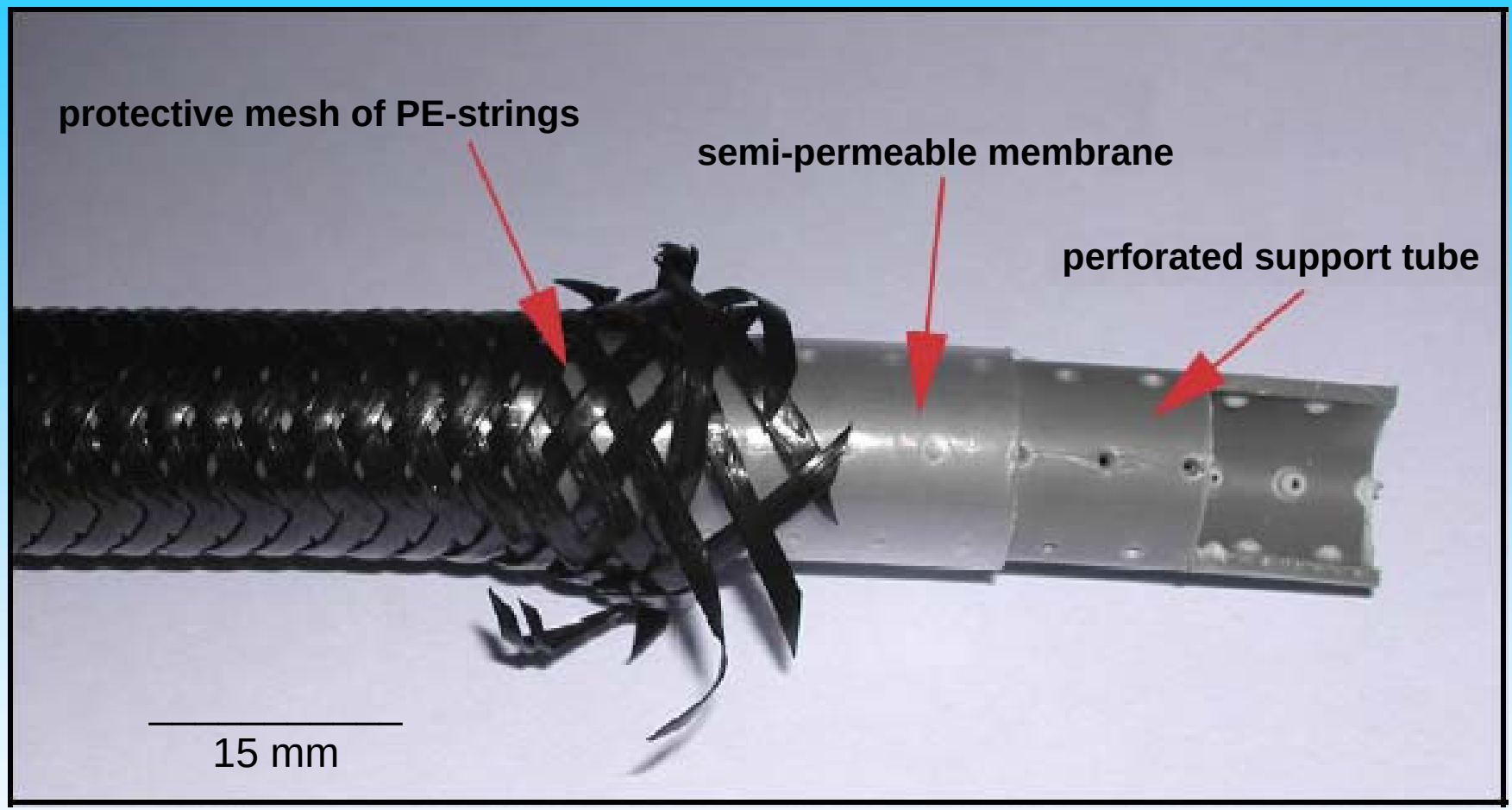
Basics of GASSYS design

GASSYS is a diffusion sampler with, presently, up to 4 diffusion chambers at different depths in one borehole

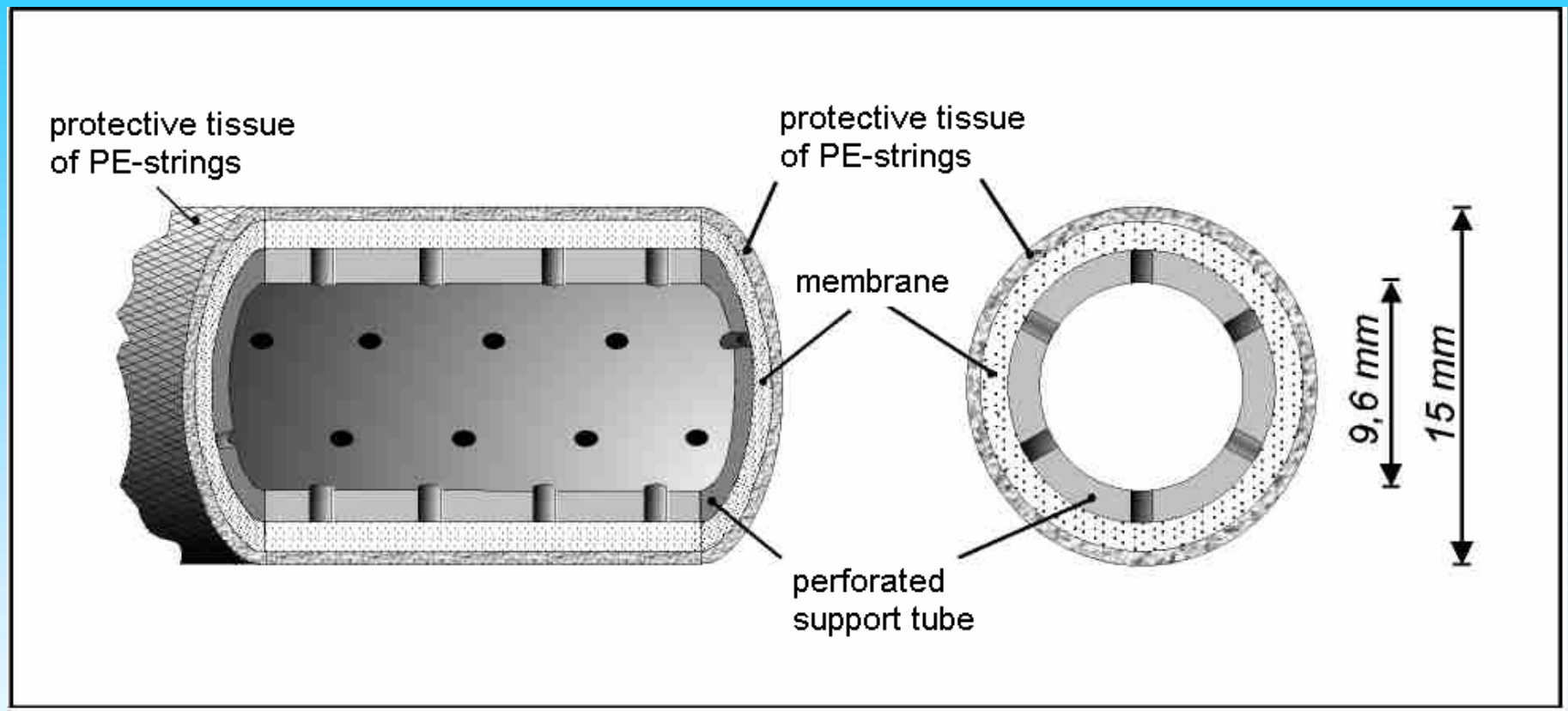


Field installation of GASSYS unit with three collection chambers.

Gas enters and leaves these chambers by diffusion to maintain a continual equilibrium with the surroundings.

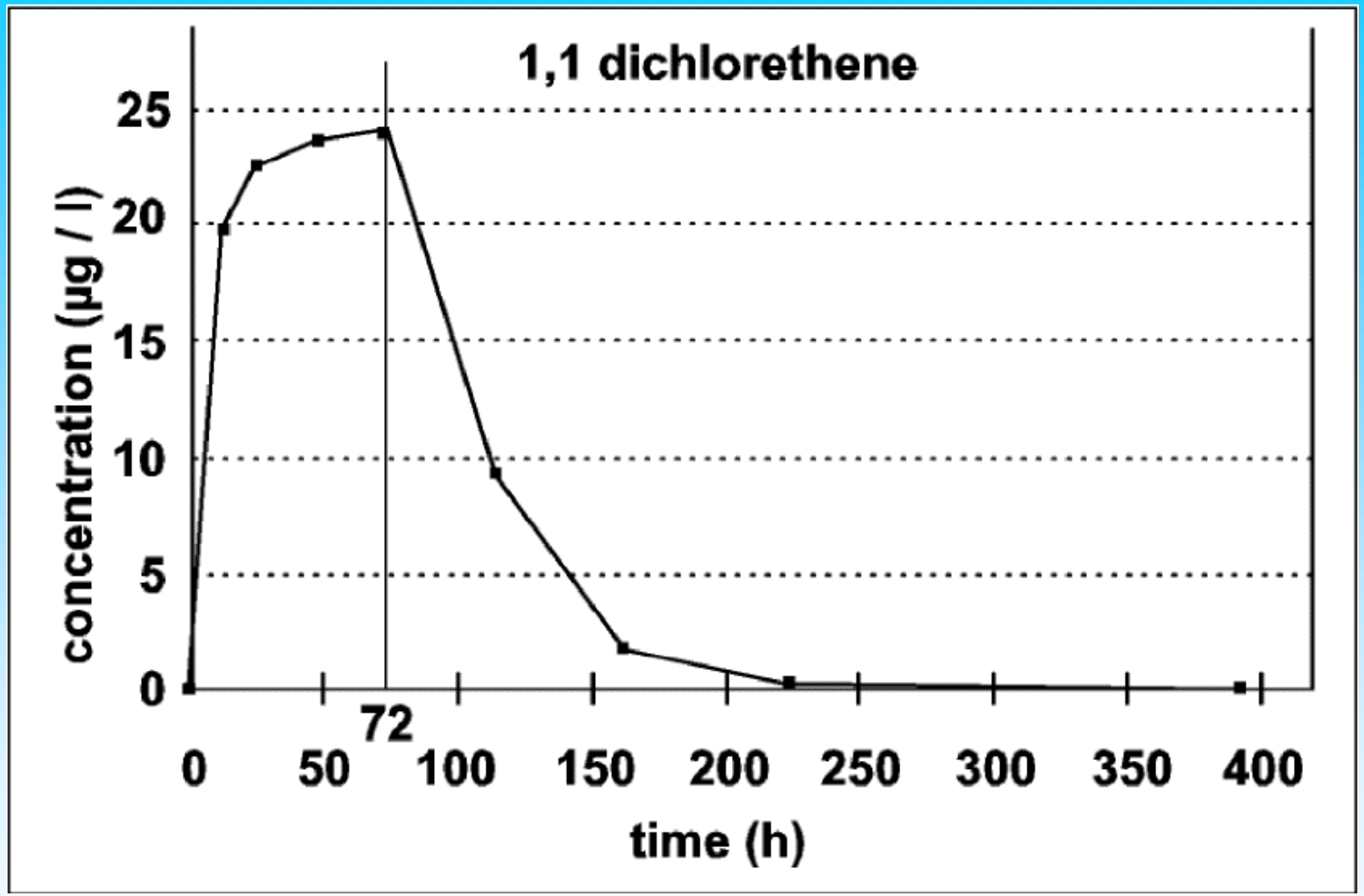


Detail of diffusion tube



Schematic diagram of EVA membrane tube used for GASSYS developed in Germany by Siemens AG for their LEOS pipeline system

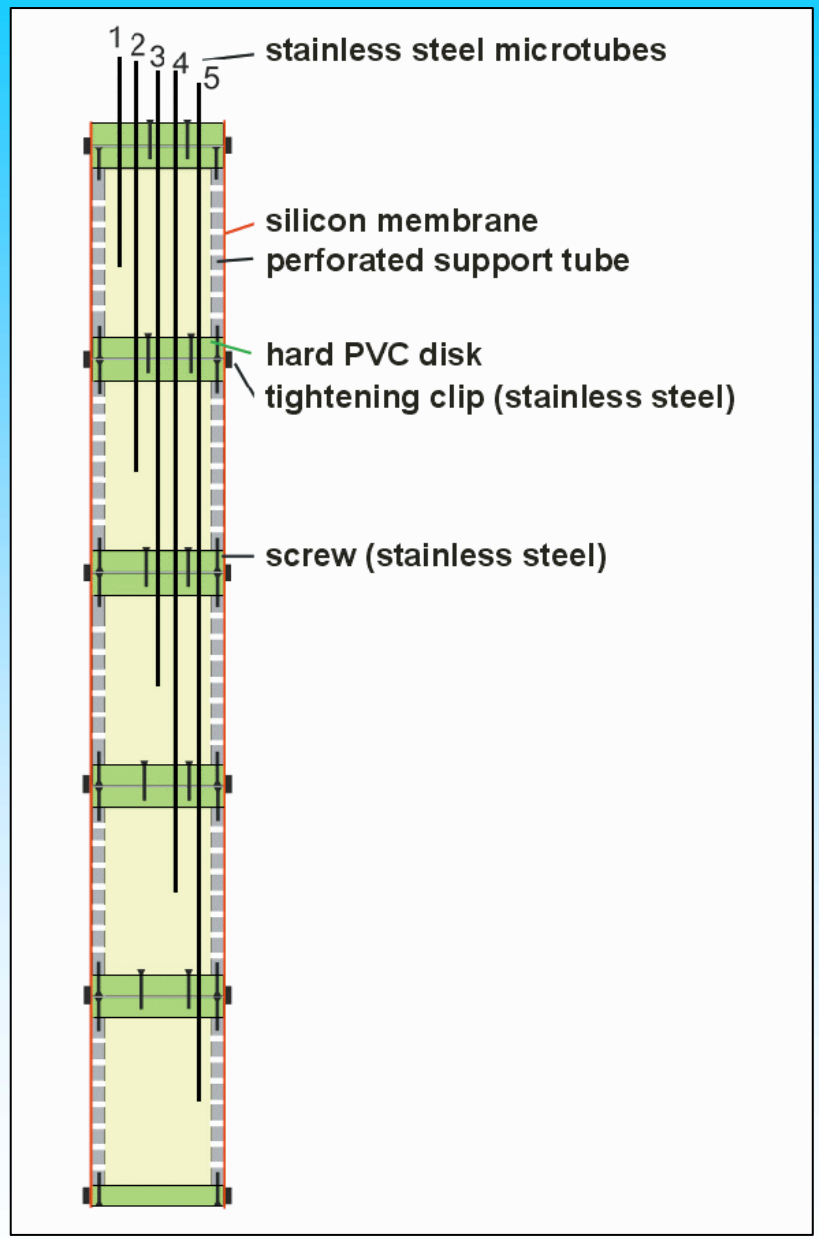
EVA = Ethylene vinyl acetate



Diffusion of 1,1-dichloroethene into a GASSYS gas collection chamber with gas present at the outer wall of the membrane [hours 0 to 72] and lowering of 1,1-dichloromethane concentration in GASSYS collection chamber [hours 72 to 400] after the source of 1,1-dichloroethene has been removed from the outer wall of the membrane. [Data from M. Hamann, University Erlangen-Nuremberg]

Top end of GASSYS installation showing the stainless steel microtubes for taking samples from four distinct collection chambers.

Access to GASSYS installation above ground.



New variant of GASSYS under development

- 10 or more chambers stacked vertically
- outer diameter 65 mm
- chamber volume 160 ml (at 1 m length)

Sampling of gas from GASSYS

Sampling set to collect gas samples from GASSYS.

Evacuation of air from a headspace vial.

Evacuation of gas from a GASSYS collection chamber by means of a special syringe. Pressure meter in front.

Measurement of gas pressure within sampled GASSYS chamber

Insertion of gas sample into headspace vial. The sample should be transported to the lab promptly for next-day analysis.

