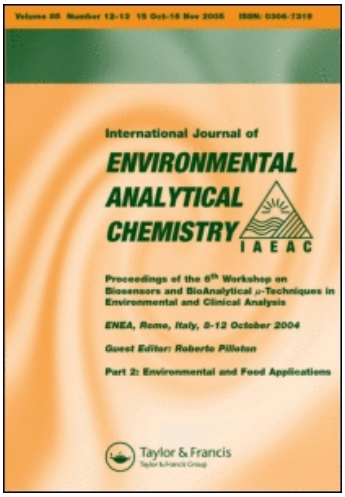

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SAMPLING TECHNIQUES FOR ORGANIC SUBSTANCES IN SURFACE WATERS

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A crucial step in the measurement of organic compounds in surface waters is collecting samples representative of the system at the time of sampling and ensuring that no extraneous materials are introduced or target compounds removed during the sampling or transport and storage prior to analysis. The various associations of many organic compounds in natural waters with colloid and suspended materials including microorganisms and algae, have led to fundamental short-comings in describing the sample matrix. Techniques are not generally available at the moment to separate compounds on the basis of their occurrence in associated forms in waters, i.e. the majority of measurements are for "whole" water samples including particulate material.

Sampling strategy is primarily determined by factors such as the overall objectives of the measurement, financial constraints and logistic considerations. This paper briefly examines sampling methodologies common to a range of non-volatile organic compounds with particular attention given to some current problem areas. There is an increasing requirement for intensive sampling to monitor episodic events in rivers that place great demands on current techniques, particularly with respect to sample integrity and stability.

KEY WORDS: Water sampling, organic compounds, pesticides, surface waters.

INTRODUCTION

The ubiquitous occurrence of xenobiotic organic substances in water is now well-known with the majority of analytical effort directed to the more toxic compounds such as PCBs, PAHs, pesticides and certain surfactant residues[1]. In this review the term "water" will refer to the "whole" water sample and includes dissolved, particulate/colloid associated and compounds bound or adsorbed to biological membranes or exudates.

The first step in the measurement involves obtaining samples representative of the matrix being sampled and maintaining sample integrity prior to analysis. General and detailed reviews of sampling and analytical methodologies applicable to waters have been available for some time[2]. This article attempts to examine some of the problems which are currently associated with sampling surface waters for trace organics.

To some extent, the chemical properties of the determinants and the expected concentrations in the samples influence the choice of methodology. Generally, the more water soluble and hydrophilic compounds are easier to measure than the lipophilic or surface active compounds. The nature of the water sample is also an important influence on the sampling strategy. Potable waters generally have a low suspended solids concentration and are therefore relatively straight forward to sample whereas river, lakes and coastal waters exhibit much greater temporal and spatial heterogeneity especially when the suspended solids or sediments are appreciable. In this context the importance of suspended solids increases as the affinity of the organic compound to the particulate matter increases

and varies according to the heterogeneity of the solids both in terms of composition and particle size. The degree of homogeneity of the particulate material usually decreases with increasing particle size but again this may depend on the specific location[2].

The high cost and time consuming nature of the analysis of waters for organic compounds means that the majority of monitoring and research is strictly targeted at specific requirements. These are quite often related to estimating the loads of particular compounds transported from river catchments, e.g. monitoring the red-list substances in the UK, or monitoring specific discharges and riverine or coastal concentrations as an aid to evaluating ecotoxicological effects in the environment. Although biological indices of water quality are essential in detecting when an ecosystem is being adversely affected, more detailed chemical analysis of the water is often needed to identify the specific contaminants which are responsible and so enable the most cost-effective remedies to be implemented.

Some of the specific problems associated with sampling organic compounds are now addressed with particular attention to areas where improvements are now possible.

THE CHARACTER OF THE SAMPLE

Organic compounds may be distributed in the water sample in the following compartments:

(a) *Dissolved in aqueous solution*

This fraction is likely to be more homogeneous than those considered below and similar in behaviour to inorganic solutes. In situations where point-source inputs are suspected, the mixing volume (or distance downstream in a river) needs to be assessed independently by sampling horizontal and vertical transects or by tracer studies, e.g. by fluorometry using rhodamine or conductimetric studies.

