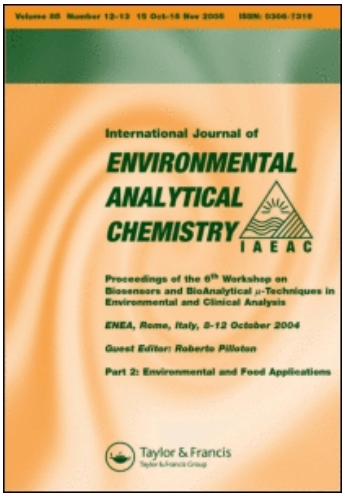

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INORGANIC CONTAMINANTS IN THE WATER COLUMN: SAMPLING AND SAMPLING STRATEGY

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Nowadays, intercalibrations, availability of certified reference materials (CRMs), clean room techniques, etc. have resulted in a situation where many laboratories seem to provide acceptable data for trace metals analysed in water, sediment or biota. Unfortunately, laboratory performance has, so far, only been tested through the analysis of well defined samples, e.g. from intercalibration exercises, or the use of CRMs.

It should be realized, that sampling, sample pre-treatment, transport and storage, are an integrated part of the analysis. The sample handling procedures have not received much attention in terms of quality assurance (QA) and good measuring practice (GMP). As such they should be considered carefully in the development of any monitoring strategy.

The various aspects of sample handling methods will be discussed here with the view to include QA and GMP/GLP procedures for that part of the analysis that relates to the samples before they reach the (clean) laboratory.

KEY WORDS: Water sampling, trace metals.

INTRODUCTION

The result of any test on the quality of the (aquatic) environment is no better than the result of all efforts that lead to the final result. This observation may seem logical, or even overdone. We should realize, however, that the total concept of analysis should fall within the realm of quality control and quality assurance, including the various aspects that make up the 'analysis'. After the sampling strategy has been defined (see section 2), any 'analysis' is a typical and necessary combination of many closely related parts:

- sampling;
- sample pre-treatment, e.g. filtration/centrifugation, preservation;
- transport conditions;
- storage;
- sample treatment;
- instrumental analysis;
- calculation, and
- evaluation of results.

Most programmes to improve the quality of the analysis focus on that part of the analysis that is concerned with the aspects in the laboratory analysis, thus limited to the

last 4 – 5 items in the above list. The reasonable to good analytical results that are produced today in intercomparison exercises between different laboratories (comparability), is the result of a decade of intercomparisons, the use of CRMs[1,2] and attention for quality assurance (QA) in the analytical laboratory. Unfortunately the tested procedures only involve the sample handling and analysis from the moment the samples enter the laboratory. The establishment of guidelines (e.g.[3–5]) helps to understand the pre-laboratory problems, but traditionally many chemical analysts are, unfortunately, trained in the instrumental analysis only, and have no proper training in pre-laboratory (e.g. sampling) procedures.

In this paper emphasis is placed on the extension of quality assurance to the area of analysis before the laboratory procedures, notably to the sampling strategy, the sampling and the sample handling. Although the discussion focuses on trace inorganic pollutants in the water column, it will be evident that similar reasoning can be followed for the organic pollutants, and even for other compartments (sediment, biota), after proper adaptations in materials and procedures.

SAMPLING STRATEGY

A proper, well defined sampling strategy should in all case be developed well before the actual sampling event takes place. This is essential not only for a sound logical approach, but also serves to evaluate a programme even before it starts or, in other words, will the final results give a sufficiently clear answer to the questions the environmental manager or the scientist has asked? An overview of the various aspects that are of concern for the definition of a sampling strategy, whether for surveys or monitoring studies, is presented in Table 1.

Although the design of a monitoring programme should be directed by the preset goals that need to be achieved, it happens that programmes are carried out on a routinely basis, without the question ever being asked whether the results meet the desired quality to support environmental management. It is our firm belief that in the process of the design of a monitoring programme specialists from various disciplines, including analytical and environmental chemists, and statisticians, are consulted. It is better to spend some time at the development stage, than to change the programme after few years due to e.g. logistic or financial reasons, with the result that this change of procedures results in a non-consistent data set which may render an expensive project useless.