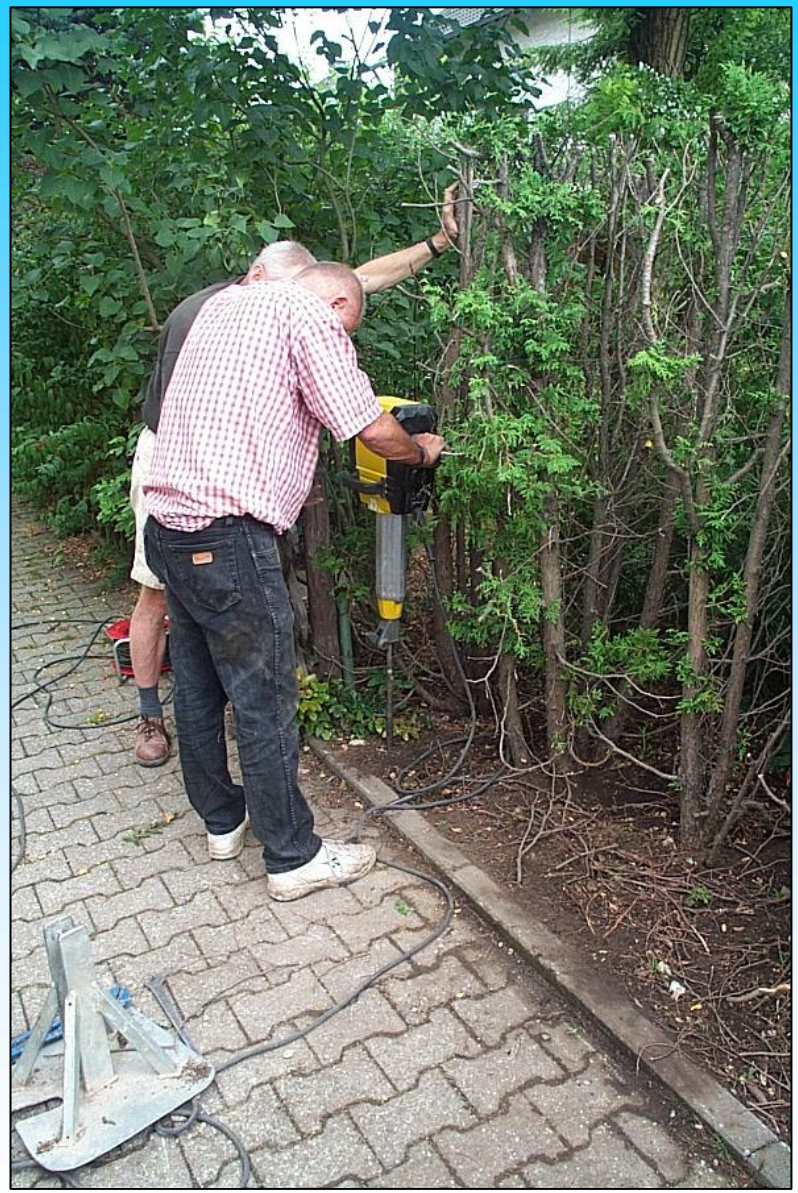
Range of gases tested and sampled thus far in EVA collection tubes

acetone	chloropicrin	ethanol	heating oil	pentyl acetate
acrylonitrile	crude oil	ethyl acetate	n-hexane	propane
ammonia	cyclohexane	ethene	hydrogen	iso-propanol
benzene	cyclohexanone	ethylene oxide	hydrogen sulfide	phenyl methanol
n-butane	dibutyl ether	formaldehyde	methane	styrene
iso-butane	dichloroethane	freon-11	methanol	tetrachloroethene
butanol	dichloroethene	freon-12	methyl acetate	tetrahydrofuran
butanone	dichloromethane	freon-21	methyl ethyl ketone	toluene
butyl acetate	diesel fuel	freon-113	methyl mercaptan	trichloroethane
carbon dioxide	diethyl ether	freon-502	nitrogen dioxide	trichloroethene
carbon monoxide	dimethylamine	gasoline	n-pentane	trichloromethane
chlorine	dioxane	halon-1211	oxygen	vinyl chloride
chloromethane	ethane	halon-1301	pentanol	xylene

Case History:
Langenfeld Waste Disposal

Methane content in unsaturated soil and in groundwater

Source of Data: WDA Consultants Inc., Calgary
[WKC Consultants, Krefeld, Germany]

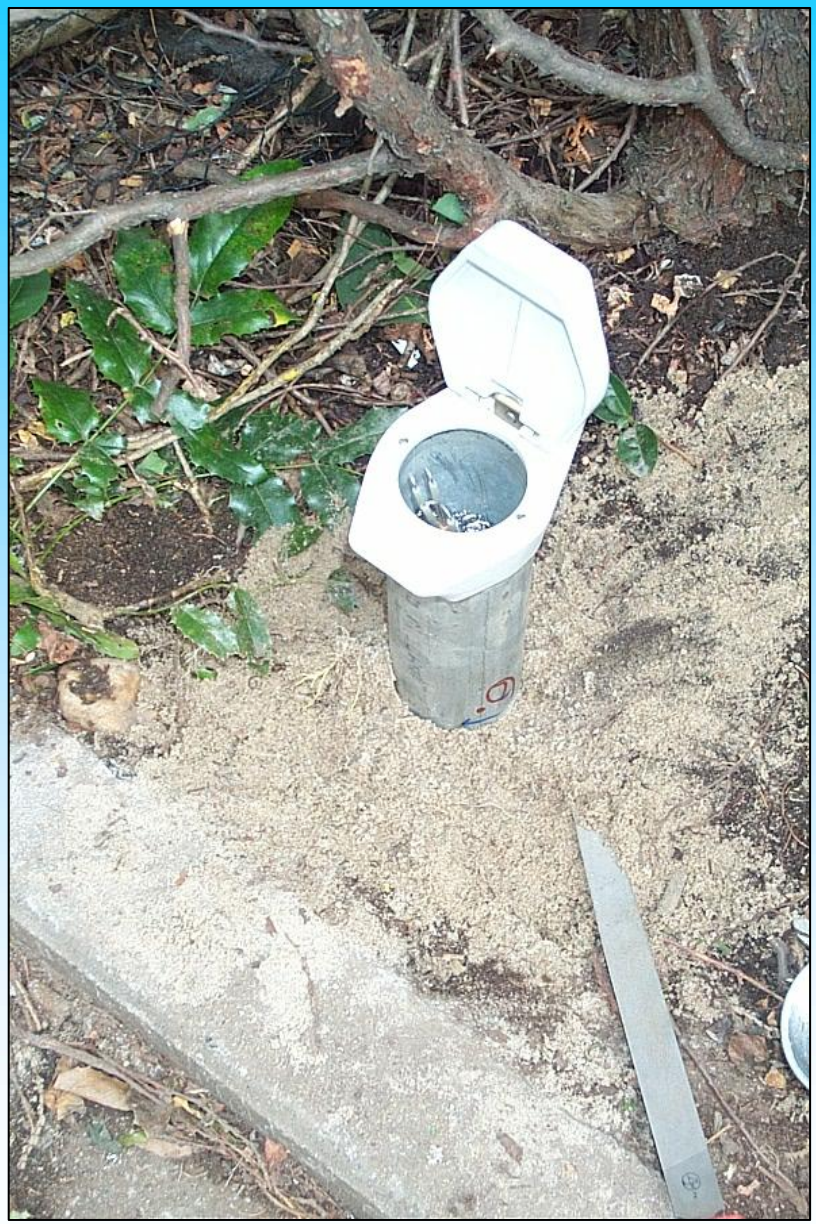


Drilling a small diameter hole with a hydraulic hammer. This drilling method can be used in tight spots. Other small diameter drilling systems could also have been used.

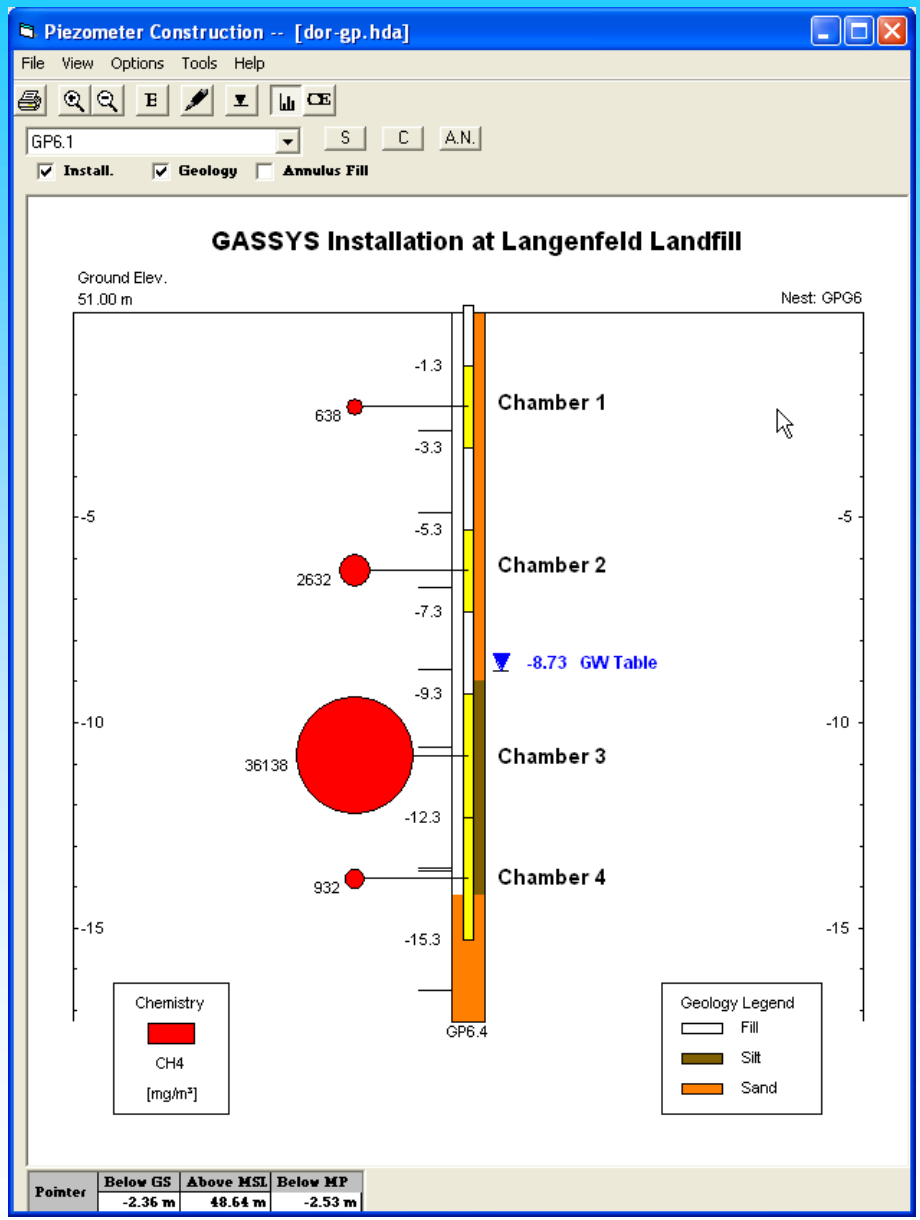
GASSYS hose with two semipermeable collection chambers prepared for installation.

Small-diameter installation casing has been drawn. Protective tube is shown.

Outer protective surface casing has been installed.



Outer protective surface casing with cap open.



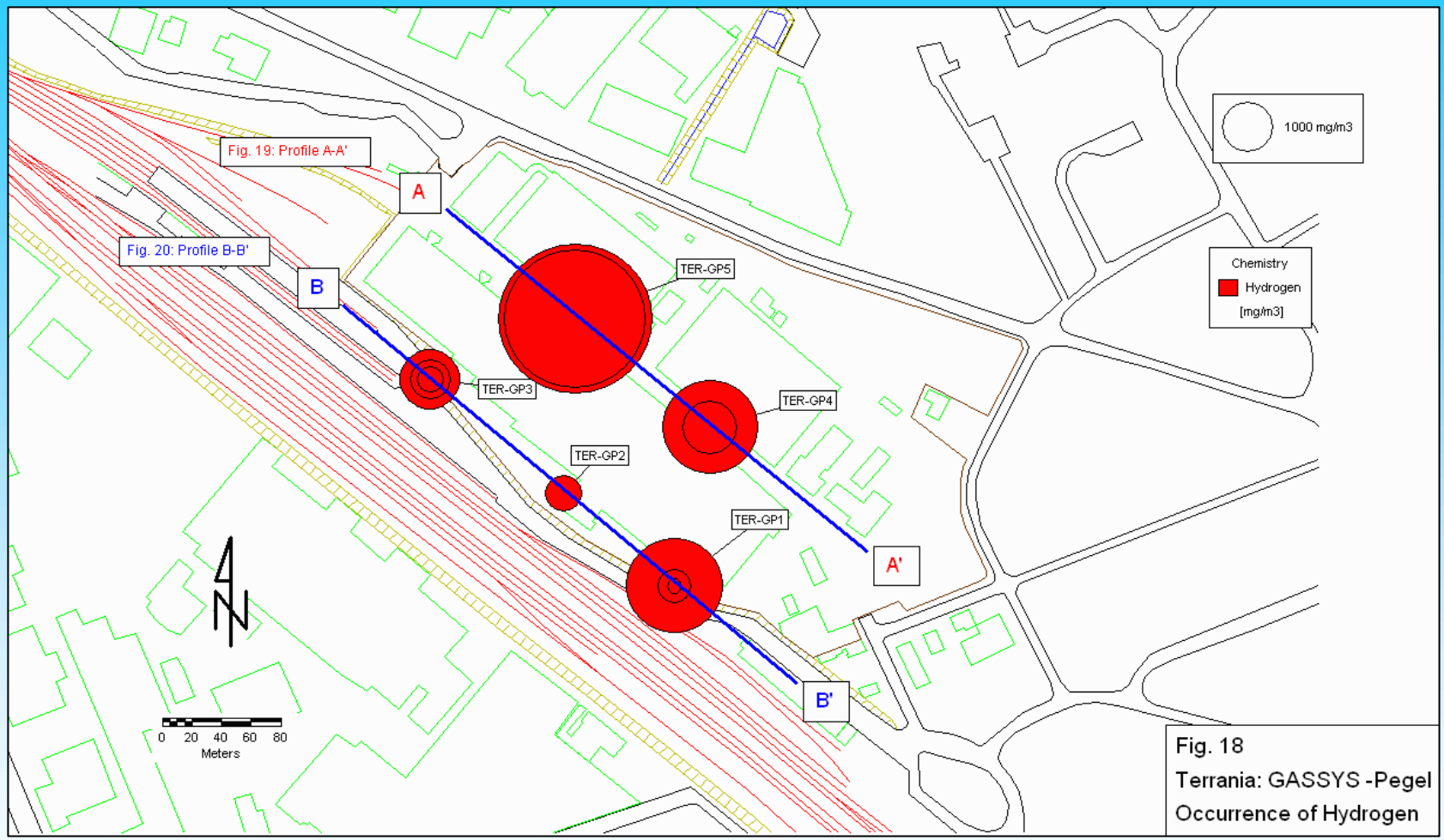
Results of methane sampling above and below the groundwater table at a landfill site, as presented by WDA's program HYDRODYNAMIK [HD].

