

SUMMARY COMMENTS AND STATUS OF HORIZONTAL DS 2. SAMPLING

RECOMMENDATIONS FROM THE STEERING COMMITTEE

The Steering Committee members felt that this desk study did not deliver on what was expected. The choice of undertaking experimental work at this stage was thought as ill advised. Thorough re-drafting is needed to fill in the gaps, in particular with regard to the existing standards in the different fields covered by “Horizontal”. An attempt should be made to characterise sampling also for untreated biowaste, although it was recognised that the contract specifications may have been not clear on this point. The Steering Committee members wished to have this aspect integrated to the extent possible, but did not ask for a variation of the terms of the contract. Emphasis was placed on bringing out the horizontal aspects of sampling, for which **A** pointed at the development of a framework in WG 1 of TC 292 (including terminology).

The Steering Committee decided to ask Mr Tim Evans to **re-draft the desk study and integrate the missing aspects by the end of March 2004**. Thus, a four-week consultation round would be organised. In principle this should not entail any increase in the budget allocated to this Work Package.

In the context of this discussion it was also decided that **Mr Bernd Gawlik** of the Soil and Waste Unit of the Joint Research Centre **would co-ordinate the aspects relative to the pre-treatment of samples**. The Steering Committee was of the opinion that sample pre-treatment was an important aspect to be dealt with in the context of “Horizontal”. However, in order not to delay the process, each Work Package team should reflect on the demands on pre-treatment for their specific topic in order to define the content of the pre-treatment standard. Mr Gawlik would ensure the necessary co-ordination among the different Work Packages.

SUMMARY OF COMMENTS

HORIZONTAL DESK STUDY 2. SAMPLING

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1 PROJECT OBJECTIVE

The sludge (use in agriculture) directive (86/278/EEC) requires that the sludge and the soil on which it is used are sampled and analysed. If and when there is a biowaste directive, this too will require that materials are analysed.

The purpose of WP2 is to facilitate implementation of these legal instruments by developing harmonised methods for sampling sludges, treated biowastes and the soils on which they might be used. It is intended that these methods will have quantified precision, i.e. the confidence limit that the sample is within a certain confidence interval of the true mean of the population. The sampling step is probably the greatest potential source of uncertainty in the overall sampling-analysis chain unless it is defined; people often overlook this fact.

WP2 was not intended to provide guidance on the whole breadth of sampling situations. For example, it was not intended to address sampling of contaminated sites, e.g. former industrial sites. Neither was it intended to address sampling stockpiles of materials whose history and origins are uncertain. Both of these require individual pragmatic sampling plans. It was intended to deal with the routine production and use of sludges and treated-biowastes on land.

After reviewing the existing standards on sampling, in particular those that dealt with the confidence and precision of the samples, the objective was to test some concepts with a limited amount of practical work so as to give guidance to future work.

2 REVIEW OF EXISTING STANDARDS

There are many standards on sampling. The ones on sludge and soil are guidances that cover a very wide range of situations; they do not deal with the precision of the samples. In general the standards that aim at achieving defined precision have been developed for sampling materials that have direct monetary value, e.g. coal, aggregate, ore and horticultural products.

3 PROOF OF CONCEPT WORK

3.1 Introduction

The only way to test a sampling protocol is to analyse the samples and compare the results. All of the samples taken in WP2 were analysed in a single automated laboratory with QA/QC in order to eliminate laboratory error as a variable in this work as far as possible. Samples were analysed for DS, LOI, pH, Zn, Cu, Ni, Cd, Pb, Cr because they are in the sludge directive and they are relatively inexpensive. pH was measured in water and calcium chloride, and the trace elements were extracted with aqua regia, nitric acid and CAT (calcium chloride DTPA) to see whether these methods in combination with sampling had any different relevance to environmental significance. The sample handling from the point of taking the samples to the laboratory reception was standardised and horizontal for all sample types, so that this too was removed as a variable. For the soils, environmental significance was tested by analysing wheat ears taken from the same locations as the incremental soil samples.

