

# 4-dimensional monitoring of aromatic hydrocarbon groundwater contamination

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## Abstract

This poster addresses the problem of measuring strongly adsorbable and volatile substances directly in bore holes. A chemical company faces the problem of an old contamination in deeper soil regions (< 30 m) that covers an unknown area of their premises. As a first step the contamination has to be evaluated by quantification of the geometrical boundaries and the mass of contaminating substances adsorbed onto soil and diluted in soil water. A new submersible UV/VIS spectrometer ("spectro::lyser" by s::can Messtechnik GmbH, Vienna) was developed for in-situ measurements of Benzene in bore holes. This instrument was successfully used for measuring Benzene profiles. This poster focuses on the new measuring technique.

## Keywords

contaminated sites, in-situ measurement, natural attenuation, UV/VIS-spectroscopy.

## INTRODUCTION

As a first step for remediation of contaminated sites the contamination has to be evaluated by quantification of the geometrical boundaries and the mass of contaminating substances adsorbed onto soil and diluted in soil water. A new submersible UV/VIS spectrometer was developed for in-situ measurements of Benzene in bore holes. It was possible to measure benzene groundwater contamination without sampling, directly in the aquifer by means of a submersible spectrometer ("spectro::lyser" by s::can Messtechnik GmbH, Vienna). Measuring the contaminant distribution in 3 dimensions and over time gives a detailed picture of the contaminant distribution. The method proved to be useful for the detailed assessment of contaminated sites and is not restricted to benzene. It could be adjusted to other contaminants containing chromophores. Concentration mapping is a valuable means to identify pollution sources and to describe contaminant transformation, dispersion and propagation in the aquifer. Such detailed assessments can be also applied for the validation of groundwater contaminant transport modelling, for monitoring natural attenuation and for alarm systems in situations where other water uses are endangered. This poster addresses the new measuring technique.

## THE PROBLEM

Figure 1 shows the area map of the contaminated site. Since the contamination is suspected to be more than ten years old, only few is known about the origin and composition of the contaminant matrix. By first analysis it was found that Benzene is always a major constituent and was defined as the target contaminant. Geological profiles showed that several geological layers in different depths can be a continuous source of contamination (Figure 2).

The geological layers are expected to behave quite differently regarding their hydraulic properties as well as their adsorption and diffusion behaviour. Therefore a 3D quantification of the contamination with consideration of the time-dynamic behaviour is necessary to model contaminant transport in the aquifer, and to evaluate the optimum strategy for remediation. Up to now no methods are known to do such comprehensive measurements in the underground quantitatively.





Figure 1. Area map of the contaminated site.

One of the prominent question was if concentration profiles of contaminants in the bore holes could be distinguished and if the concentration profiles are correlating with the behaviour of contaminants in the corresponding adsorbed phase of the soil layers. An answer to this question is crucial for the evaluation of the most promising remediation strategy.

In a first stage, discrete measurements were done in the liquid phase - in existing bore holes - only. In a second stage, time resolved and dynamic measurements in the bore holes along with multi stage pumping experiments are planned. In a third stage, measurements directly in the solid phase are planned.

Usually samples are taken with a submersed sampling pump/tube, transported to the lab followed by GC analysis. By this method, it is not possible to measure a concentration profile, since the liquid volume of the bore hole is mixed during pumping.

Another well known drawback of this strategy is that high the precision of laboratory measurements is more than outweighed by the error resulting from sampling (adsorption, purge), transport, and sample handling (Weingartner et al., 2000). Sampling of volatile substance produces an error that tends to underestimate especially high concentrations. A typical error of around 1 % of GC analysis

is, for critical substances, accompanied by a typical error of around 10 % from the sampling procedure.