Case History: Terrania

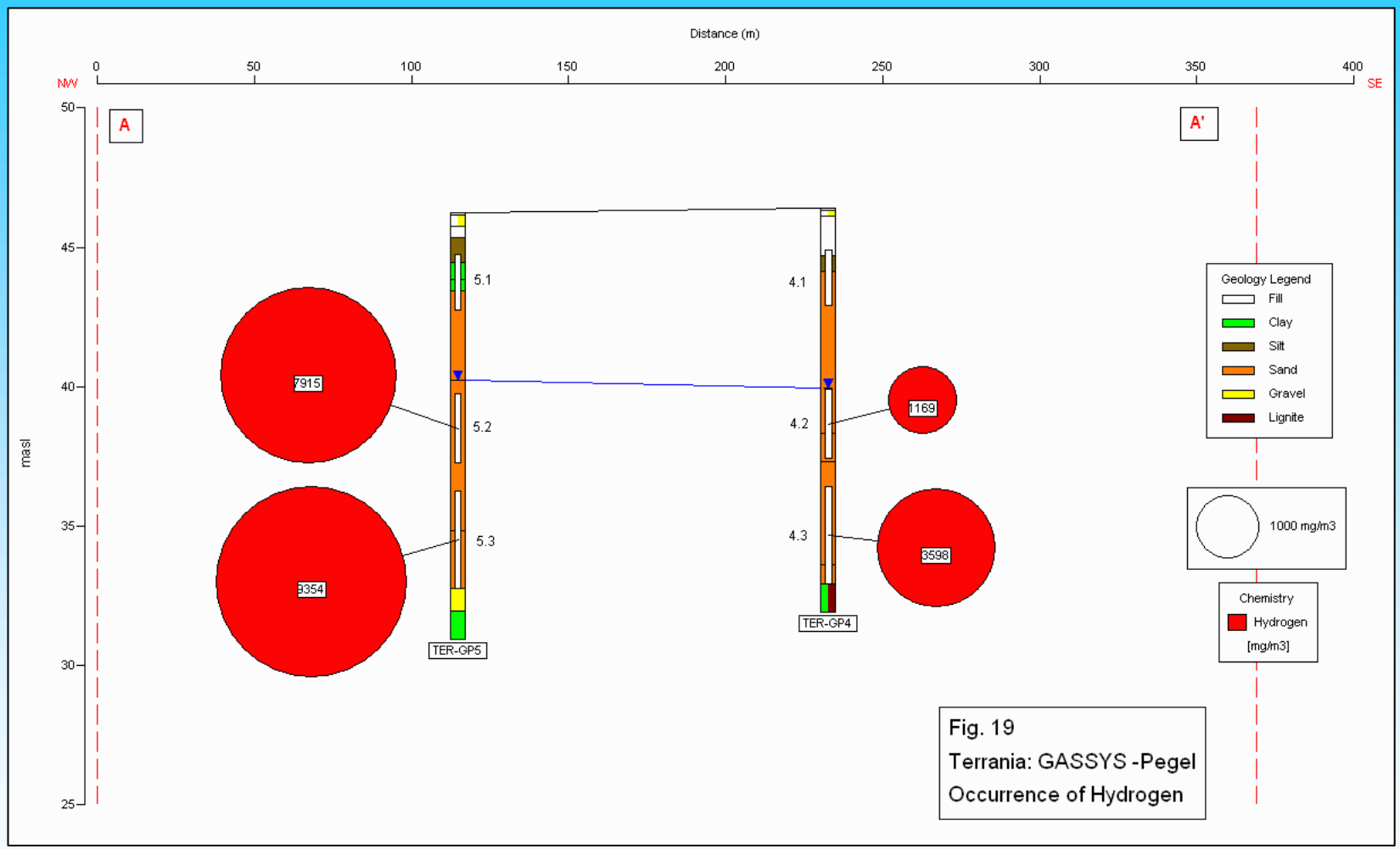
Hydrogen gas content in groundwater

Source of Data: WDA Consultants Inc., Calgary
[WKC Consultants, Krefeld, Germany]

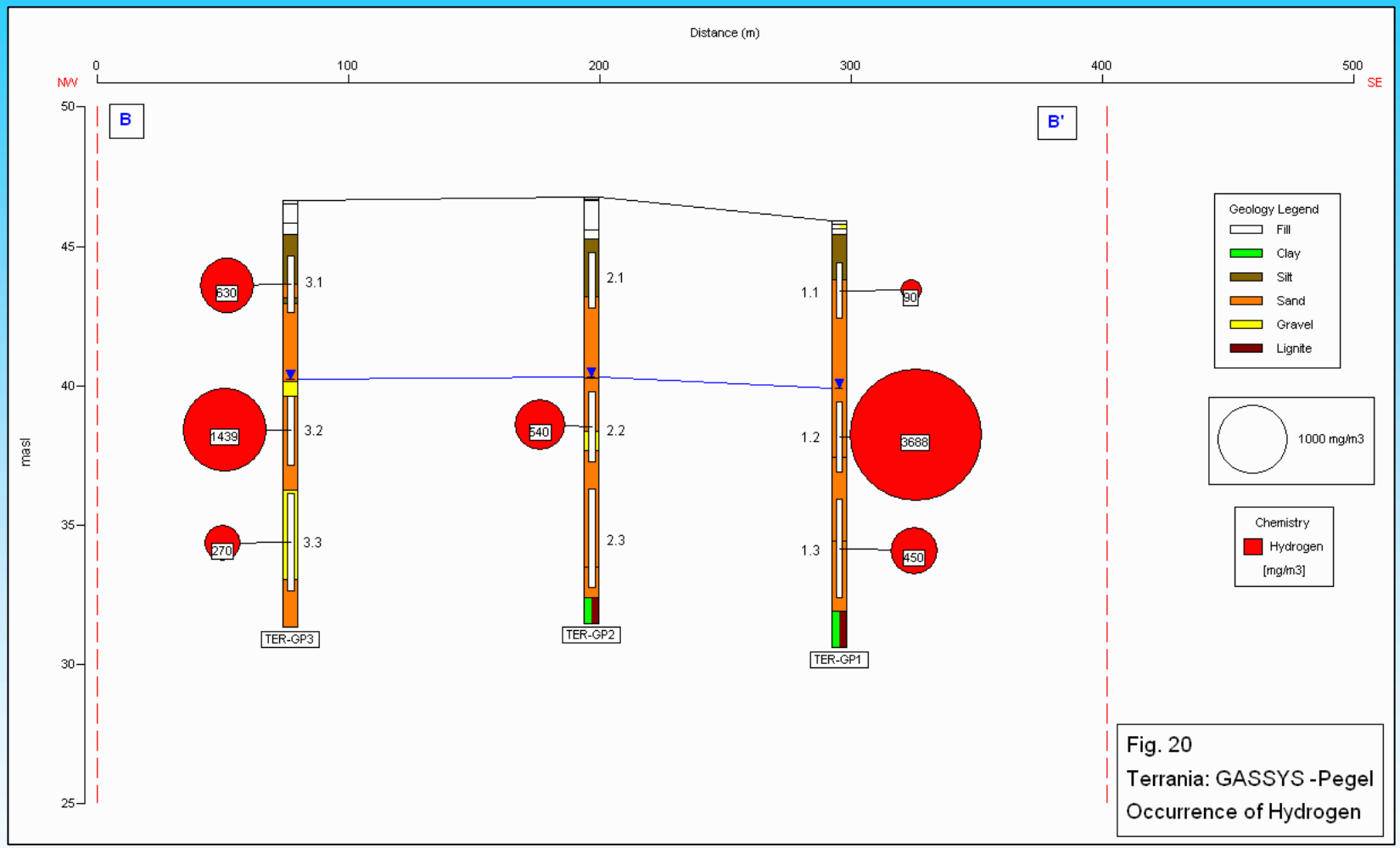
Access to installation below ground in a paved area at plant site.



Terrania - GASSYS installations: Occurrence of hydrogen gas



Terrania – GASSYS installations: occurrence of hydrogen gas

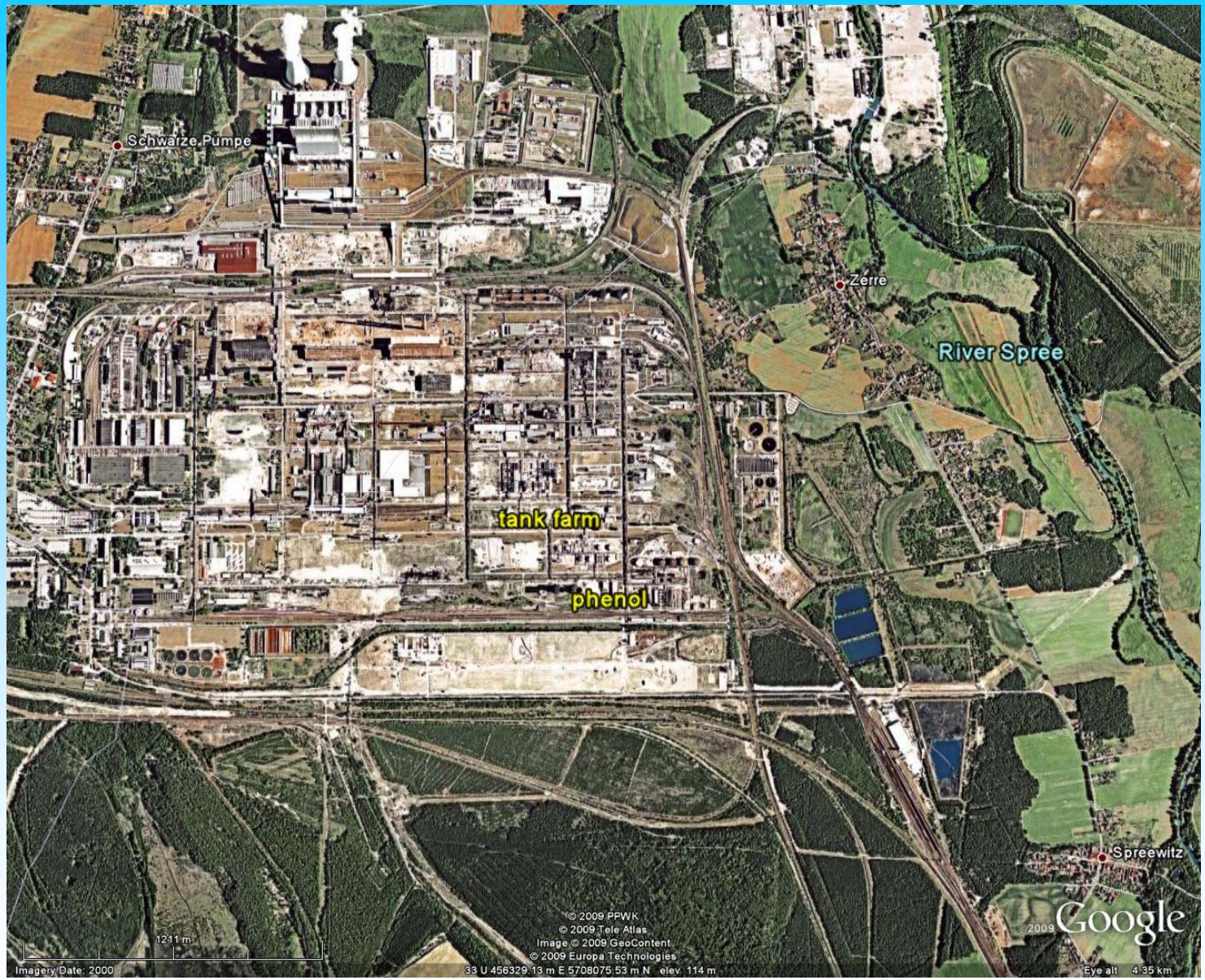


Terrania – GASSYS installations: occurrence of hydrogen gas

Case History: Schwarze Pumpe
Remediation of benzene/toluene plumes

GASSYS: sampling of BTEX, H_2S, and methane gases in groundwater

Data provided by Büro DR. BEERBALK
Ingenieurtechnische Projekte für
Umwelt, Altlasten und Entsorgung,
Berlin



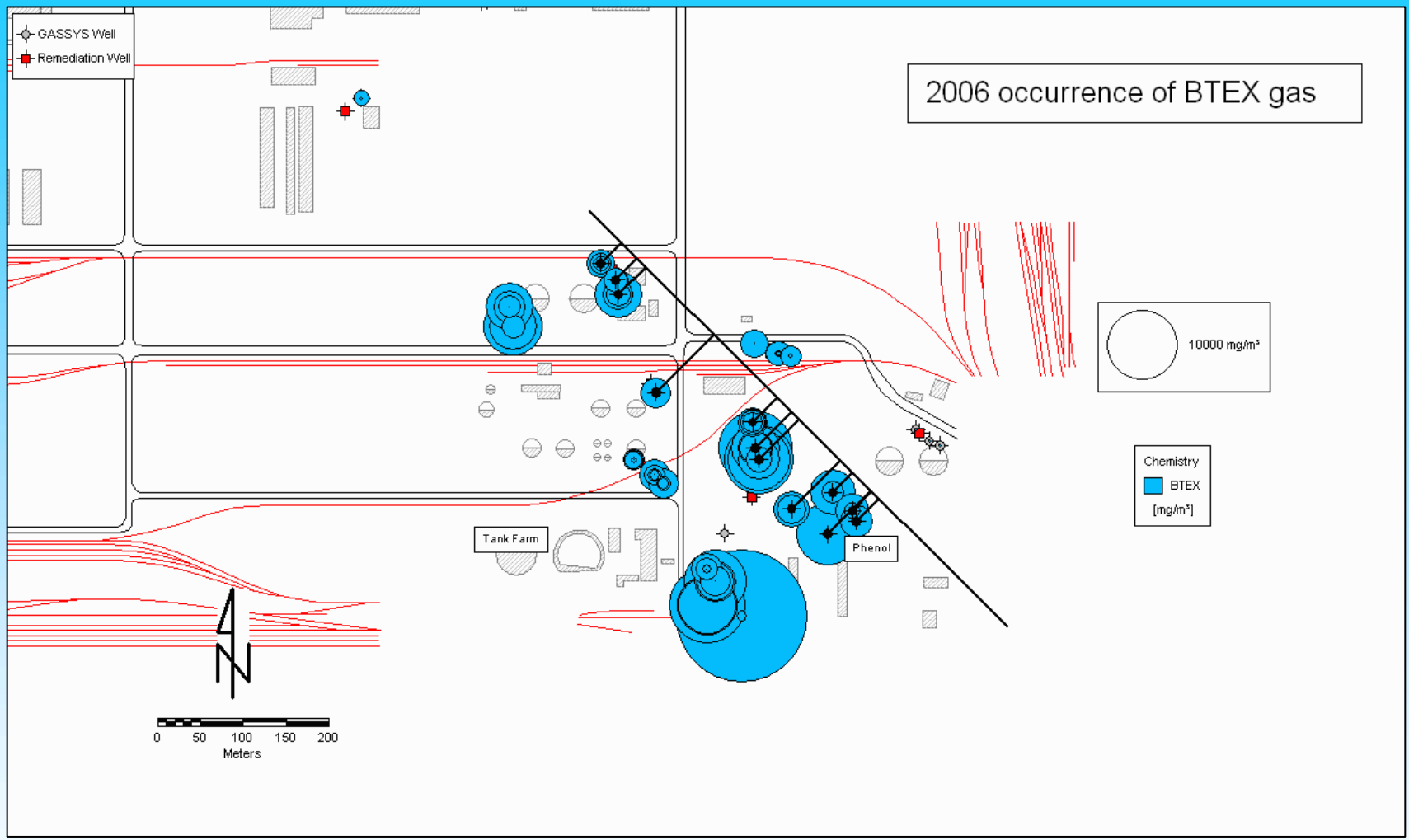
Industrial plant site ‘Schwarze Pumpe’.

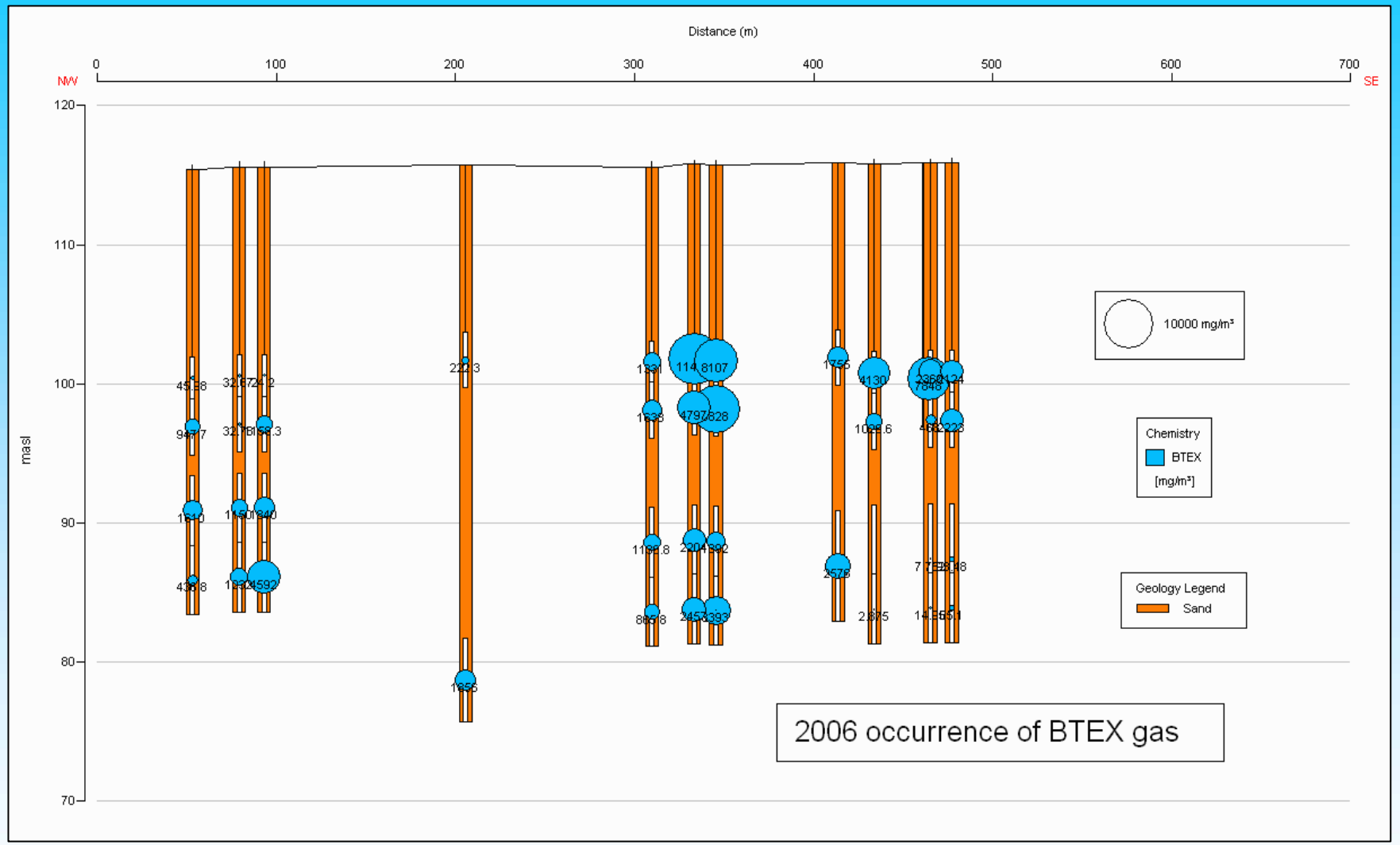
Drilling of auger hole for installation of GASSYS

GASSYS installation above ground.