SAMPLING

The objective of sampling is "to collect a portion of material from an environmental compartment (either water, sediment or biota) small enough in volume to be transported conveniently and handled in the laboratory, while still accurately representing the part of the environment sampled." Representativity has a central place in this passage not only in terms of whether the portion of the sample really represents the original environment, but also whether the sampling and following sample handling is under sufficient control that no change i.c. addition (e.g. contaminant leaching from containers) or loss (e.g. sorption to filters) occurs[6].

Next to the sampling strategy important aspects of sampling which may interfere with the final (total) analytical result include the following (sub)-tasks: definition of locations and sampling frequency, of sampling platform (logistics), of sampling method and device, of sample bottle and, not in the last place of methods for contamination control.

Table 1 Strategy to design environmental (chemical) monitoring programmes (adapted from:[7]).

I. Problem definition; objectives, functions

IIa. Selection of subjects and targets
- selection of the area or ecosystem with regard to:
  - expected pollution sources
  - expected toxic compounds
  - expected concentration ranges
  - assessment of expected environmental hazards
- selection of pollutant(s) with regard to their:
  - expected behaviour (sorption characteristics, complexation, transport routes)
  - expected bioavailability, bioaccumulation, bio-concentration factors, toxicity)
- selection of compartments: water and/or seston (sediment, biota)
- selection of sub-compartments e.g. chemical species or fractions (grain size fraction, specific organs)

IIb. Execution of a field survey to:
- establish IIa subjects and targets,
- test logistic means
- validate methodologies

III. Definition of the actual monitoring programme:
- description of the area, pollutant(s) and (sub)compartmets
- logistics (transport, ships, equipment, laboratory actions)
- sampling
  - type of sample (spot, integrated or continuous)
  - sample characteristics (size, materials, bottles, preservation)
  - sampling frequency and density
- chemical analysis (available techniques, detection limits, QA)
- requirements of (future) mathematical data treatment (trend analysis, time series)
- documentation and data storage
- data evaluation
- financial constraints
- frequency and format of reporting

Sampling location and frequency

The geographic location of sampling will be largely determined during the initial planning phase, and will follow the goals of the monitoring programme. One should realize that in most cases the sampling location (including depth) may bias the final analytical result, which is in contradiction with the representativity principle.

In Figure 1A, a cross-section of a river or lake is depicted. Often the logistic possibilities will determine the location of sampling, e.g. at the locations A or C, since for location B a boat (or bridge) is required. Neither A nor C will be representative for the actual situation, however, as an effluent is discharged near location A, and the limited

water depth prevents proper mixing at location C. We may assume that location B is representative, but is it? When observing Figure 1B, the vertical inhomogeneity is depicted, e.g. as the amount of suspended particulate matter. It will be obvious, that in our original option, location B1 is probably not the most representative choice; may be B2 is, but for a better estimation we may need three sampling depths (B1, B2, B3) or even more samples (which could be eventually by pooled into one integrated sample). In an examination, performed prior to the actual sampling activity and using an *in situ* continuous measuring device (conductivity, turbidity, etc.), the vertical (in)homogeneity of the water body may be estimated. The sampling strategy should then the be based on the interpretation of the results. In most cases special care should be given to avoid either sampling the enriched surface microlayer, or the near-bottom waters that may contain a high load of resuspended sediments. Similar discussions can be given in a lateral context, e.g. along a river with a discharging effluent line. An approach could be to sample mid-stream above and below the emission source (Figure 1C; stations K, L). When, however, taking into account currents and mixing dynamics, it may become clear that several additional stations will be needed to get information on the overall distribution and load of the contaminants emitted, and that neither of the L-stations can be considered as representative (Figure 1D). Formulas have been drafted to calculate distances down-stream of an effluent line where homogeneity should be reached, but these are to be taken with care, as natural conditions (e.g. bathymetry) may interfere substantially. Also here, a preliminary survey using a characteristic parameter (pH, temperature, oxygen, etc.) may assist in the definition of the sampling locations and their validation.