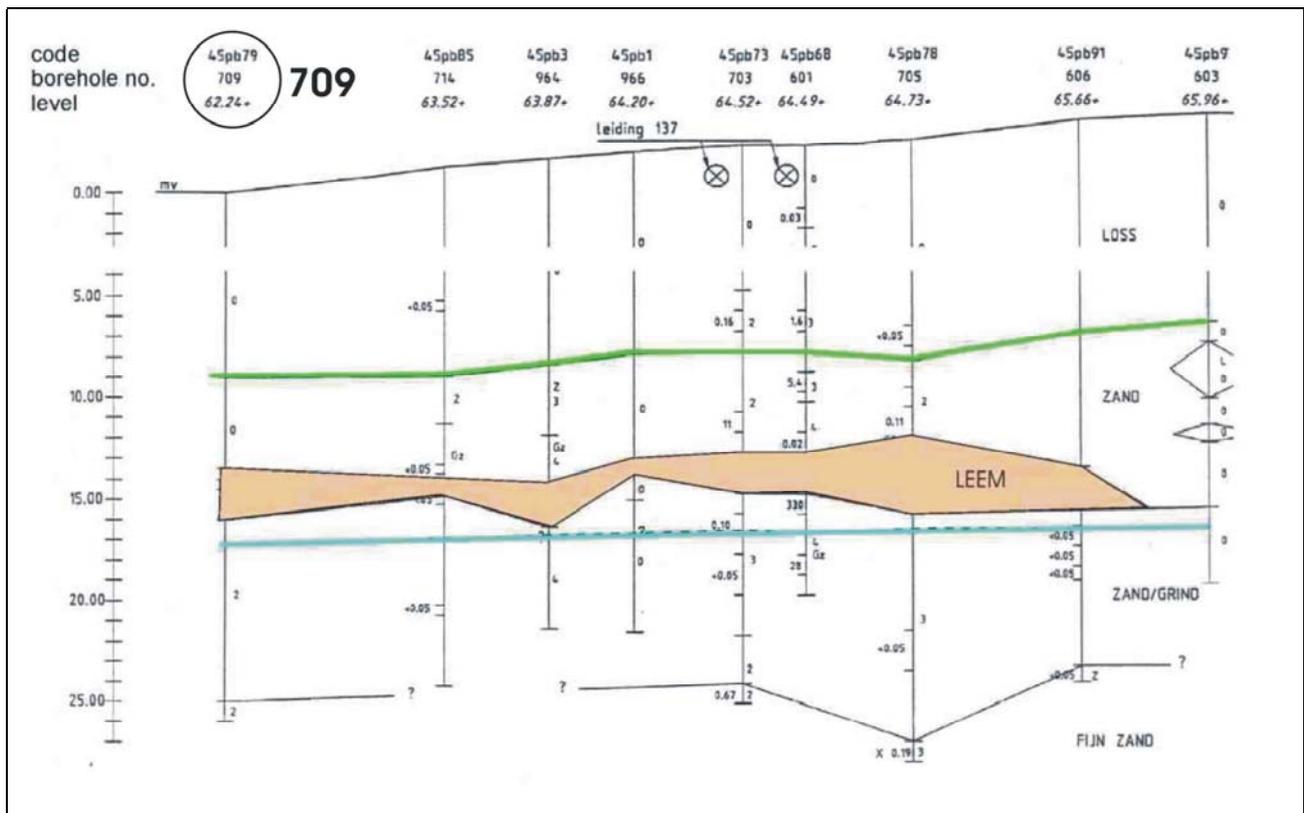


Figure 2. Geological profile (cross-section B-B) of the contaminated site.

### THE SUBMERSIBLE SPECTROMETER

UV/VIS spectroscopy is a well known and accepted method for BTX measurement on higher concentration levels (Rinke and Hartig, 1994). It is wide spread not only in laboratories, but also often used by a new generation of fibre-optic process spectrometers. However, none of these instruments can be used inside small bore holes (about 2"). The new developed "spectro::lyser" (s::can Messtechnik GmbH, Vienna) has been, after a phase of evaluation, successfully used for measuring Benzene profiles in bore holes.

The "spectro::lyser" is a spectrometric probe of about 0.6 m length and 4.5 cm diameter (Figure 3) and displays and/or communicates the result in real time. It is a 2-beam 256 pixel UV/VIS spectrometer, with a Xenon lamp as a light source and a path length of 80 mm. All of the controller electronics including a data logger and a water level meter are included in a 44 mm tubular anodised aluminium housing. The communication is via RS232 or RS485 interface.

The measurement takes place directly in-situ in the bore hole without sampling or sample treatment. A single measurement typically takes about 15 seconds. The "spectro::lyser" automatically registers the water depth as well as the UV spectrum (200 to 380 nm) and the Benzene concentration. It automatically plots the concentration profile online on a connected laptop screen or stores it on board. Of course it has to be certified in advance that the water within the 2" groundwater well is representative for the surrounding aquifer.



Figure 3. “spectro:lyser” by s::can Messtechnik GmbH, Vienna.