Access to GASSYS installation below ground in the field.

Training for gas sampling at ‘Schwarze Pumpe’ plant site.





Assumed Microbiological Processes

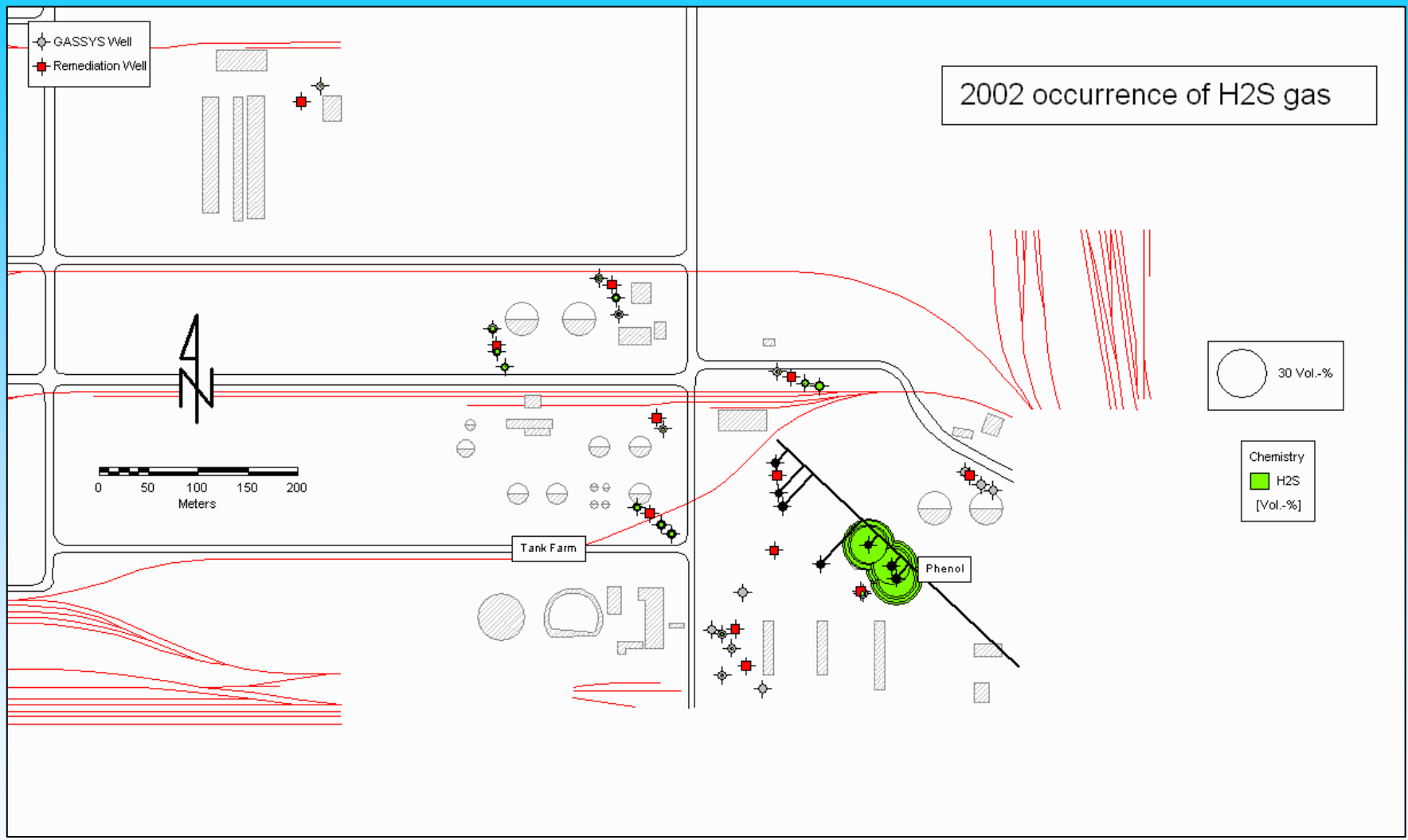
(A) Process of Sulfate Reduction

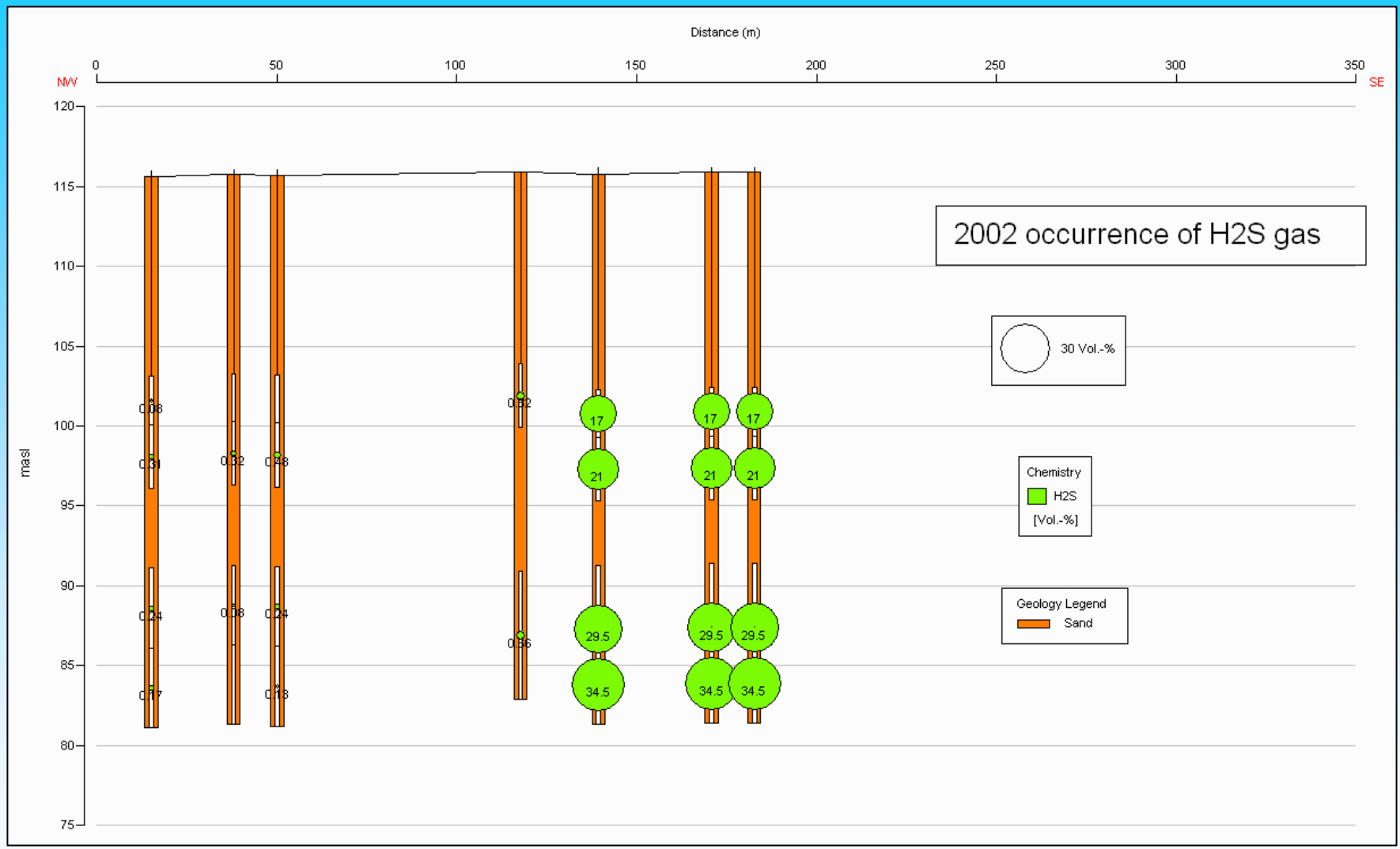
$$C_{10}H_8 + 6\ SO_4^{2-} \rightarrow 10\ CO_2 + 4\ H_2O + 6\ H_2S$$

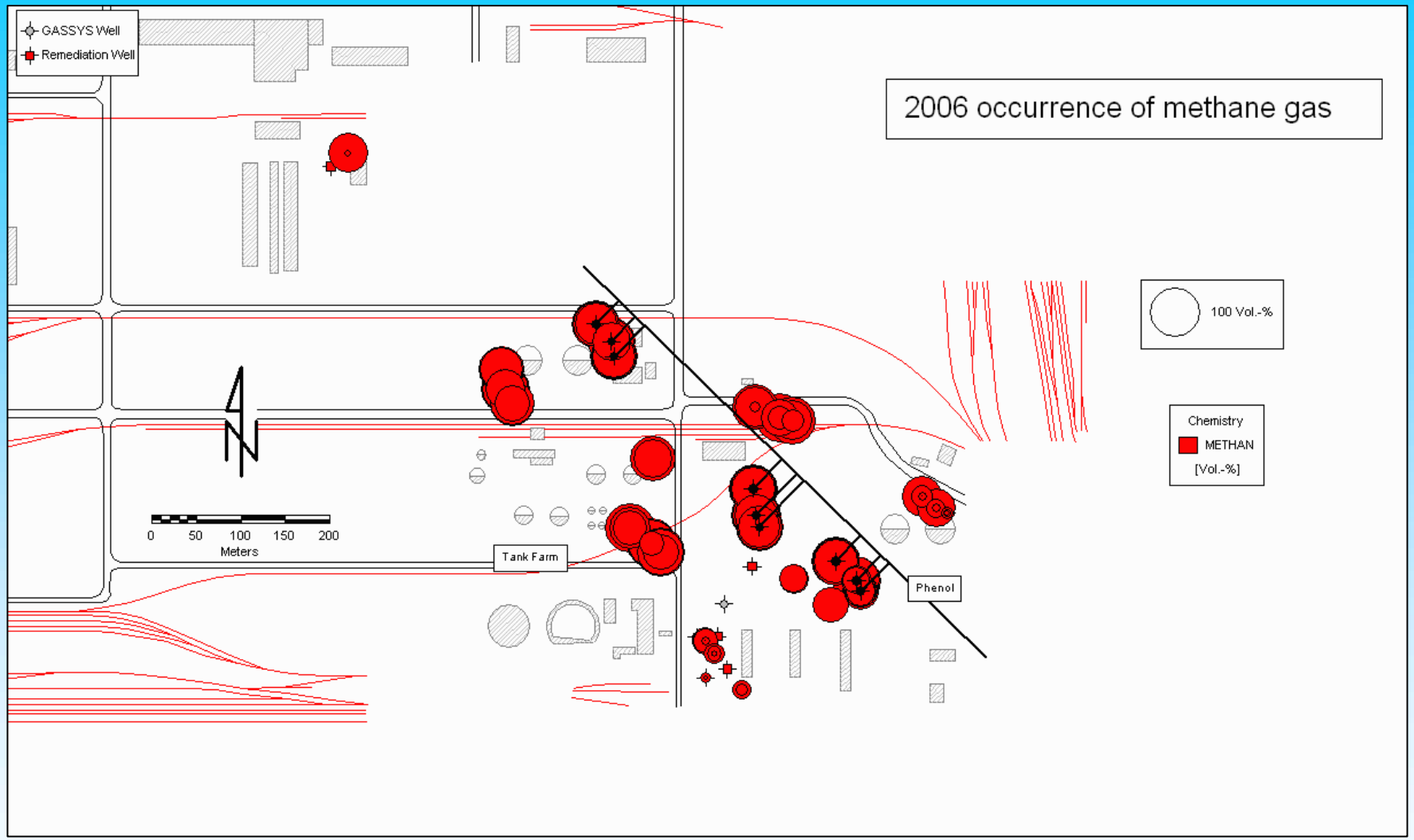
was dismissed as H_2S was generally found in minor amounts only

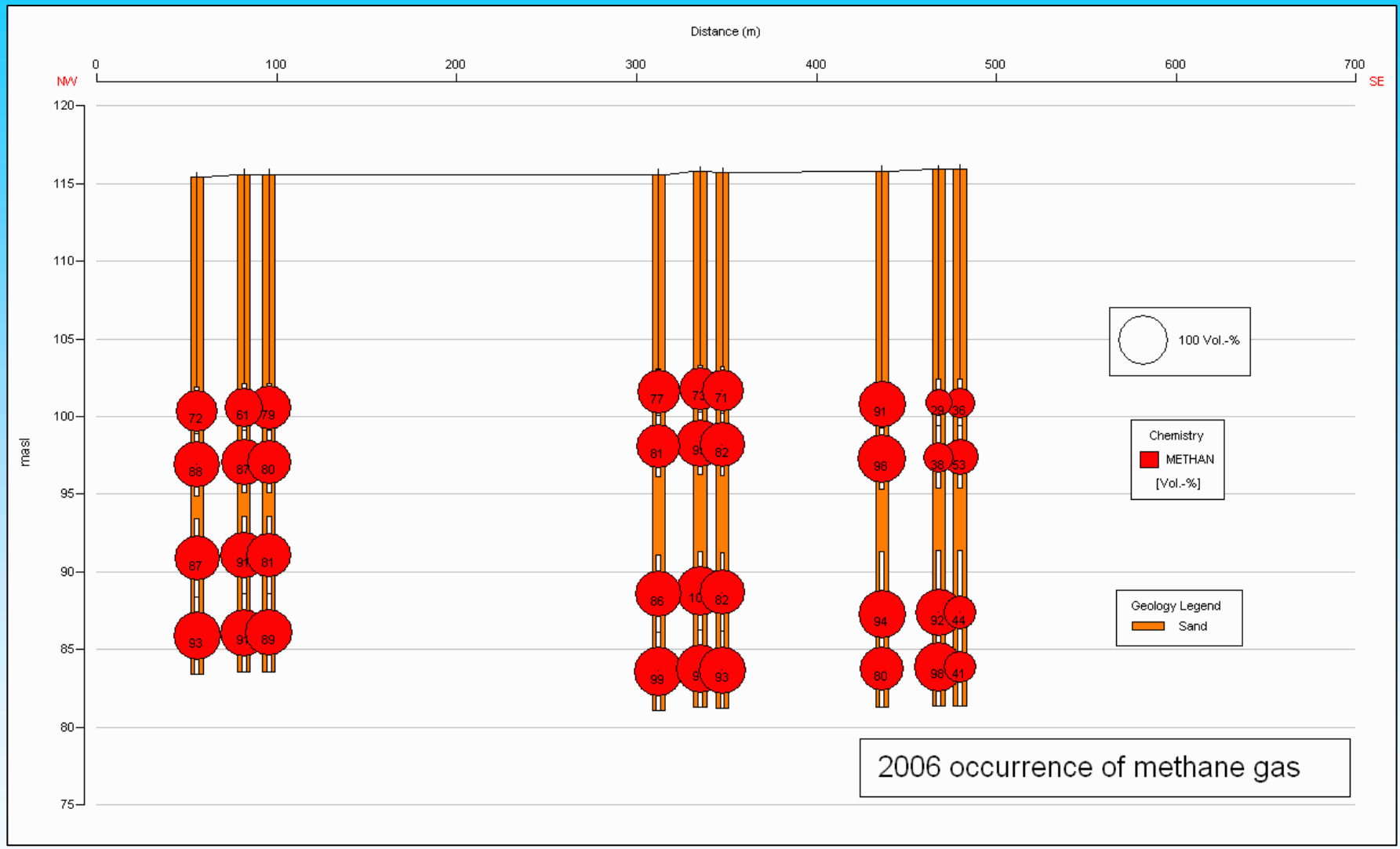
(B) Degradation of Benzene under Anaerobic Conditions

