CASE STUDY

MERCURY ONSITE MONITORING IN SOIL AND WATER SAMPLES USING THE PDV6000 AND SOIL EXTRACTION DEVICES

This report describes a field demonstration of the PDV6000 at a former mercury-cell chlor-alkali plant site containing mercury in the ground water and soil.

Background

The purpose of the evaluation was to show the effectiveness of on site analysis in managing site characterisation and remediation. The PDV6000 is a low cost and simple to use device and takes a few minutes to set up and condition the electrodes. It uses the principle of Anodic Stripping Voltammetry to detect concentrations of most heavy metals down to 5 µg/L in water and 0.5 mg/kg in soil.

For this demonstration, all the samples analysed were taken by a sampling crew using normal field sampling techniques and brought back to a central location on the site, where they were analysed. The sample extraction and analysis took between 15 and 20 minutes, but simultaneous extraction of samples meant that between 10 and 20 samples an hour could be analysed. The results generated were used to make a rapid assessment of the contamination level in each sampling area. This information was used to make an evaluation and decision about whether the soil should be disposed of as costly hazardous waste or re-used on site. The data was also used to direct the sampling team to other contaminated areas. The results showed that the PDV6000 could generate data that could be used to assess soil as contaminated or clean.

Introduction

Contaminated land sites are among the most common environmental problems and their assessment is highly reliant on chemical analysis. Traditionally, this would be performed in a central laboratory, using techniques such as Flame Atomic Absorption Spectroscopy (FAAS), and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Although these specific and sensitive analytical techniques are routinely used, the analysis is rather costly and time-consuming (typically 24 hours or more). Errors associated with storage, transportation and identification of samples can also occur. For remediation projects where removal of soil for disposal in landfill or for thermal treatment is required, the excavators cannot wait 24 hours to confirm no contamination remains. This means they will over excavate by as much as 30% to ensure all pollutants are removed.

This has led to the need for rapid and cost-effective on-site methods of monitoring for a range of contaminants. Heavy metals, such as lead (Pb), copper (Cu), cadmium (Cd), arsenic (As) and mercury (Hg) are of particular concern as they are non-biodegradable, persistent and, even at low concentrations, can produce undesirable effects to human health and the environment.

Due to its ability to measure these metals in soil the PDV6000 has fulfilled this need. A field demonstration of the instrument was carried out on the site of a former mercury-cell chlor alkali plant at Roermond which has ground water, sludge and soil all contaminated with mercury.

Analytical Procedure

Sampling Procedure

Soil, water and sludge samples were taken by a sampling crew using standard sampling techniques. These were taken to a central location on site where the analysis was carried out. A total of 16 samples were taken.

Soil and Sludge sample extraction procedure

Using the Cogent Environmental field extraction kit, 2g of each sample were digested in 4 mL of concentrated nitric acid and 4 mL of hydrogen peroxide. Organic compounds found in the samples create an exothermic reaction with these reagents that increases the temperature of the extract to ~60°C. Due to the low ambient temperature (~5°C) the digestion time was set to ~10 minutes. This time is normally 5 minutes. The samples did not give this exothermic reaction, indicating a low organic content. After the initial digestion, 20 mL of electrolyte and 10 mL of pure water were added to the mixture to dilute the sample. The sample was left for 5 minutes to settle. Samples were extracted simultaneously so that 10 - 20 samples could be analysed per hour.

Soil and sludge sample measurement procedure

Cogent Environmental field reagents and standard kits were used for this evaluation. The analytical procedure selected was a standard method that would quantify between 4 and 100 mg/kg of Hg in soil. This range reflected the 10 mg/kg decision level for this site and the anticipated higher concentrations of Hg. The procedure is not designed to be quantitative over a wide range, but in a narrow band around the pollutant trigger concentration. Each measurement took 120 seconds to perform. A single calibration standard was prepared for this set of analyses. The standard was matrix matched to the extraction solution. New analysis cups were used for each sample and a 5 second rinse in sodium hydroxide plus a 5 second rinse in distilled water was used between each sample to clean the electrode assembly to eliminate carryover. Standard checks were run once every 10th sample in order to confirm the stability on the electrochemical signal.