Benzene estimation consists of three steps: Substance identification being the first, turbidity and linear baseline correction the second, and quantification by fitting a reference spectrum to the measured spectra the third. The benzene spectrum has a distinguished “5-finger”-shape around 250 nm, therefore it was possible to reach a high selectivity and to exclude cross sensitivities to other substances to a high degree. Even multi-component groundwater contamination at some of the measuring stations did not hamper the quantification.

The Benzene concentration can be measured selectively from 0,1 (1) ppm to about 700 ppm (high concentrations with path insert). Figure 4 shows calibration results. The obtained correlation coefficients are high ( $R^2 = 99.92\%$  for lower concentrations and  $R^2 = 99.89\%$  for the whole calibration range).

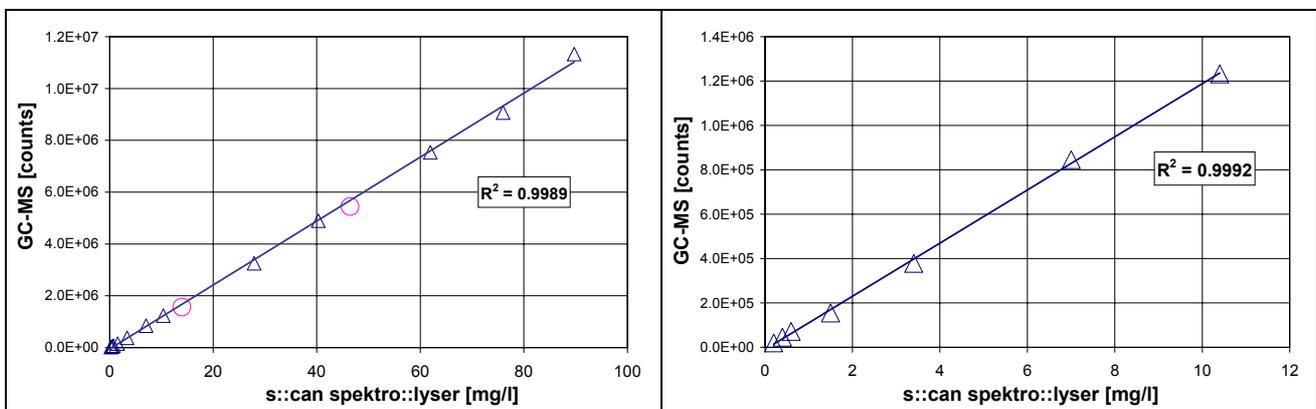


Figure 4. s::can “spectro:lyser” calibration results using 3rd party calibration with aqua dest. (triangles) and GC-MS in native groundwater matrix (circles).

## RESULTS AND DISCUSSION

The contamination covers an area of about 15.000 sqm. The groundwater level is in a depth of around 19 m beneath surface, and a not very homogenous clay layer was explored between depths of 14 and 19 m. Above and beneath this separating layer sands of different transmissivity are typical. About 10 years ago, the upper sand layer was decontaminated but the clay layer and the lower sand layer were not. Therefore the strongly adsorbing clay layer is supposed to have kept near saturation and is supposed to be the main source of contamination.

Concentration profiles have been measured several times in 20 ground water wells, on sometimes very high levels. Four of these profiles are pictured in Figure 5.

Bore holes 712 and 708 are situated close to the border of the more or less saturated area (708 inside, 712 outside). In 712 the groundwater touches the clay layer, what leads to a steep concentration profile from clay to water that could result from diffusion of Benzene from the clay layer into the water. The very close well 711 has a relatively low contamination possibly because it does not touch the contaminated clay layer.

Bore holes 713 and 709 are situated inside the source area. In 709 the clay layer is not touched by the water and therefore the concentration profile (concentration increasing with water depth) indicates convective transport of Benzene in the liquid phase from upstream. Since the thickness of the clay layer varies rapidly within short distances the source/valley behaviour can change even between neighbouring wells.