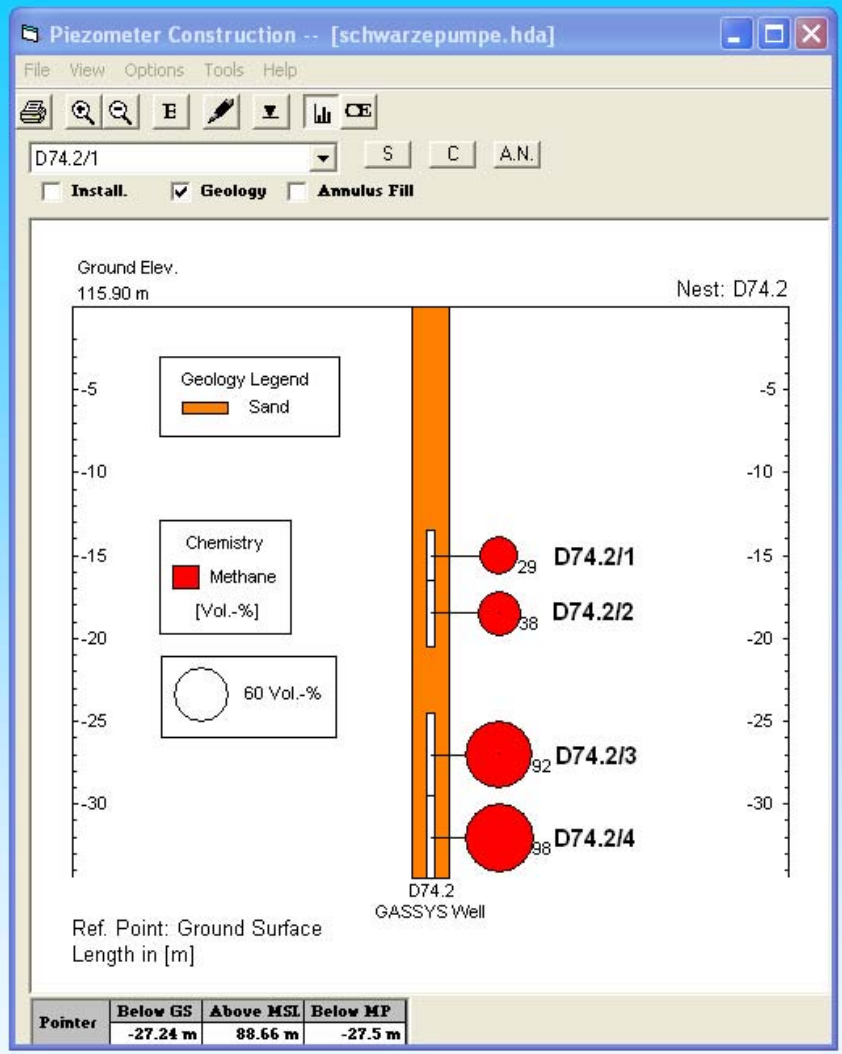
$$18\ H_2O + 4\ C_6H_6 \rightarrow 9\ CO_2 + 15\ CH_4$$

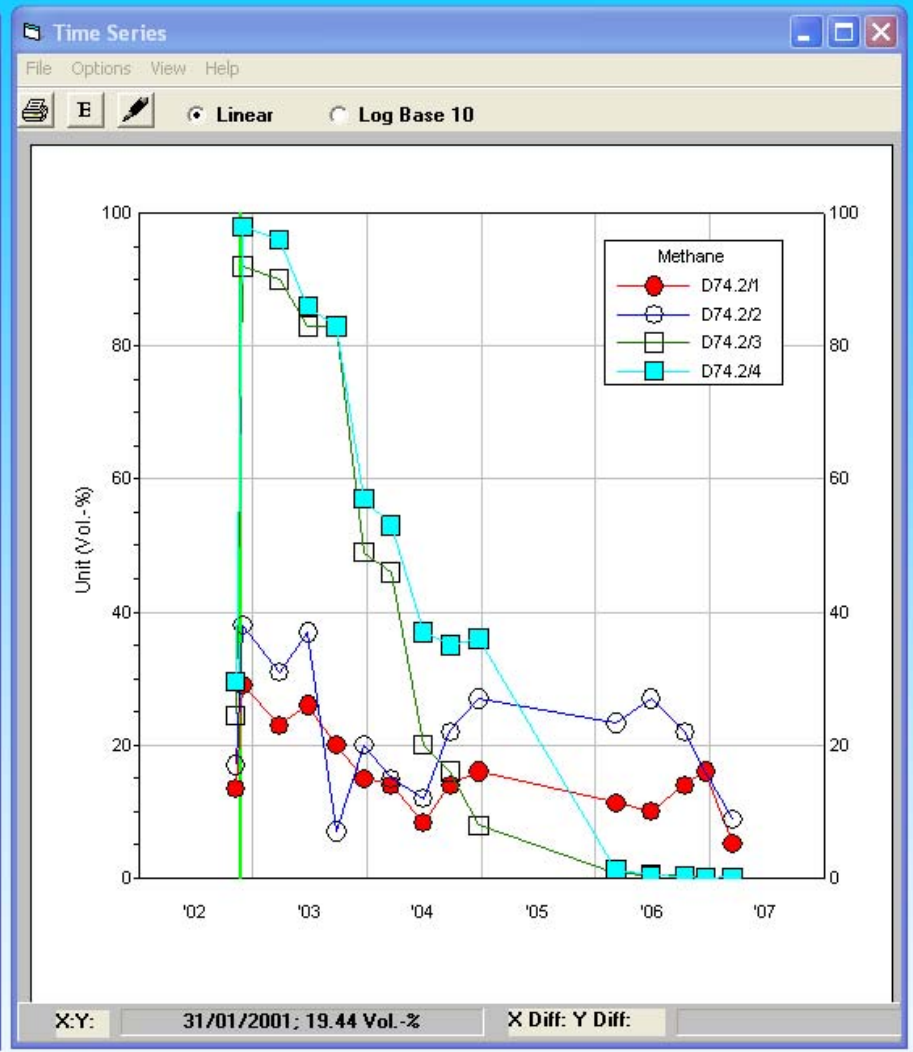






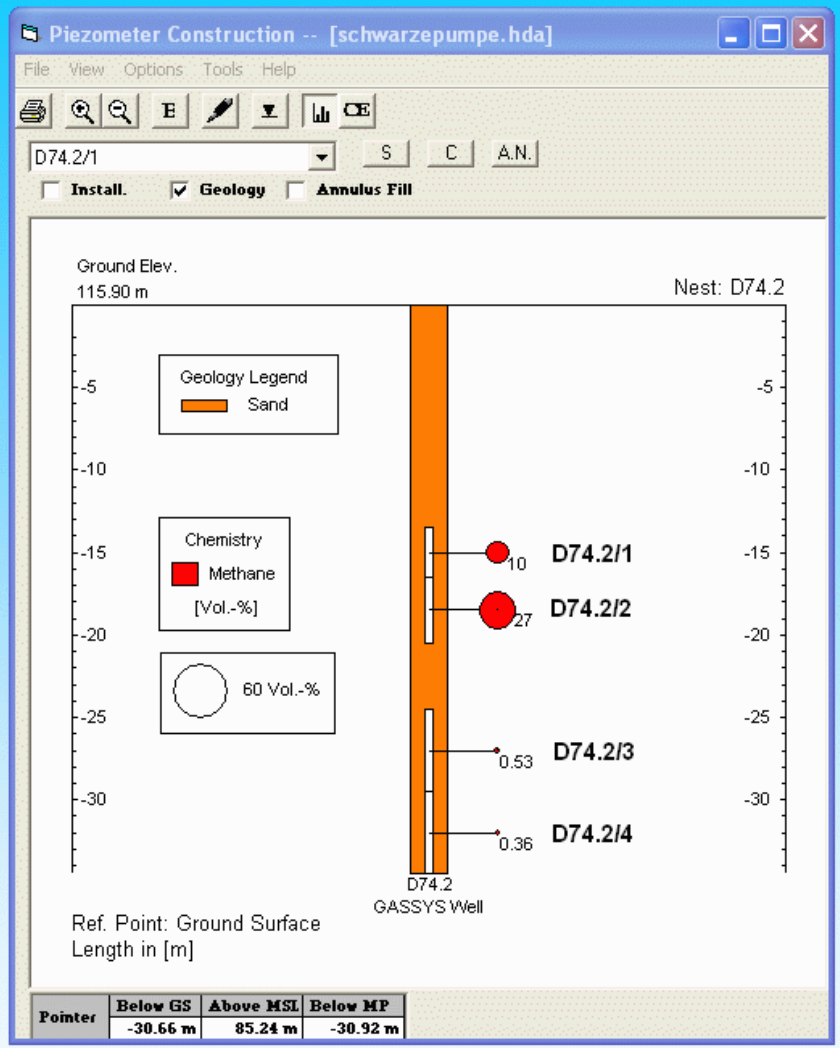


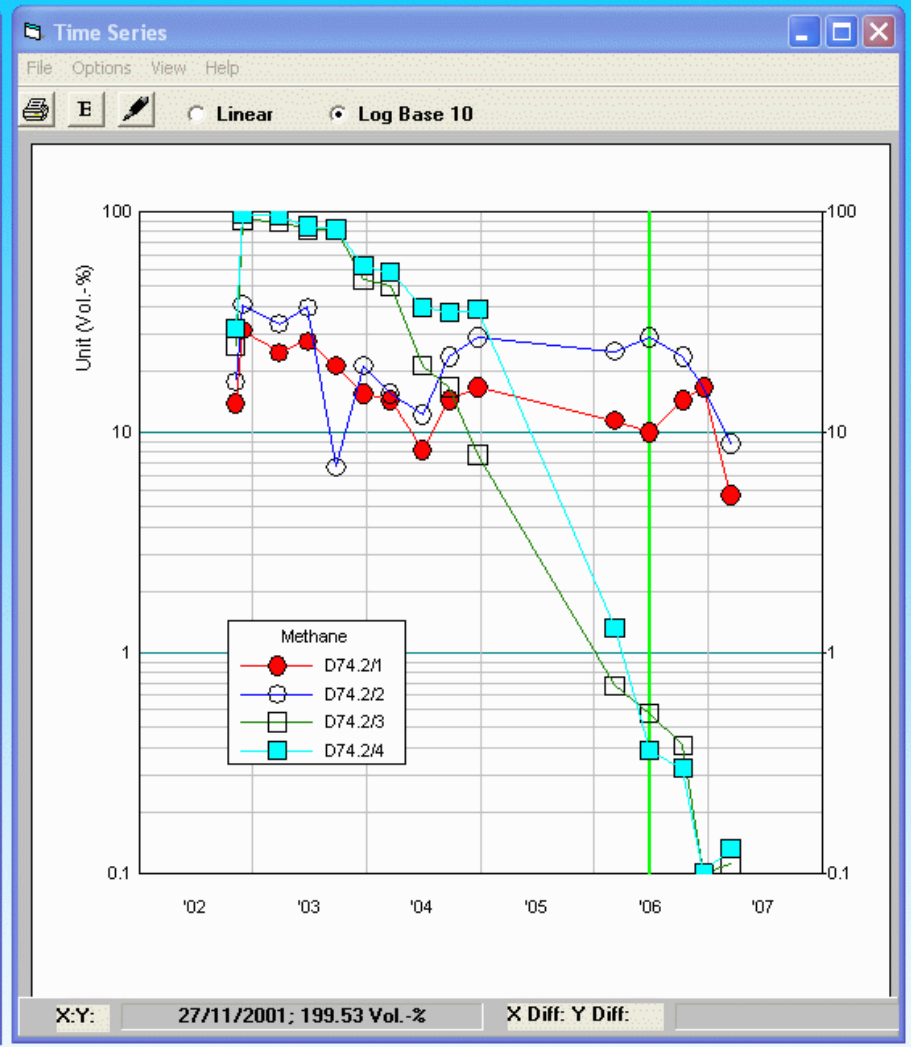




Methane trends measured with GASSYS in nest D74.2

Left diagram shows methane values in individual chambers for 28/11/2002.
Right diagram [linear scale] shows decline of methane gas from 2002 to 2007.





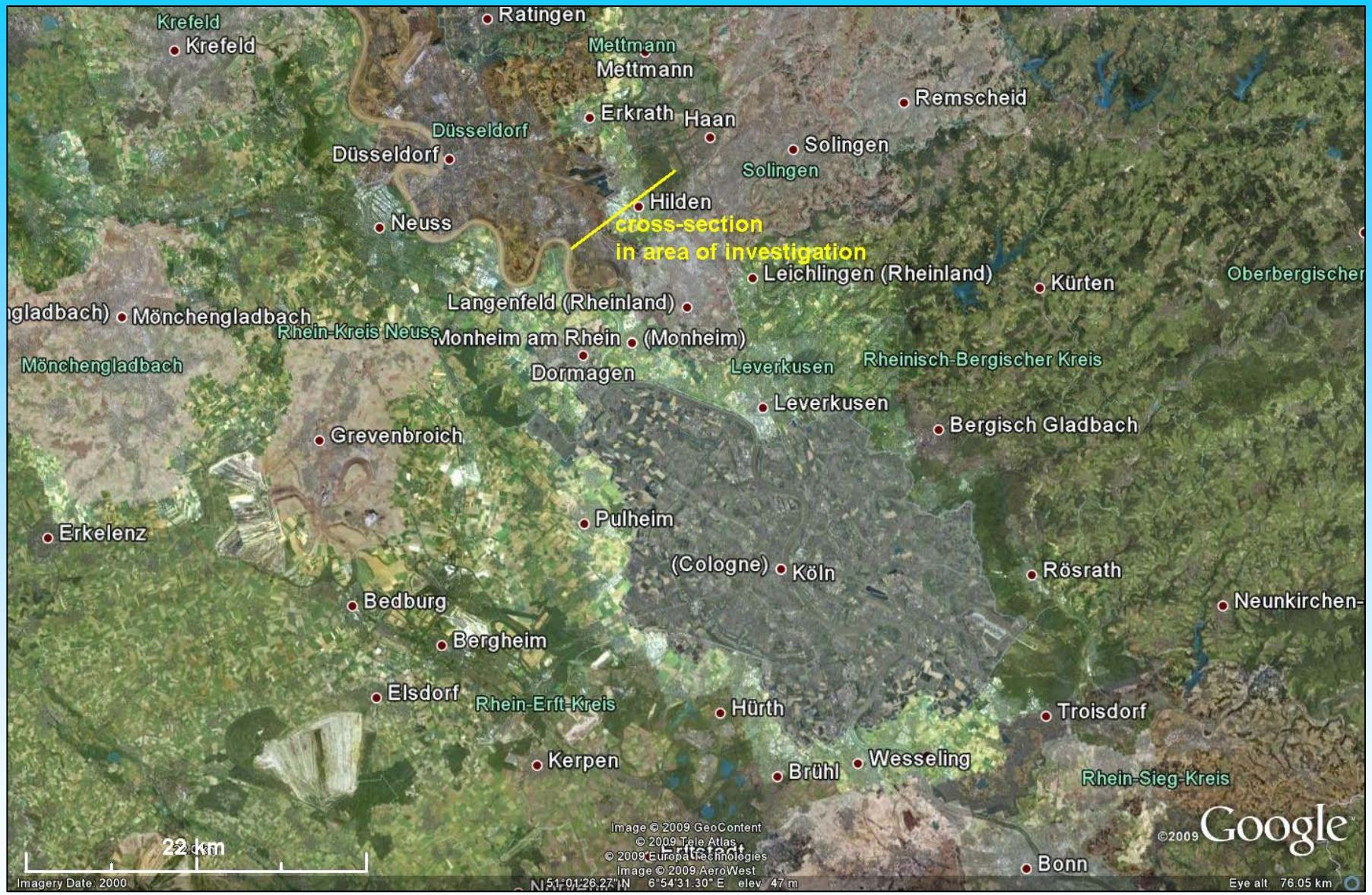
Methane trends measured with GASSYS in nest D74.2

Left diagram shows methane values in individual chambers for 26/06/2006.
Right diagram [log scale] shows decline of methane gas from 2002 to 2007.