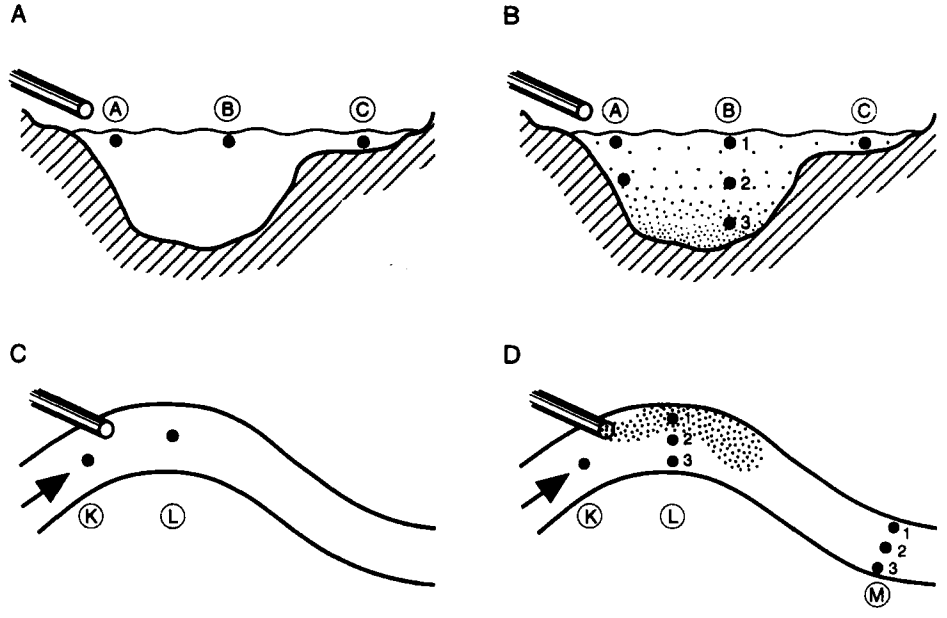

Figure 1 Schematic presentation of the representation of sampling locations. A, B) Cross section of a river or lake; C, D) Locations along a longitudinal transect (see text for details).

Validation of the sampling locations (geographic position and depth) is therefore an important aspect of the sampling strategy. Also the documentation and training of the sampling staff should be such, that it can be guaranteed that the same locations are sampled throughout the (multi-year) monitoring study.

Sampling frequency may vary from continuous measurement and (semi)continuous sampling, to once or four times a year. It will be obvious that for the compartment water with its rapid changes, no representative result can be achieved when the sampling frequency is too low. One should even seriously consider to collect at one occasion replicates in order to get information on the variability of the samples collected.

The number of samples that can be collected and analyzed is usually a function of available staff and thus follows financial constraints. For simple, on line detection of e.g. temperature, pH and chlorophyll, continuous recording will be feasible, but for the expensive trace metal analysis this is not yet possible.

Sampling may be restricted to 'typical' periods of the year, but nature is often not very predictable. As an illustration, a two-year period of monitoring the river Rhine at Lobith is presented, where the results for the discharge, the amount suspended particulate matter and the total zinc concentration are given (Figure 2). The discharge is measured semi-continuously, while the other parameters are based on weekly measurements. Interestingly, the discharge shows large changes often over short periods. The SPM content follows this pattern (due to increased resuspension at higher flow rates), but only to some extent. As the total zinc content is also linked to SPM amounts, its pattern