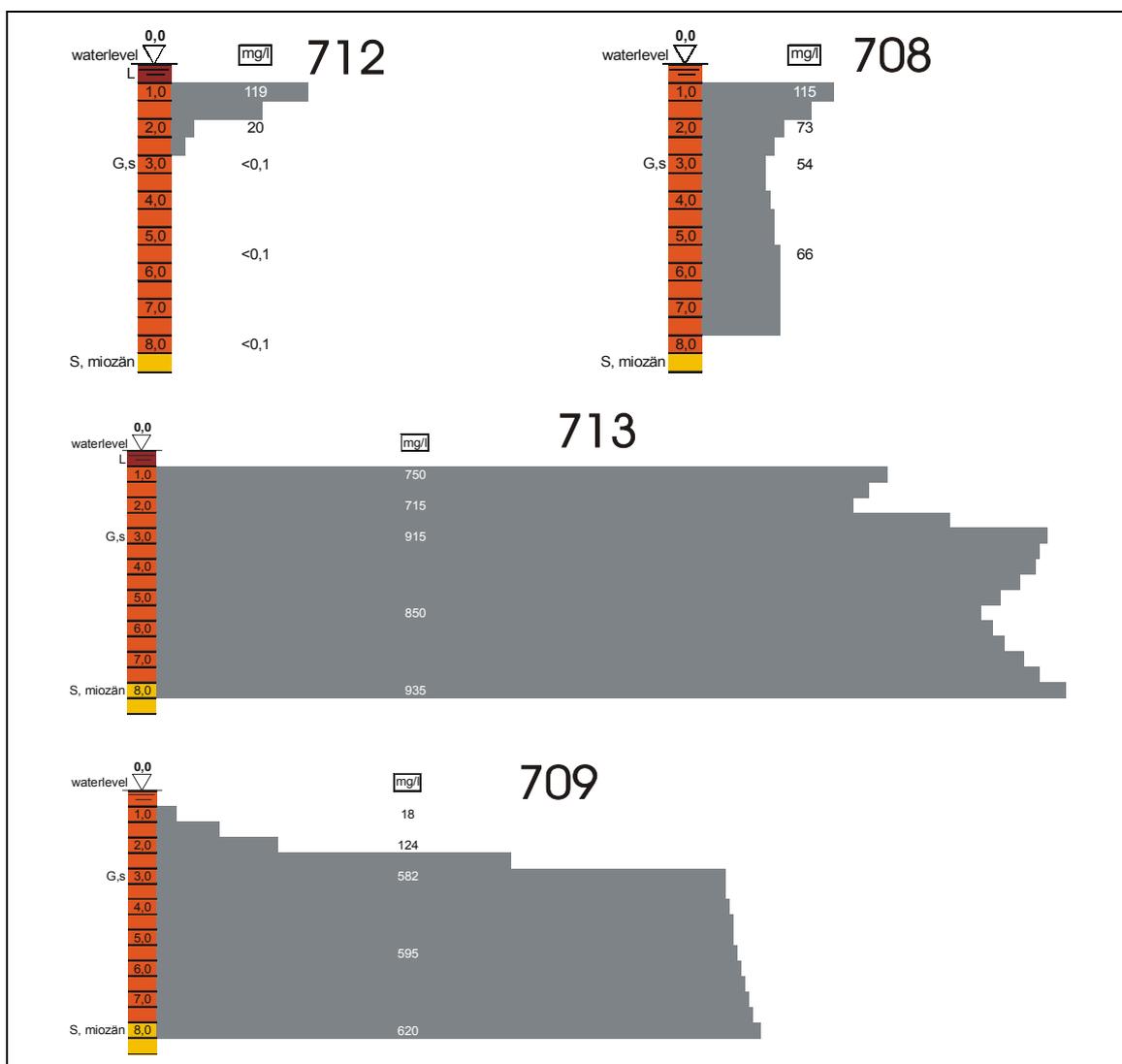


Figure 5. Concentration profiles of Benzene in different bore holes in the contaminated area (concentrations interpolated).

## **5. SUMMARY**

The prerequisite for remediation is a good characterisation of the contamination of the site. The determination of concentration profiles in bore holes gives a 3D information on the distribution of the contaminant. Profiles can only be measured with in-situ measurement techniques. When using in-situ measurements one can also avoid errors from sampling, transport, and sample handling.

A new submersible UV/VIS spectrometer is available now. The “spectro::lyser” has successfully been used for measuring Benzene profiles in bore holes. Due to the very special shape of the Benzene spectrum it was possible to reach a high accuracy and a high selectivity. The instrument has been used by plant staff in a regular manner for several months now and so far no problems occurred.

## **REFERENCES**

Weingartner A. (2000). Monitoring ohne Probenahme. In: D. Depisch (ed.): *Innovative Messtechnik in der Wasserwirtschaft – Präsentation eines Forschungsprojekts. Wiener Mitteilungen 161*, pp.97-115.

Rinke G. and Hartig C. (1994). Mehrkomponenten-Prozeß-UV-Spektrometer. *Technisches Messen* **61**(5).