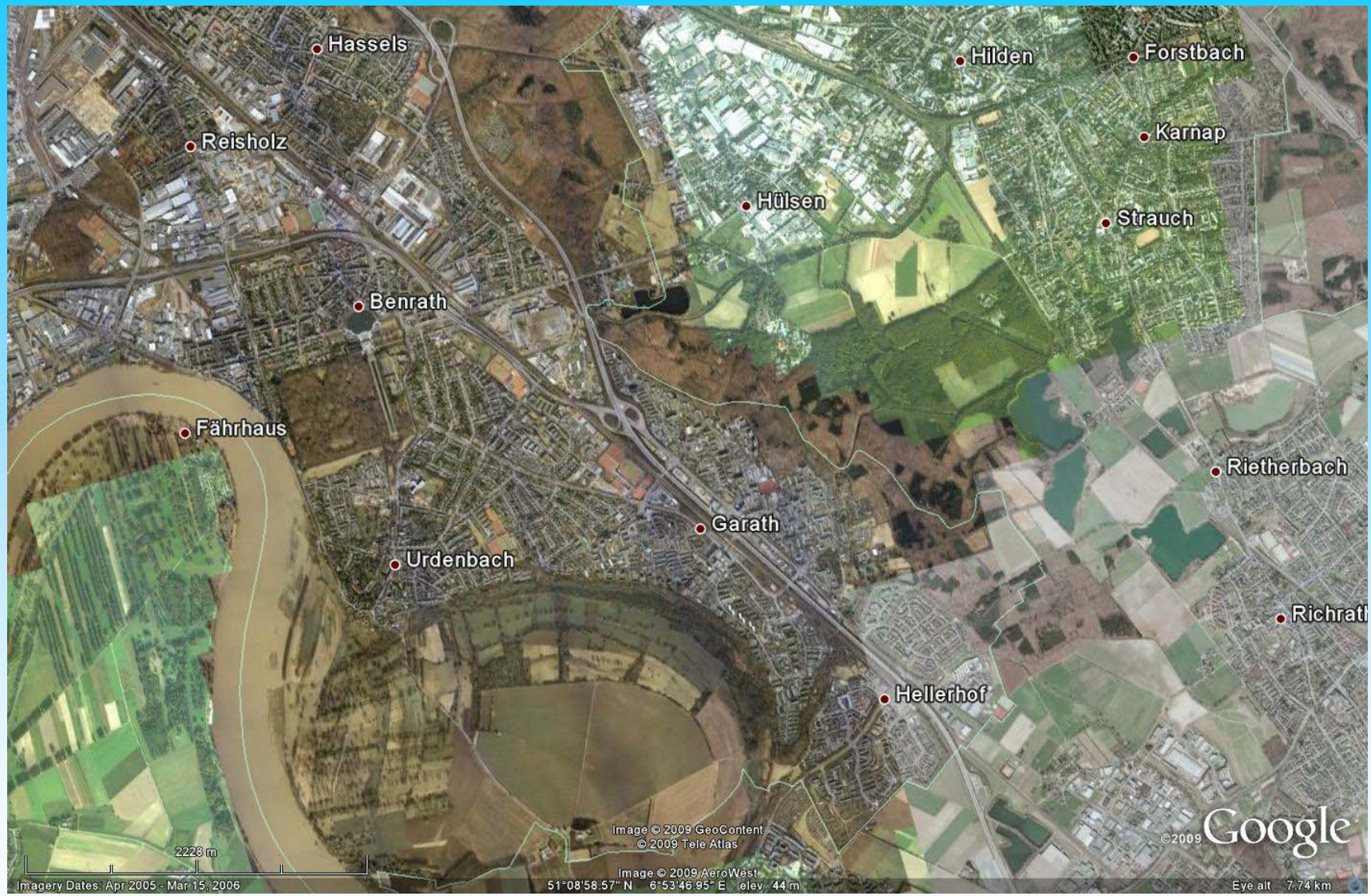
Case History: Düsseldorf/Hilden
investigation and remediation of CHC plumes

GASSYS: sampling of CHC, VC, ethane, ethene, and hydrogen gases in groundwater

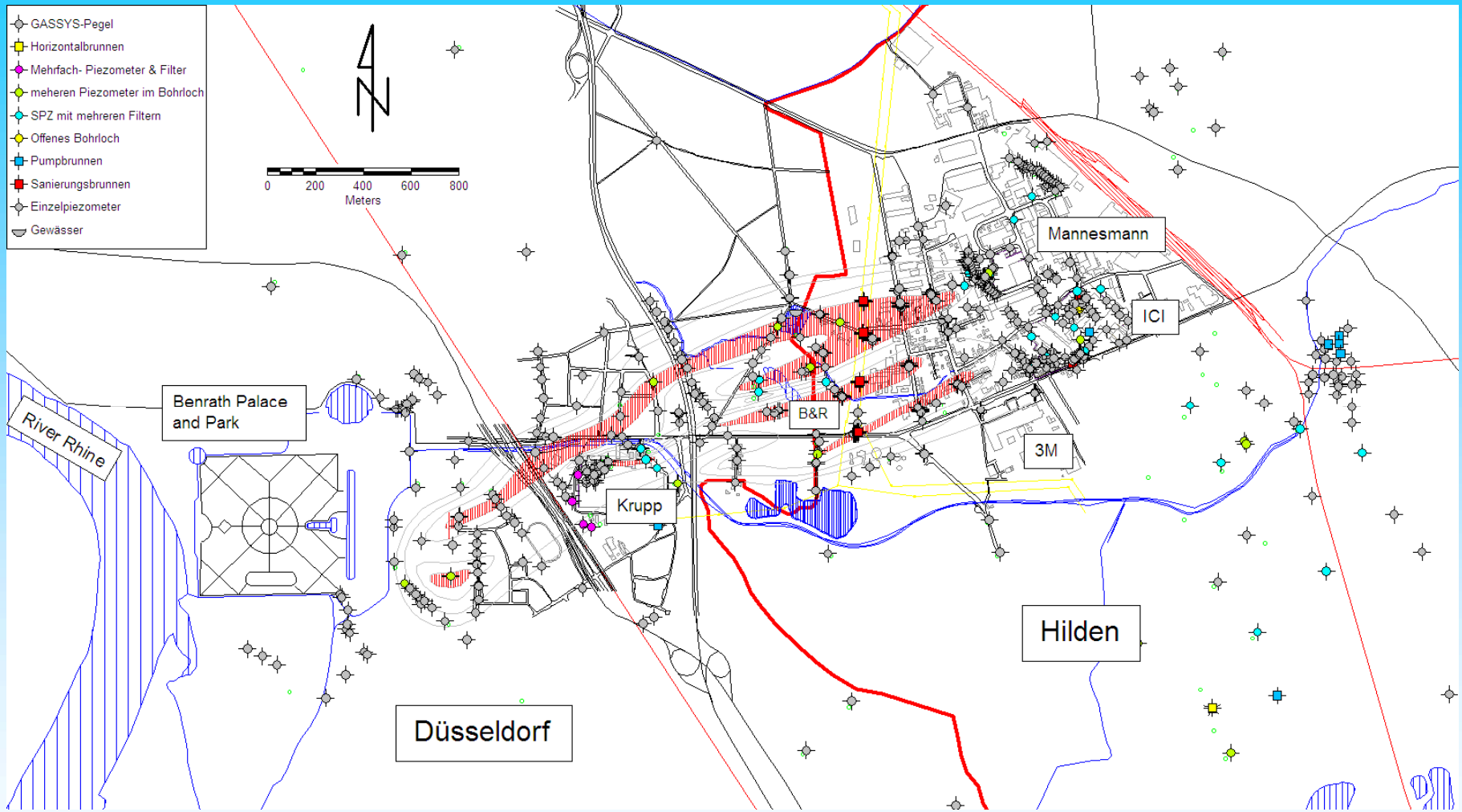
Source of Data: WDA Consultants Inc., Calgary
[WKC Consultants, Krefeld, Germany]



Region Düsseldorf/Hilden with deep open pits (up to 500 m depth)

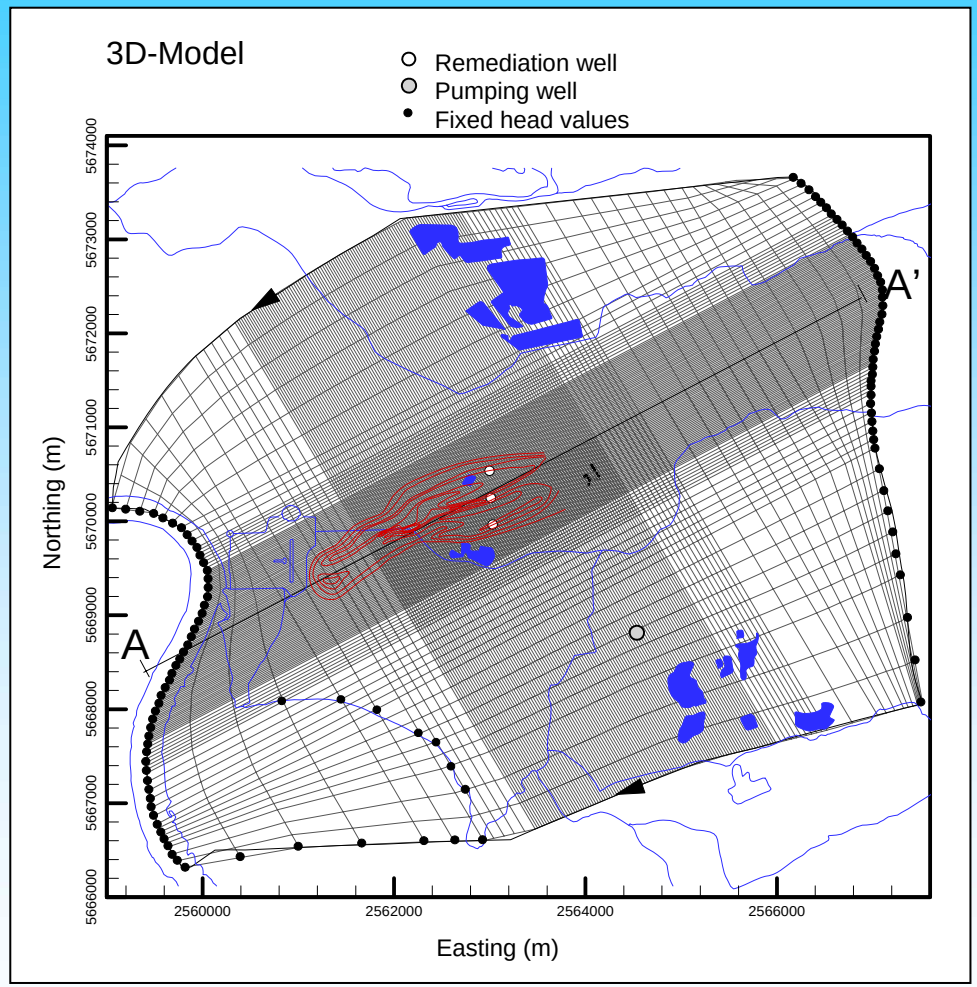


Close-up of area of investigation and remediation



Overview Düsseldorf/Hilden CHC plumes

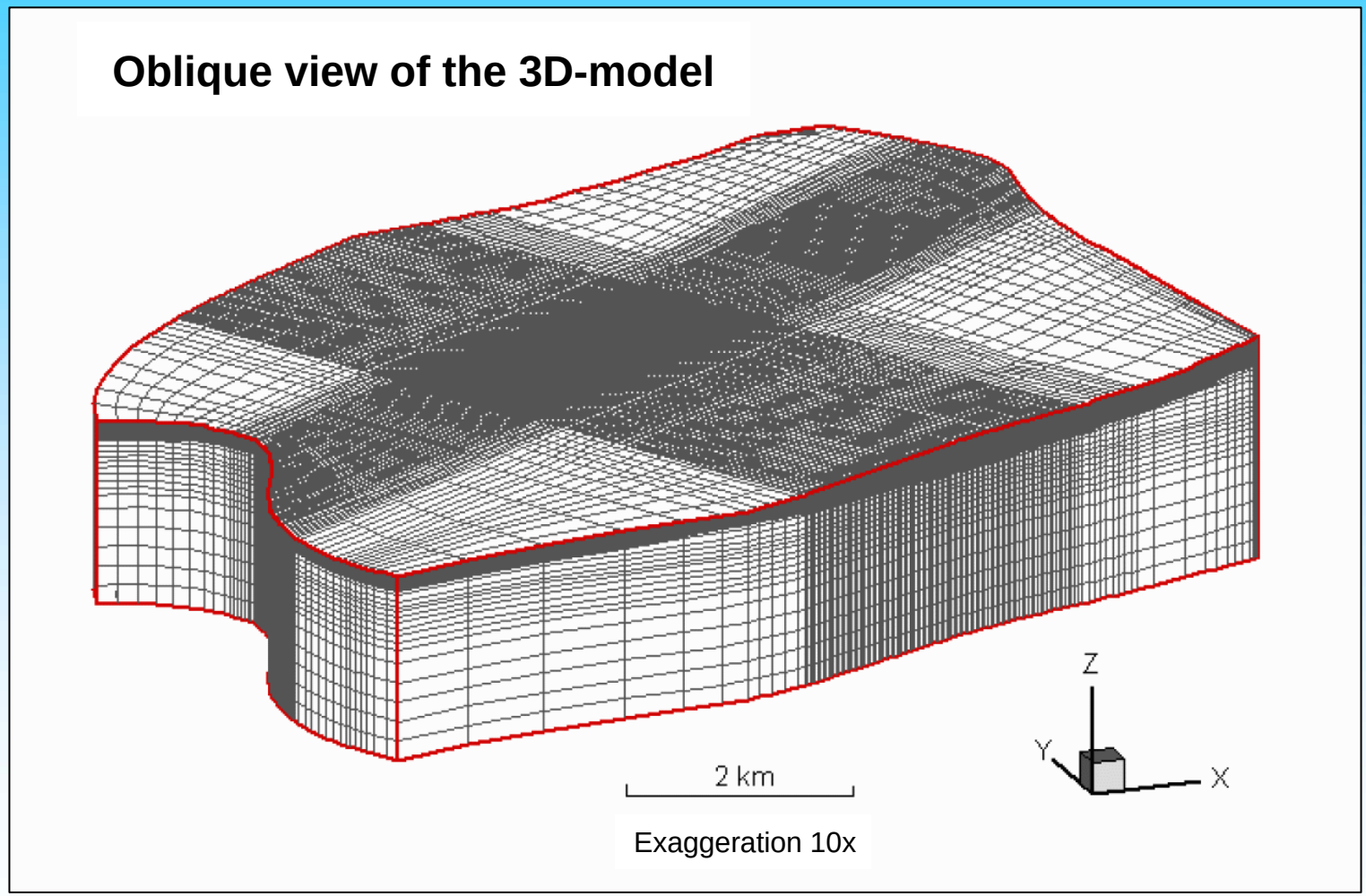
Plan view of model area



after Weyer and Molson, 2004

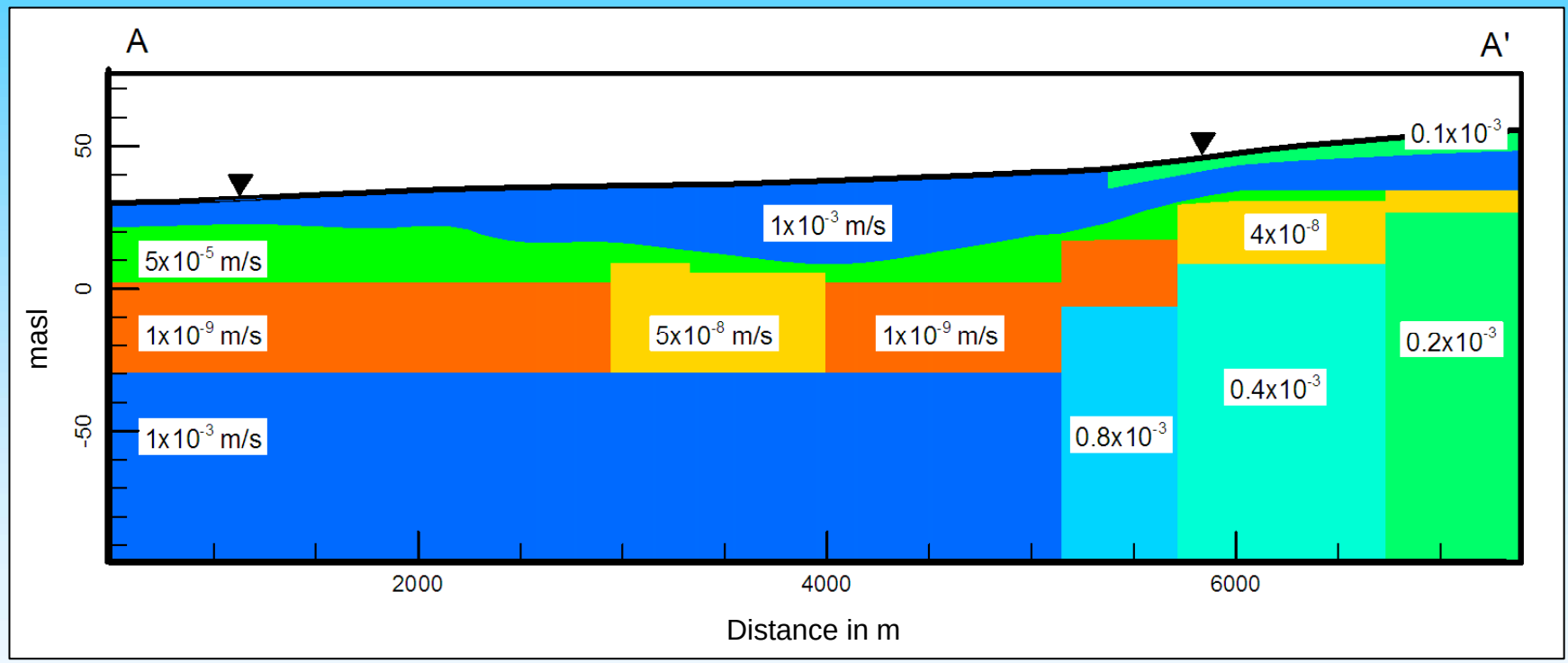
- Location of contaminant plume (in red) and trace of cross-section A-A' shown
- Length of sides of diagram about 8 km
- Western fixed heads follow the River Rhine