(b) *Associated with colloids*

The association with colloids is usually through specific interactions with clay minerals or the interaction between lipophilic organic compounds and organic polyelectrolytes, such as naturally occurring humic, fulvic and acidic polysaccharides. Several studies reported in the literature have provided evidence for the interaction of hydrophobic organic compounds and colloidal macromolecules in water[3–6]. Sometimes this has been investigated in terms of the enhanced solubility of the compounds in water containing humic and fulvic acids. This approach has arisen because of the common procedure of filtering freshwater samples through 0.45 μm membranes to separate the particulate bound and soluble components of the analyte. The observed enhancement has been accounted for by the partition between the organic colloids and the solution. The strength of the interaction is thought to be closely related to the molecular size and composition of the colloids and the intrinsic water solubility of the solute[6].

The relative importance of the interaction with organic colloids is illustrated in Figure 1 for compounds with distribution coefficients below 50,000 $dm^3\ kg^{-1}$ assuming a linear adsorption isotherm applies at low concentrations of the trace organic compounds. The

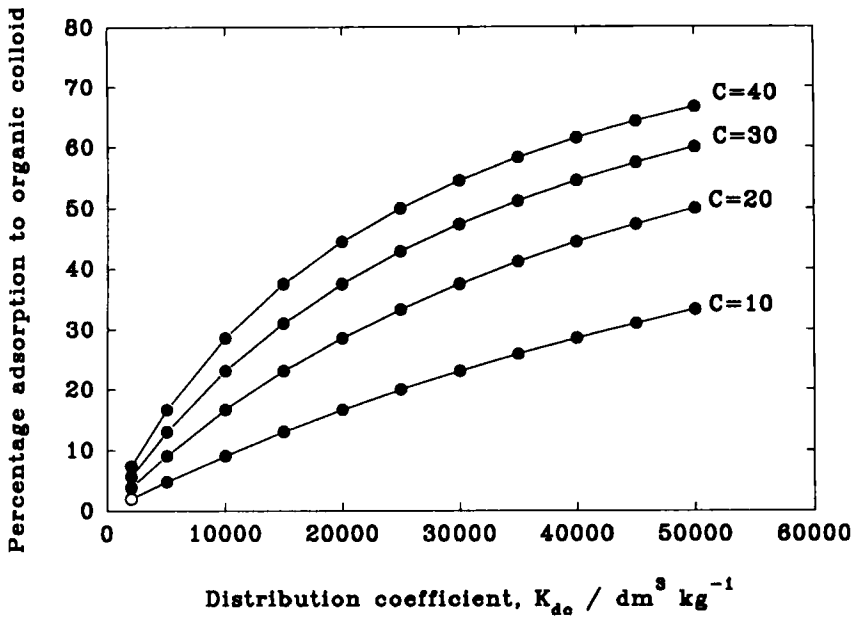

Figure 1 Theoretical relationship illustrating distribution of compounds between the dissolved and colloid fractions. The concentration of the colloids, C, is in mg dm^{-3}. The distribution coefficient, K_{dc}, is defined as the ratio of the concentration of the compound associated with the colloid (ng g^{-1}) to the concentration of the dissolved compound (ng ml^{-1}).

results of Means and Wijayaratne[7] indicate K_{dc} values for atrazine of between 1690 and 13,600 for various estuarine colloids, Preliminary results of House *et al*[8] for a pyrethroid, permethrin, produced values of approximately 30,000 dm^3 kg^{-1} for humic material released from a freshwater sediment. Various approaches are possible to quantify the amount of trace organics associated with the colloid phase. These include estimates from measurements of the dissolved organic carbon (DOC), separations of the higher molecular weight fractions by dialysis or ultra-membrane filtration and the application of turbidity methods to measure colloid concentrations.