The PDV6000 can be programmed to work with any concentration band for a range heavy metals. To simplify the analysis on-site 2 alternative standard methodologies were pre-programmed into the instrument, Hg Low (0.5-5 mg/kg) and Hg High (100 1000 mg/kg). These methods were used to re-analyse the samples that could not be quantified using the initial procedure.
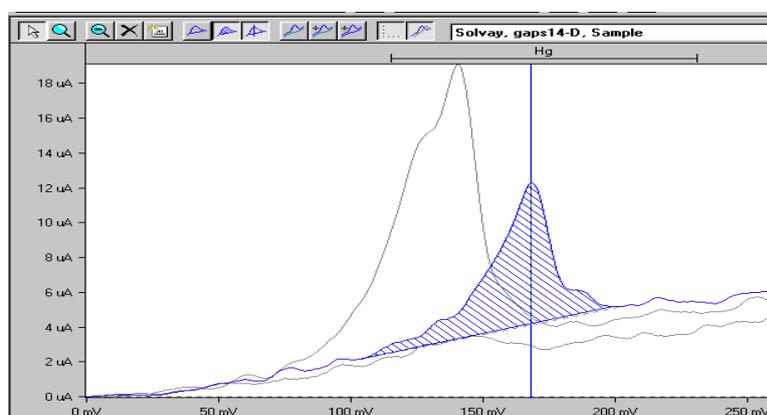
This trace shows a typical soil extract measurement with Hg peaks. The blue dashed curve represents the sample; the greyed curves represent the standard and the blank. The Hg concentration in the extract analysed was approximately 20 µg/L.

Water Sample Measurement Procedure

A similar procedure to the soil analysis was used for the water samples. Cogent Environmental field reagents and standard kits were again used for this evaluation and the analytical procedure selected was a standard Cogent Environmental method. Hg can be detected in water down to the 5 µg/L level. The main difference with water samples is they can be analysed directly without the need for the extraction procedure, indicating efficient analysis. The sample is simply added to an electrolyte for conductivity and analysed. The standard was again matrix matched to the sample.

Results

Sample I.D.	Sample type	Hg concentration as mg/kg	Comments
GAPS1	Soil	0.86	CLEAN
GAPS2	Soil	746	CONTAMINATED
GAPS3	Soil	35.5	CONTAMINATED
GAPS4	Soil	>>10 (estimated 80)	CONTAMINATED
GAPS5	Soil	103	CONTAMINATED
GAPS6	Soil	3.6	CLEAN
GAPS7	Soil	Less than 4	CLEAN
GAPS8	Soil	Less than 4	CLEAN
GAPS8-A	Soil	Less than 4	CLEAN
GAPS8-B	Soil	Less than 4	CLEAN
GAPS12	Soil	Less than 4	CLEAN
GAPS12-A	Soil	10	*CLASSIFIED CONTAMINATED*
GAPS12-C	Soil	42.5	CONTAMINATED
GAPS13	Soil	8.5	BORDERLINE CONTAMINATED
GAPS14-O	Pool sludge	13.2	CLASSIFIED CONTAMINATED

GAPS14-D	Pool sludge	10.5	**CLASSIFIED CONTAMINATED**
PP9-1	**Water**	**225 µg/Kg**	**CONTAMINATED**
PP9 –2	**Water**	**Less than 1 µg/L**	**? Sample degraded**
PP30-1	**Water**	**Less than 1 µg/L**	**? Sample degraded**
PP30-2	**Water**	**Less than 1 µg/L**	**? Sample degraded**

Results obtained post-Roermond:

Sample I.D.	1.1.1. Sample type	1.1.2. Hg concentration as mg/kg	1.1.3. Comments
GAPS14-A	Pool sludge	1.2. 6.4	CLEAN
GAPS14-B	Pool sludge	1.1	CLEAN
GAPS14-C	Pool sludge	7.5	CLEAN
GAPS14-E	Pool sludge	3.5	CLEAN