Configuration of 3D-finite-element flow model
(about 800,000 elements)



after Weyer and Molson, 2004

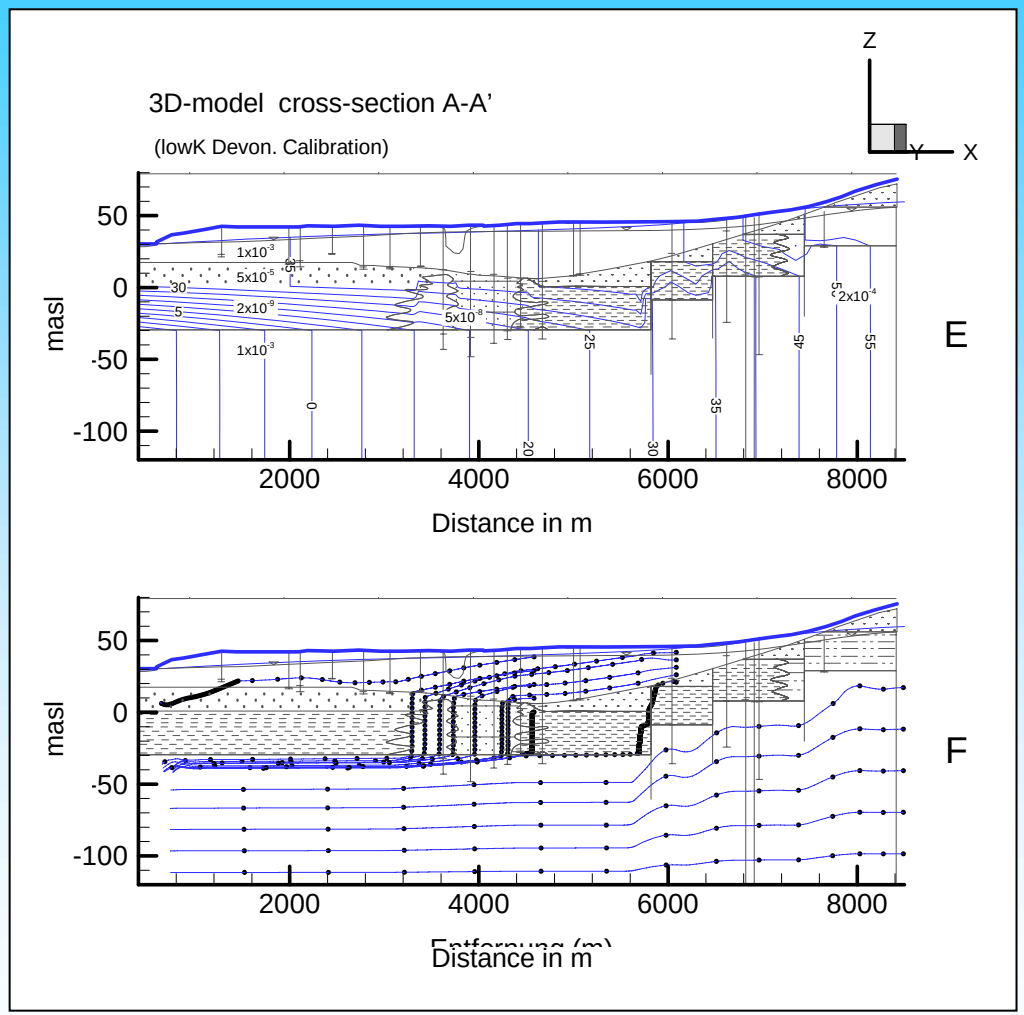
Geologic SW-NE cross-section through middle of model



after Weyer and Molson, 2004

Dark blue = quaternary and Devonian dolomite
Orange = clay layer
Yellow orange = silt window

Equipotential lines and flow lines in cross-section A-A' in state of calibration

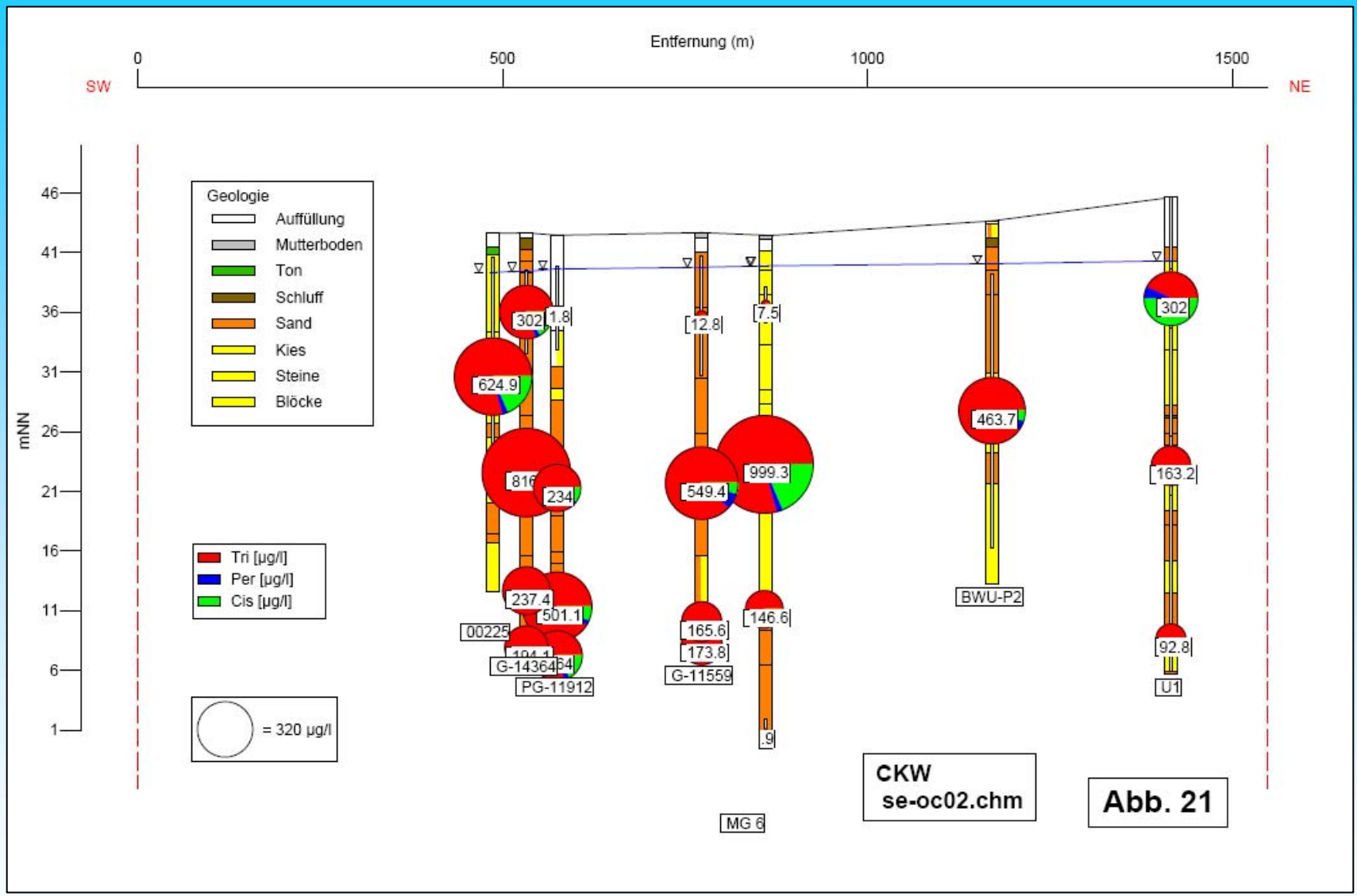


E: equipotential lines in cross-section

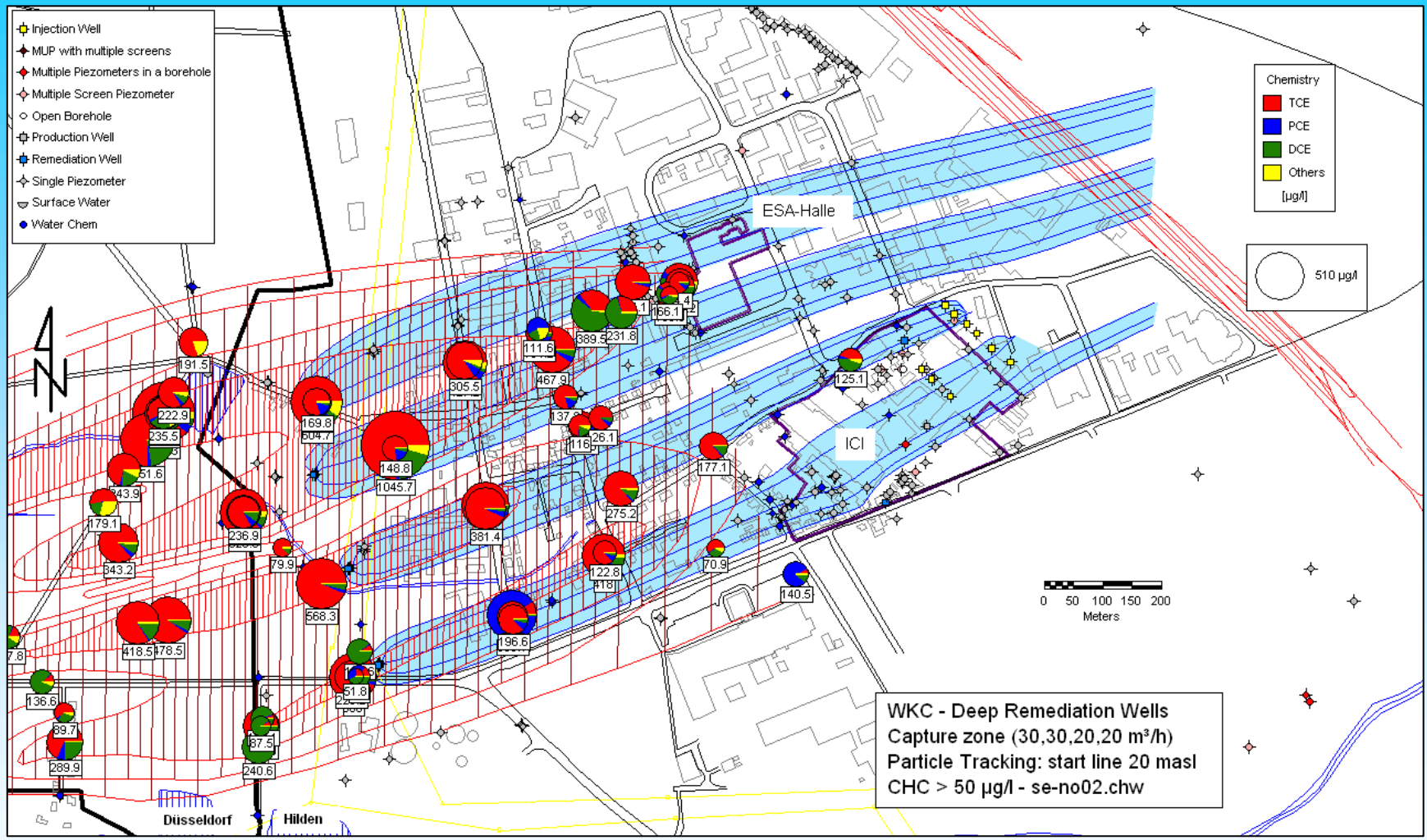
F: Flow lines in cross-section

- Both equipotential and flow lines emphasize the hydraulic role of the silt window
- Annual flow distance (distance between dots) calculated by particle tracking
- For geology and permeability see slide 83