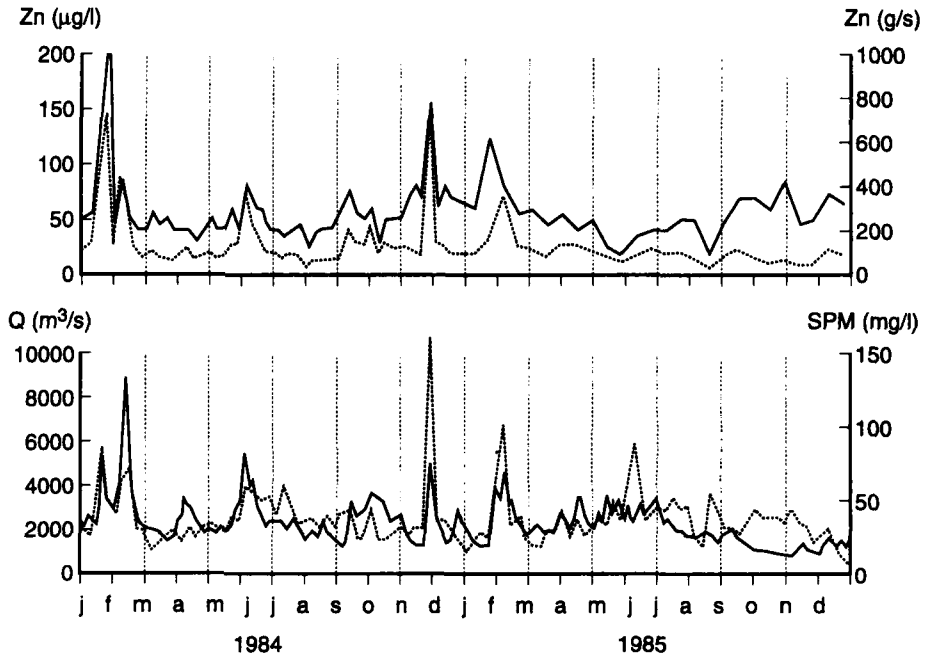

Figure 2 Representativity and sampling frequency. Two-year example of data from the river Rhine, collected at Lobith at weekly intervals. Upper graphs: the zinc concentration (in µg/l, solid line) and total calculated load (in g/s, dotted line); Lower graphs: the discharge (in m^3/s, solid line) and the amount suspended particulate matter (in mg/l, dotted line)(After:[21]).

follows the SPM, but also here: to some extent. For logistic (and statistical) reasons sampling is often performed at regular intervals. When sampling is not performed at weekly intervals, but e.g. every two months (see Figure 2), we observe that in most cases the 'peaks' are not detected, which usually results in an underestimation of the calculated load, whatever the calculation method applied[8-9].

For these type of studies one may combine (semi)-continuous measurement of e.g. SPM with periodic sampling for contaminants, in order to try to interpolate the data.

A reduction in the analytical costs may also be achieved by making use of (biological) early warning systems. The standard sampling frequency can then be set at a rather low frequency. A rapid environmental change detected by continuous measuring of physico-chemical or biological sensor(s), will induce an additional sampling event.

Sampling methods

One may distinguish the use of various approaches for the collection of a representative sample:

- Spot samples are usually collected, and involve any sampling device that collects a sample at a given location and time; hence they are in principle representative only for these conditions. When the water body is not too inhomogeneous (in space and time), these samples may still provide valuable information.
- Integrated samples give a better estimate of the water body sampled. The sampling covers a given transect or area and/or period of time. Usually several (spot) samples are collected and pooled, but the continuous collection by pumping system is also possible. The sampling may be initiated by preset time intervals (time-proportional) or by the amount discharged (volume-proportional).
- Continuous sampling/analysis. Some sensors may provide a continuous analytical signal, such as temperature, conductivity, turbidity. These signals can, based on a continuous recording, be useful to describe the behaviour of the water mass, which may help to interpret analyses from spot-sampling. It is expected that new continuous (bio)sensors will become available.
- Use of biota. The ability of biota, e.g. mussels, to accumulate contaminants in their tissues to elevated levels reaching concentrations that are in equilibrium with the ambient water concentrations, make these biota useful 'samplers'. Apart from the relative ease of detection of these elevated concentrations, the biota are time integrating, and may thus reduce the number of samples to be analyzed[10].
  Another use of biota is the incorporation of a biological early warning system (BEWS)[11]. Here biota, e.g. fish or mussels, detect a wide range of pollutants and indicate through an alarm function the adverse environmental conditions.