3.2 Sampling Sludges and Treated Biowaste

Three sites allowed us to test the following questions:

- Does time-series sampling from the feed to a centrifuge differ from time-series sampling from the out-feed conveyer belt?
- Do the time-series samples differ from sampling the stockpile?
- Does it matter how the stockpile is sampled?
- Is sampling from the outside different from digging into a stockpile with a mechanical shovel?
- Is there any stratification in a bag of dried granules?
- How does the analysis of composted greenwaste vary with time?
- Do all of the parameters vary similarly?
- What is the variance associated with incremental sampling?
- What is the bias associated with composite sampling?

3.3 Sampling a farmer's field

A field that had been treated with sludge over many years allowed us to test the following questions:

- How does the sampling pattern affect the result of sampling soils in the landscape?
- How do the results correlate with crop uptake?

3.4 Results and Discussion

The analyses of time series samples taken from the feed to a centrifuge were different from those taken from the conveyer belt because of the different partitioning between liquid and solid phases.

There was very little difference between time series samples taken from the conveyer feeding to the heap, those taken from the outside of the heap, those taken by cutting into the heap and those taken by cone and quartering the heap.

There was no stratification within a bag of granules so it is acceptable to sample from the top of a bag.

The number of increments combined to make a composite sample and the frequency with which composite samples should be taken were particular to a site and the parameter being analysed; they were not a function of the quantity of material being treated by the site.

Soil pH values measured in water were consistently different from those measured in calcium chloride.

There was no consistent bias when comparing the content of trace elements extracted by aqua regia and nitric acid, however there was a much more dispersion of results in aqua regia extracts compared with nitric acid extracts for the sludge and treated biowaste. The dispersion of results was greater the greater the %LOI.

None of the soil trace element extracts correlated well with grain composition, though CAT was somewhat better correlated than aqua regia or nitric acid. Soil pH was not correlated with grain composition either.

The bias of the non-systematic sampling patterns compared with the systematic pattern was trivial for pH and LOI but it was significant for trace elements, however the total number of sampling locations was less than adequate.

WP2 has identified the desirability of doing further work to test whether the observations about nitric acid versus aqua regia are general; if they are, the balance of advantage would appear to be in favour of the former.

4 RECOMMENDATIONS FOR A FUTURE SAMPLING STANDARD

The review of standards and the proof of concept work have indicated that it should be possible to prepare harmonised methods of sampling that will achieve samples that are within a pre-determined confidence interval of the true mean of the whole with a pre-determined level of confidence. For example that there is X% confidence that the result of analysing the sample will be within $\pm Y\%$ of the true mean for the whole.

This would be a considerable improvement on the current situation where we do not know anything about the representativeness of the sample and as a consequence whether two results are statistically different or the same. In the present situation there is also the risk of false compliance or non-compliance.

Regarding the future harmonised methods:

- It should be possible to have horizontal modules for sample containers, labelling and transport for each type of parameter – inorganic, organic and microbiological.
- Sampling sludges and treated biowastes should have considerable horizontal commonness. Sampling soils in the landscape (farmers' fields, etc.) present a different situation.
- The harmonised method for sludges and treated biowastes would include a protocol for initially characterising the production stream statistically. This characterisation would determine the required frequency for taking composite

samples and the required number of increment samples in each composite. The statistical formulae for defining this would be part of the method.

- The frequency for taking composite samples and the number of increment samples in each composite would be entirely objective and characteristic of the production stream and the parameters being analysed.
- The method could also include a procedure for assessing the trend in the monitoring results statistically in order to identify when the inherent characteristics of the production stream had changed such that it needed to be re-characterised to either increase or decrease the frequency/increment-number of sampling whilst maintaining the confidence limit and interval.
- There are indications that the method for sampling fields would define the non-symmetric pattern and the number and spacing of incremental samples that achieves the statistical confidence.
- The modules for sample containers, labelling, packaging and transport can be horizontal for all 3 media.

Further work is needed to verify that the concepts tested and preliminary conclusions are general and to develop robust protocols. The work to date indicates very good probability of success.