Discussion

All soil sample concentrations calculated in this evaluation are uncorrected for moisture content. Soils always contain some water as an integral part of their normal structure. Disposal costs are based on actual soil weight, not estimated dry weight. At Roermond, the soil samples (sandy) contained roughly 15% of moisture. The sludge samples contained approximately 25%. Laboratory values usually report for dry weight and this should be taken into consideration when reporting the onsite results to the laboratory. In practice, for real time decision-making the wet weight concentration is more useful.

The soil sample GAPS4, has an estimated value of 80 ppm. The operator used an incorrect sample volume and the analysis was therefore out of the calibration range. For the purpose of the evaluation however, the analysis showed the sample was far above the 10 ppm decision level soil concentration for the site. This situation shows the robustness of the technique in the field, even if a mistake is made in sample manipulation. Some samples were re-analysed using the other methodologies in order to quantify the soil concentration, but GAPS4 was not re-analysed.

The water samples were collected in 1 glass and 3 plastic bottles and were left overnight before analysis. The PDV6000 could not detect Hg above 5 µg/L in the sample in plastic bottles, but detected Hg in the glass. Analysis of these samples by an alternative technique showed Hg in the fresh samples, but subsequent analysis the next day with this technique also showed that all the Hg had disappeared from the plastic bottles. This shows the importance of the correct sampling and

preservation method as even 12 hours can cause samples to completely degrade. The advantage of real time analysis is clearly demonstrated by this event.

Estimating the recovery of Hg from the soil samples using any of the techniques is difficult as the samples were non-homogeneous and samples taken from the same location cannot be assumed to contain identical concentrations. Comparison of the results with the other techniques and laboratory data will therefore be relative. Other experiments (US EPA ETV) showed that the recovery with the Cogent Environmental cold extraction procedure was approximately 80%.

For decision making on site, data quality objectives should always be set that dictate how data generated can be used. The same approach should also be taken when using laboratory data. All analytical techniques have a percentage of error, but the largest source of variability comes from the way the sample is selected, preserved and prepared for analysis. The data quality objective should estimate this source of error and use this information to assess the confidence of the result obtained.

For example, with a trigger concentration on this site of 10 mg/kg, would the 8.5 mg/kg result be classified as below 10 or above? The homogeneity of the soil in the sample area could mean that a sample taken just 0.2 metres away could have a soil concentration of 15 mg/kg. A data quality objective that assumes the average errors associated with sampling and analysis of +/-20% would classify a sample containing 8.5 ppm as contaminated. The advantage of on-site analysis in this situation is that another sample from the same location can be acquired and analysed within a few minutes, confirming the first result. Several results in the sample area showing less than 10 mg/kg would be a good indicator that the area is indeed clean.

For most of the samples, the results were very clear-cut, with either an Hg result significantly above or below the 10 mg/kg threshold concentration, even when applying a 20% uncertainty to the values. Four samples were borderline and analysis of additional samples from these areas would have increased the confidence in their classification.

Conclusions

16 soil samples were extracted and measured under field conditions in real time for screening purposes. The reported values ranged from 0.86 mg/kg to 746 mg/kg in the wet soil. The speed of analysis was such that the data could be used to manage site operations in real time. The evaluation clearly demonstrated the ability of onsite analysis to manage contaminated land characterisation and remediation. The main excess cost of any remediation is due to the unnecessary removal or treatment of uncontaminated soil. Additional costs in site characterisation are incurred when contaminated areas remain unidentified due to the wrong areas being selected for sampling. Minimising this has financial as well as environmental benefits. The PDV6000 showed that it could be effectively used as a tool to rapidly identify soil concentrations and therefore allow real time management of soil characterisation and removal operations.

The four samples which couldn't be extracted and analysed on site were classified later as CLEAN and are reported above for information.