For sampling of the water column, three different methods are commonly used:

- water sampler,
- pumping system (even while sailing a ship[12]), or
- collection direct in the sample bottle.

The first method is most commonly used. While the other two methods are in general limited to the surface waters (down to about 20 m), water samplers usually can be applied at any depth. A special design acts by *in situ* pumping and trapping of compounds on special chromatographic columns. Despite the option of filtration, these

Table 2 Method for cleaning of (polythene) bottles used for the BCR certified reference material CRM 403 (trace metals in sea water). In the steps 2–4, the bottles are filled to the top (after[2]).

step 1	washing with demineralized water to remove dust and plastic remnants;
step 2	soaking with nitric acid (analytical grade, 2:3), ≥ 1 week;
step 3	soaking with nitric acid (analytical grade, 1:12), ≥ 1 week;
step 4	storage with Milli–Q water/nitric acid (pH 1.6) until use.

systems seem not to work well in turbid waters[13–14]. For some hydrophobic compounds, like the organo-tins (e.g. tributyltin, TBT), it is essential to collect the sample directly in the sample bottle, as adsorption to the sampler wall will negatively affect the final concentration.

Typical materials for equipment (samplers, sample bottles) used in trace element collection and storage involve polythene, polypropylene or the more expensive (FEP) Teflon (e.g.[15]). Special trace metal free samplers have been developed, (inter)comparison of samplers has been reported (e.g.[16–18]). Despite this, differences have been observed in routine sampling methods. The differences were attributed not only to different types of samplers, as could be expected due to the various construction materials and cleaning methods, but also to different sampler sizes. Obviously volume-surface ratios may interfere with the analytical result. Cleaning by soaking with acid is considered important, but due to the complicated shape of samplers, this is not always an easy task. The sample size necessary for trace element analysis is typical in the order of one litre. Information is available on proven cleaning procedures[19–20], involving a four step approach (Table 2). This procedure results in stable samples, as was proven e.g. for the production of certified reference materials (CRMs)[2].

SAMPLE PRE-TREATMENT

Without pre-treatment, samples for trace metal analysis will change. Sorption (to particles or container wall) and (micro)-biological processes will influence the distribution of the constituents which may interfere with the total analytical procedure.

The total trace element content is the sum of the dissolved and the particulate fractions. In low SPM containing samples the particulate fraction is often neglected, and total samples are then analyzed. When information on the dissolved and/or the particulate fractions is required, the analysis of total amounts becomes problematic in waters with higher levels of suspended particulate matter. Since many compounds adhere strongly to particulates such an analysis would be difficult to evaluate (Figure 2).

Even if we could properly estimate the amount of SPM before sampling, no clear boundary can be set to at what SPM level a separation technique should be applied. At present it seems that common practice within each laboratory determines whether separation is applied or not, often independent of SPM content.

Filtration

Essentially two methods are available to separate particulates from the water: filtration and centrifugation.

Most applied separation of SPM is by filtration, where water passing a pore size of 0.45 μm has become the experimentally defined dissolved fraction. Since smaller

particles exist (e.g. colloids), the distinction is not real and smaller pore sizes are in use, even down to 0.005 μm (ultrafiltration). Whatever filter used, the effective pore size will decrease during the filtration process as a result of clogging of the filter, and hence be a function of the amount and the grain size distribution of the suspended matter[22].