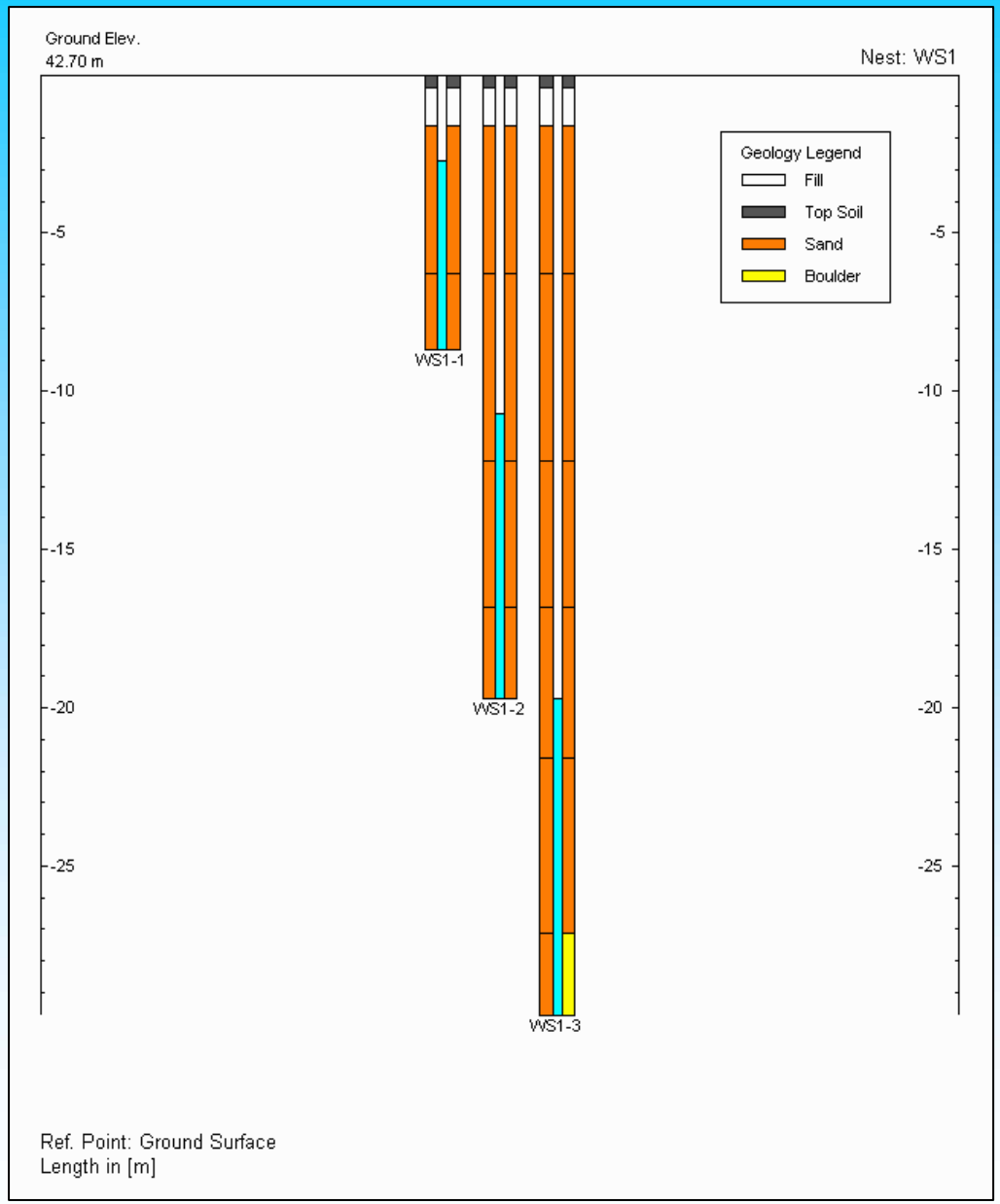
Weyer and Molson, 2004



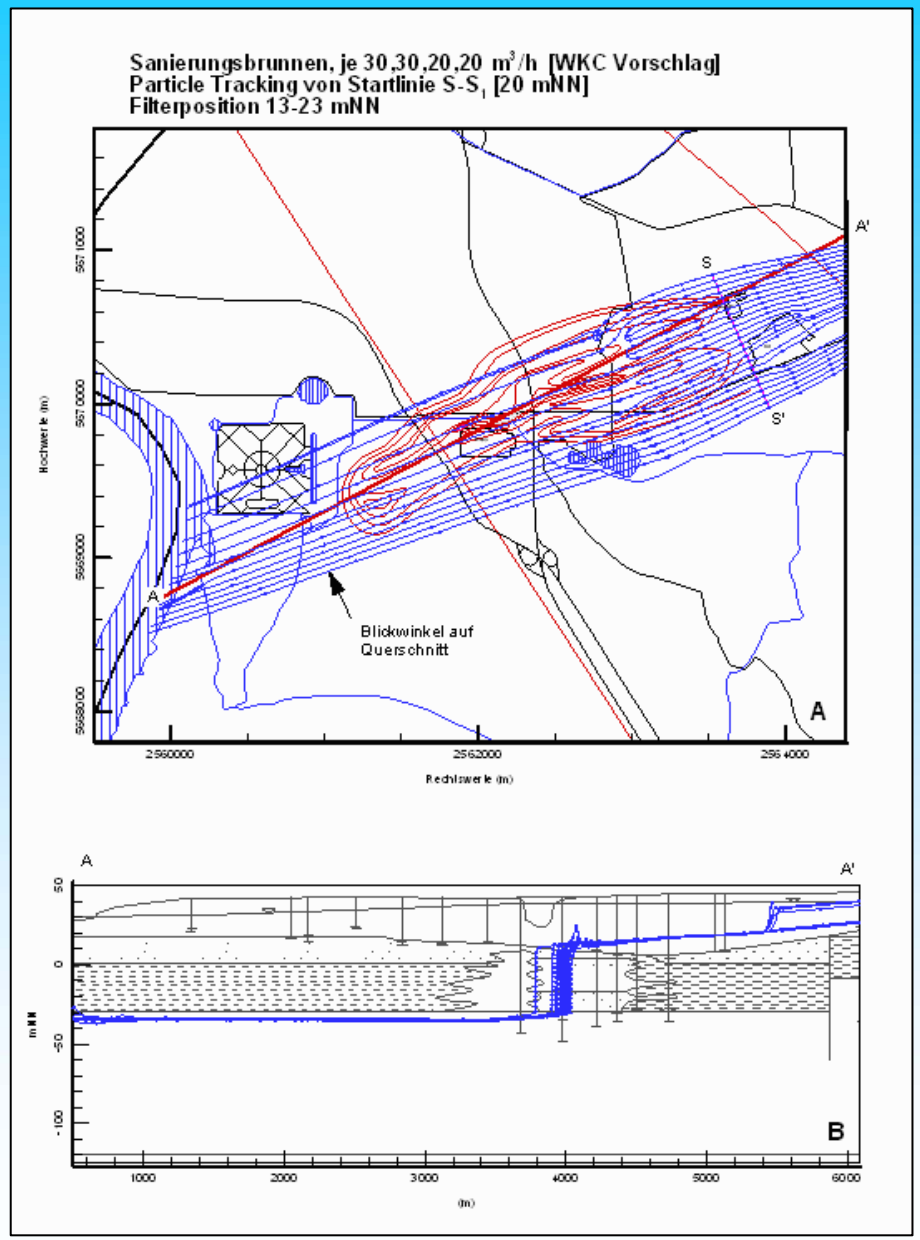
Occurrence of TCE [Tri], PCE [Per] and DCE [Cis] along inclined flow lines



Capture zones for proposed pump-and-treat wells



Design of well groups for pump-and-treat remediation



Effect of deep remediation well pumping at 30, 30, 20, 20 m^3/h

Installation of GASSYS at a large-diameter remediation well.

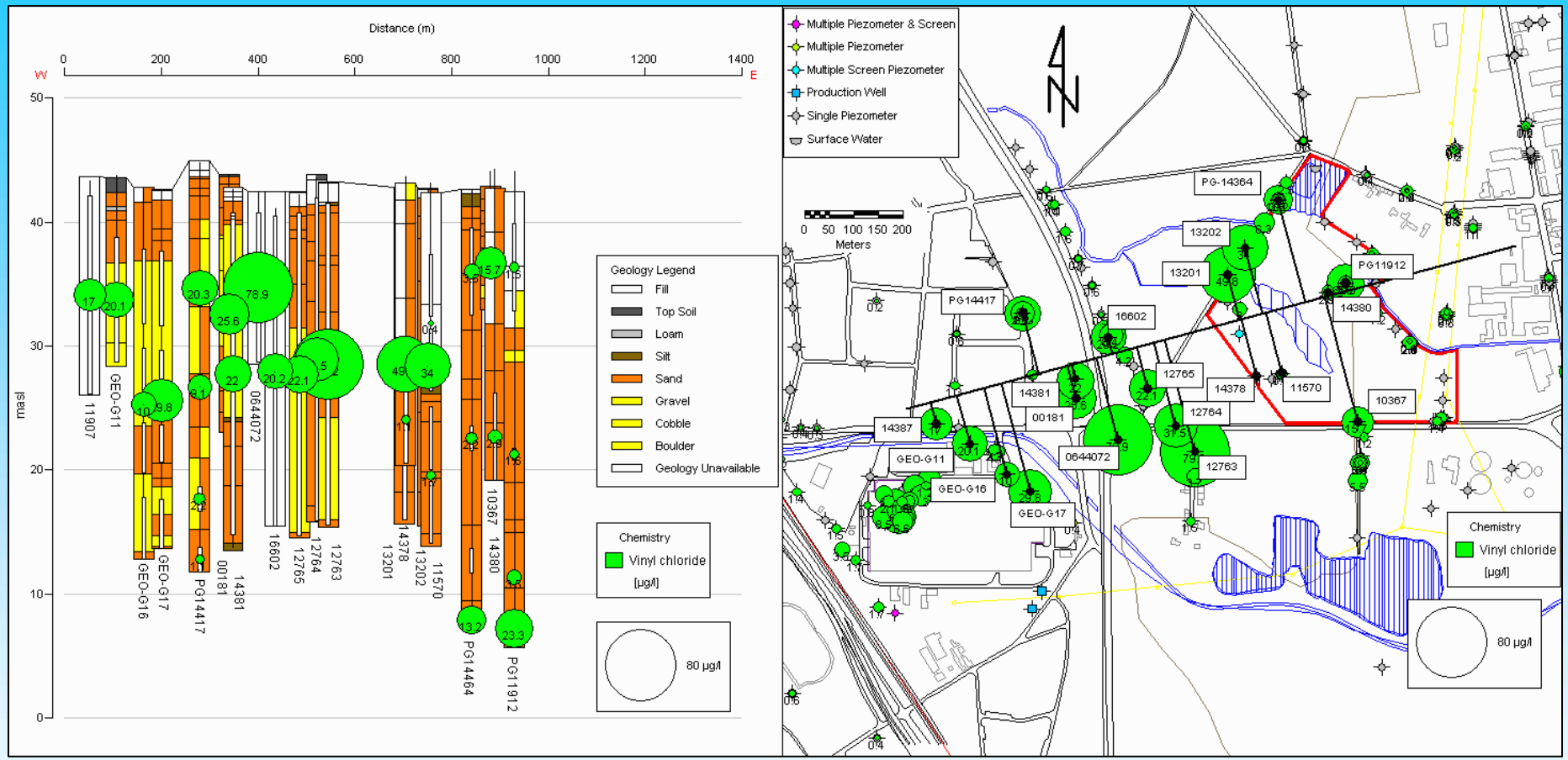
Screen of well (blue), screen of 2” piezometer (black), and chamber of GASSYS system (black/blue, diameter 15mm) are on same level, allowing for concordant sampling of groundwater and gas in groundwater.

Bottom of GASSYS tube (black/blue) attached to screen of a remediation well (blue) with nearby screen of 2” piezometer (black)

Project "Remediation wells Hilden (2007)" - Analyses of gas samples from GASSYS

Well group	1			2			3			4		
GASSYS-depth	15 m	25 m	35m	15 m	25 m	35m	15 m	25 m	35m	15 m	25 m	35m
Laboratory results (RUK-Report-No.: 80712152-73 of 20/12/07) corrected with volume correction factors by KaiserGEOconsult GmbH												
RUK sample number	0712152	0712154	0712156	0712158	0712160		0712162	0712164	0712166	0712168	0712170	0712172
GASSYS-field numbers (a)	1.1a	1.2a	1.3a	2.1a	2.2a	2.3a	3.1a	3.2a	3.3a	4.1a	4.2a	4.3a
	[mg/m³]	[mg/m³]	[mg/m³]	[mg/m³]	[mg/m³]		[mg/m³]	[mg/m³]	[mg/m³]	[mg/m³]	[mg/m³]	[mg/m³]
clorinated hydrocarbons												
Dichlorodifluoromethane	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1		< 0,1	< 0,1	< 0,1	< 0,1	**1.7**	0.7
Vinyl chloride	**0.2**	< 0,1	< 0,1	< 0,1	**0.4**		< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
Trichlorotrifluoromethane	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1		< 0,1	< 0,1	< 0,1	< 0,1	**0.4**	< 0,1
1,1-Dichloroethylene	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1		< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
Methylene chloride	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1		< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
1,1,2-Trichloro-1,2,2-trifluoroethane	<0,1	<0,1	<0,1	<0,1	<0,1		<0,1	<0,1	<0,1	<0,1	<0,1	<0,1
trans-1,2-Dichloroethene	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1		< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
1,1-Dichloroethane	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1		< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
cis-1,2-Dichloroethene	**1.4**	**2.2**	< 0,1	< 0,1	**1.0**		**1.1**	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
Chloroform	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1		< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
1,2-Dichloroethane	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1		< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
1,1,1-Trichloroethane	< 0,1	0.4	< 0,1	< 0,1	< 0,1		< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
Carbon tetrachloride	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1		< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
Trichloroethylene	**7.4**	**33.5**	**12.8**	< 0,1	**7.8**		**8.0**	< 0,1	2.3	< 0,1	**4.3**	**3.6**
1,1,2-Trichloroethane	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1		<0,1	<0,1	<0,1	<0,1	< 0,1	< 0,1
Tetrachloroethylene	< 0,1	0.5	< 0,1	< 0,1	< 0,1		< 0,1	< 0,1	< 0,1	< 0,1	0.2	1.2
1,1,1,2-Tetrachloroethan	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1		< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
Sum (Chloride)	**7.2**	**29.4**	**10.3**	< 0,1	**7.2**		**7.3**	< 0,1	1.9	< 0,1	**5.3**	**4.4**
Sum (Fluoride)	<0,1	<0,1	<0,1	<0,1	<0,1		< 0,1	< 0,1	< 0,1	< 0,1	0.7	0.2
BTEX												
Benzene	<0,1	<0,1	<0,1	<0,1	<0,1		<0,1	<0,1	<0,1	<0,1	<0,1	< 0,1
Toluene	10.0	7.9	11.6	0.5	7.0		10.4	1.3	2.4	0.5	1.6	2.8
Ethylbenzene	0.2	0.2	0.2	< 0,1	0.1		0.2	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
m-/p-Xylene	0.7	1.0	0.8	< 0,1	0.5		0.8	0.1	0.3	<0,1	0.2	0.2
o-Xylene	0.5	0.7	0.5	< 0,1	0.5		0.6	< 0,1	0.2	< 0,1	0.1	0.1

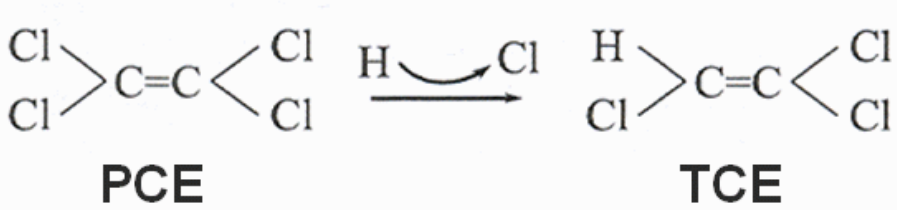
RUK sample number	0712153	0712155	0712157	712159.0	0712161		0712163	0712165	0712167	0712169	0712170	0712173
GASSYS-field numbers (b)	1.1b	1.2b	1.3b	2.1b	2.2b	2.3b	3.1b	3.2b	3.3b	4.1b	4,2b	4.3b
various gases (Vol.-%)												
Methane	<0,1	<0,1	<0,1	<0,1	<0,1		<0,1	<0,1	<0,1	<0,1	<0,1	< 0,1
Carbon dioxide	3.0	3.5	4.4	1.3	4.2		3.5	<0,1	0.6	<0,1	2.9	4.6
Oxygen	18.5	18.3	14.4	14.1	15.3		11.7	19.2	18.1	19.2	18.5	12.3
Hydrogen (ppm)												
Hydrogen (ppm)	13	16	14	< 3	10		8	8	9	< 0,3	10.4	6
Pressure measurements (_____) before and after sampling (17/12/07) and volume correction factors												
Pressure before sampling	1061	1029	1034	defect	1044	defect	1033	defect	defect	defect	1042	1044
Pressure after sampling	1031	836	922		854		795				1037	856
correction factor for sample a	1.20	1.20	1.21	1.20	1.20		1.20	1.20	1.21	1.20	1.20	1.21
correction factor for sample b	1.31	1.30	1.29	1.31	1.30		1.31	1.30	1.29	1.31	1.30	1.29



Maximum occurrence of vinyl chloride in groundwater.
Data indicate landfill [red outline] as source.

REDUCTIVE DECHLORINATION OF CHLORINATED HYDROCARBONS

PCE Degrades to TCE



PCE **TCE**

Full Degradation

PCE → **TCE** → **DCE** → **VC** → **ETHENE** → **ETHANE** → **CO_2**

$CCl_2=CCl_2$ $CHCl=CCl_2$ $CHCl=CHCl$ $CH_2=CHCl$ $CH_2=CH_2$ C_2H_6 CO_2

VC = Vinyl Chloride / Chlorethene

CONCLUSIONS

- GASSYS is well-suited for individual and long term (decades) investigations of changing gas contents in unsaturated soil and within groundwater
- Physical and geological conditions are kept constant during the life time of the installation, thus allowing valid and accurate comparison of sampling events
- GASSYS is a valuable additional tool for the determination of processes at work in Natural Attenuation and the observation of progress achieved
- GASSYS installations have been applied in the determination of explosive and toxic subsurface conditions at plant sites
- The proven life time of the installed EVA diffusion tubing has exceeded 25 years along pipelines [Leos system by Siemens]
- The proven lifetime of GASSYS installations is approaching 10 years
- The functionality of the system can be measured at any time by means of pressure recordings
- Pressure measurements allow the direct determination of summary gas pressures in groundwater which at some sites exceeded 2 bar significantly.

OUTLOOK

Additional applications of GASSYS:

- Gas leakage measurements in CBM areas
- Gas leakage measurements in CO_2 storage areas
- Gas leakage measurements at operating and abandoned, sealed and unsealed boreholes

Thank you for listening