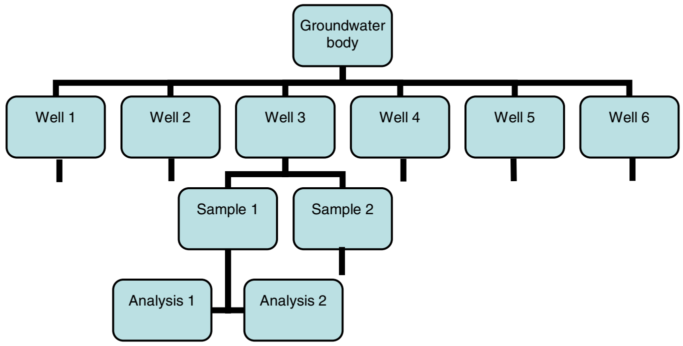
Case Study – Århus County, Denmark

Background information
Title/Name of case study: Estimation of groundwater monitoring uncertainty
Type of case study: Local monitoring study as part of international guidance cooperation
Web-Link: http://www.samplersguide.com
Objective of case study: Demonstration of the use of simple methods for estimation of monitoring uncertainty and for monitoring quality control
Contribution to…
WFD focus: Groundwater quality monitoring
Specific contributions: Uncertainty from analysis, sampling and aquifer heterogeneity, methods for estimation of uncertainty, use of uncertainty estimates to identify points of improvement as well as fitness for purpose (compliance with set quality objectives)
Characterisation: A group of groundwater bodies that are an important drinking water resource for the city of Århus, the second largest city of Denmark, has through surveillance monitoring been identified as at risk for deterioration of the quality due to intensive drinking water abstraction. An operational monitoring program was established in order to control the trend in water quality development. The groundwater body is in glacial outwash sands with Miocene sands and clays below and glacial till above. The natural quality of the groundwater is anaerobic without nitrate, with sulphate and reduced iron, but without hydrogen sulphide and methane. One of the threats to the groundwater bodies is oxygen intrusion into the aquifer as the result of the water abstraction and concomitant groundwater table draw down. One groundwater body representing the group, 2 km x 2 km x 10 m, starting 20-30 m below the surface, was selected for the operational monitoring. In the operational monitoring planning, it was decided to use dissolved iron as a target parameter that would be a sensitive indicator of aquifer oxidation (decreasing iron concentration with increasing oxidation). It was further decided to aim at monitoring one well twice per year and the objective of the operational monitoring was set to having a 95% probability of recognising a 20% quality deterioration. This requires a measurement uncertainty including both sampling and analysis of not more than 10% (comparison of two means each for two samples, 95% confidence interval, two sided test) corresponding to an expanded measurement uncertainty of 20%. To ensure the compliance of the monitoring program with this stated objective, a sampling validation study was initially conducted including all wells available and based upon the results from this, a routine sampling quality control program was set up for implementation with the monitoring program for the selected monitoring well.
Experiences gained - Conclusions – Recommendations The empirical approach was selected as study design in order to provide estimates of heterogeneity in the groundwater body (between-target variation well to well or over time) and measurement uncertainty, split into sampling uncertainty and analytical uncertainty. The basic principle of the empirical approach is to apply replicate measurements. Sampling was done using the groundwater monitoring sampling protocol developed by the county. Analyses were performed at an independent, accredited (ISO 17025) laboratory using accredited methods subject to the required quality assurance and analytical quality control. Estimates of laboratory uncertainty and analytical detection limits were obtained from the laboratory quality control scheme and evaluated with the data from the monitoring validation and quality control. The objective of the validation study was to ensure that measurement uncertainty meeting the set quality objective could be obtained and to describe the components of uncertainty in order to identity points of improvement, if required. The validation study was set up with sampling of the 6 wells, two independent samplings per well and 2 sub-samples per sample analysed, see overleaf

figure. The validation study thus included one sampling round with a total of 12 samples taken and 24 sub-samples sent for analysis.



The objective of the quality control programme for the operational monitoring was to ensure that measurement uncertainty did not increase over time during the monitoring. The quality control programme was set up after careful evaluation of the results from the validation study and was designed including duplicate sampling on one of the two annual sampling occasions of the monitoring programme.

The replicate data were treated using the range method (ISO 3085), see below table for results. The applied calculation methods are demonstrated in the guide on uncertainty from sampling, calculations are easily done using standard spread sheets, and an example can be downloaded from http://www.samplersguide.com. The data treatment provided estimates of analytical, sampling and total measurement uncertainty, in addition to the uncertainty due to heterogeneity (in space or time). Only random errors were included, whereas the occurrence of systematic sampling errors was not assessed quantitatively, but the consistency of the obtained results for different chemical parameters was used as a qualitative control of systematic errors.

Dissolved iron	**Expanded uncertainty, coverage factor 2**			**Between-target**
in groundwater	**Analysis**	**Sampling**	**Measurement**	**Heterogeneity**
Validation	2.1%	10%	10%	35%[1]
Quality control			4.0%	9.9%[2]

The data show that the requirement for less than 20% expanded measurement uncertainty could be fulfilled for dissolved iron (sampling validation), and that the required measurement uncertainty was in reality achieved during the routine monitoring (sampling quality control). Furthermore, the data show that if an improvement of the certainty of monitoring was required, the obvious point of improvement would be increased monitoring density (between-target heterogeneity dominating).

Outlook - Next steps – Accessibility of results

In planning groundwater monitoring, fitness for purpose (monitoring uncertainty corresponding to set quality objectives) can be ascertained by a simple monitoring validation approach. If required, points of improvement of monitoring can be identified from the contributions to monitoring uncertainty (analysis, sampling, heterogeneity). With a simple and cost efficient quality control, it can be ascertained that the routine monitoring uncertainty remains as required for the purpose.

Considering the total costs of groundwater monitoring and the costs associated with decisions on measures taken from monitoring data, the costs of including an initial monitoring validation during planning and a subsequent monitoring quality control during routine monitoring seem justified.

The principles applied are described in the Eurachem/EUROLAB/CITAC/Nordtest Guide "Estimation of measurement uncertainty arising from sampling".

[1] In the validation study, between-target variability was between wells

[2] In the quality control, between-target variability was between sampling occasions, first 6 sampling occasions included