Only limited information exists on filtration procedures. An intercalibration exercise was carried out for the collection of SPM from coastal waters for trace metal analysis[23], while e.g. Laxen and Chandler[24] and Horowitz *et al.*[25] compared different filter types for their use in trace metals analysis.

For trace metals, the influence of filtration method, as function of filter type, filter size, pore size, amount SPM present and amount of material discarded prior to sample collection, has been demonstrated by Horowitz *et al.*[25]. All these variables could influence the concentration of a 4.9 mg/l iron solution.

Membrane filters (cellulose acetate or -nitrate) or Nuclepore type filters (polycarbonate) of 0.45 μm or 0.4 μm, respectively, are commonly used for trace metal analysis. For ultra trace concentrations the filters require to be cleaned using an acid treatment step.

Centrifugation

The second option of separation of dissolved and particulate fractions is centrifugation, either in batch or in flow-through systems[26]. The method is sometimes favoured due to the relative ease to collect large amounts of suspended matter, which enables laboratory analysis of the SPM that is much less subject to contamination. The mechanism of separation is, however, totally different from the filtration process and discrepancies may be expected[27-28]. Since density and size of the particles will mainly determine the deposition rate, the lighter and smaller particles may escape from collection[29]. The finest fraction that contains the highest amounts of pollutants, and plankton cells that may have accumulated pollutants, may thus be included in the dissolved fraction and bias the analytical result.

In a comparison between filtration and centrifugation methods, the centrifugation method underestimated the SPM amount[6].

PRESERVATION, TRANSPORT AND STORAGE

With or without filtration, the sample is usually best analyzed as soon as possible after collection. This will not always be possible, and storage according to validated procedures and conditions will be necessary[30-31].

The addition of chemicals to ensure that the sample stays unchanged during storage, is often necessary. For trace metal analysis acid is added to filtered samples (1 or 2 ml/l HNO_3). The added chemicals should be of highest quality to ensure a minimum of contamination. This procedure was followed for the production of certified reference materials of sea- and estuarine waters, and samples can thus be stored for longer periods at ambient temperature[2,20]. We should realize, that addition of acids to non-filtered samples will seriously affect the distribution of trace metals over the dissolved and particulate phases, and only a total analysis will then be possible. When treatment (filtration and preservation) in the field is problematic or impossible, these processes may be delayed until the sample has reached the laboratory. Proper conditions should be applied (cool or deep frozen, dark) and methods should be validated, as changes in the sample are to be expected.

When samples, rich in organic matter, are not analyzed immediately, flocculation/precipitation of newly formed particulate matter may occur, even after the initial 0.45 μm filtration. This particulate matter renders the sample inhomogeneous, but it seems not to affect the trace metal analysis[32].

It should be realized that there is a maximum storage period, despite the existence of preservation methods. CRMs for trace metals in seawater proved to be stable for over one year. Storage conditions should be applied from the moment the sample has been collected and/or preserved. Often appropriate conditions during transport are neglected.

The aspects of sample storage will be treated in a separate communication in this issue[33].

CONTAMINATION CONTROL

It seems obvious that during all steps of the analytical process contamination control is of utmost importance. Within the confined space of the (clean) laboratory this is relatively easy to achieve, but during sampling and sample treatment in the field one tends to forget its necessity. In the marine environment most trace metal concentrations tend to be much lower than in freshwater systems, and it took years to marine chemists to combat the threat of contamination. It is the author's firm belief that at least part of the trace metal concentrations reported for surface waters, are an overestimation of the real situation. In these situations one would be surprised to see the differences in the results when open sea methodologies could be implemented.

Closed sample handling systems may be preferred to eliminate contact with the polluted, dusty atmosphere, else a portable clean bench is advised. Equipment should be cleaned appropriately and stored contamination and dust free until use in a double set of plastic bags.

It is our opinion that the analytically skilled laboratory staff, which is used to combat contamination, should be responsible for the cleaning of equipment and bottles. They should provide appropriate instructions and training to all involved in the sampling and sample handling process.

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