Generally colloids are defined as < 0.2 μm in size[9] and include many clay components which pass through 0.45 μm membrane filters. If the water is derived from catchments containing peat soils, the humic substances are usually well-mixed and present no problems for obtaining representative samples. Only if such waters mix with ones of different composition, e.g. hardwaters draining karst catchments, is it necessary to examine the hydrodynamics and mixing downstream of the confluence as mentioned in (a) above. For clay colloids, surface run-off, resuspension of bed-sediments or river bank erosion are likely to contribute to the colloid component and so techniques are needed to assess each situation in the field. In the past very little attention has been given to the colloid associated fraction, i.e. the concentration of trace organics in the filtrate has included a contribution from the pesticides bound to colloids. The efficiency of the extraction process, e.g. using solid-phase extraction columns, may be altered by the presence of colloids because of the increased mobility of the colloid fraction through the

extraction column leading to rapid "breakthrough" of the target compounds. Although this is an important post-sampling problem, there are important implications for planning the sampling strategy and also the pre-extraction handling of the water samples.

(c) *Associated with suspended solids*

This component, like the colloid associated fraction, is troublesome because of the heterogeneity in composition, size and distribution of the particles (here defined > 0.2 μm). Many organic compounds, particularly the most toxic, e.g. the PCBs, organochlorine and pyrethroid insecticides, are sparingly soluble in water but strongly sorbed to sediment minerals and organic particles or organic layers associated with inorganic particles. The larger size of these particles results in greater difficulties in obtaining representative samples, particularly in situations where suspended sediments are a major contribution to suspended solids. In this situation, e.g. during wind induced turbulence in a lake or storm event in a river, some caution is necessary in the interpretation of the analytical results from spot samples if spatial as well as temporal variability is probable.

For compounds with a moderate water solubility and low octanol-water partition coefficient, e.g. the triazine herbicides such as simazine with a $\log K_{ow}$ = 1.5 to 2.3[10] and solubility of 3.5 mg dm^{-3} at 20°C[11], the amount of analyte associated with suspended solids is estimated as < 10% of the total herbicide concentration for suspended solids as high as 1 g dm^{-3} and organic matter content of 40%[8]. In contrast, under the same conditions, compounds like DDE and the pyrethroid insecticides are mainly (> 70% of total amount) associated with suspended solids[12]. As shown in Table 1, the sample heterogeneity introduced through suspended solids could explain some of the variability found in the analysis for these lipophilic pesticides. Compounds with a lower $\log K_{ow}$ such as lindane, are less strongly attached to organic matter and show less inter-sample variability compared with *cis*- permethrin, the most lipophilic compound listed.

SAMPLING STRATEGY

Sampling techniques will depend largely on the purpose of the measurement. The discussion here will primarily focus on research although certain aspects are common to regulatory and monitoring requirements. The latter usually consist of relatively

Table 1 Example of the sample variability for γ-BHC (lindane), dieldrin, DDE and *cis*-permethrin for water samples taken from the same location and at the same time. The octanol-water partition coefficients, K_{ow}, are taken from the recent compilation[10]. The values in brackets are the standard deviations for triplicate analysis be glc. The results are taken from reference 8. All compounds were quantitatively analysed by GC-ECD and the peaks confirmed by GC-MS[8].

compound	*log K_{ow}*	*replicates/ng dm^{-3}*		
γ-BHC	3.66 – 3.72	41(3.0)	38(0.2)	34(7)
dieldrin	4.32 – 5.40	9(0.2)	8(0.1)	6(1)
p–p' DDE	5.69 – 6.96	ND	22(0.4)	4(1)
cis-permethrin	6.24	468(48)	323(2)	191(23)

infrequent (1–4 week intervals) spot sampling of pre-selected monitoring sites over long periods or more intensive sampling when water quality problems are evident as a result of either chemical or biologically based assessments.

Sampling strategy should reflect the known or expected variability of the system. Broadly this necessitates obtaining information about the spatial and temporal changes in the concentration of the target compounds. These aspects are usually considered separately although ideally both need to be quantified for an assessment of fluxes or ecological impacts on the system.

(a) *Spatial variability*

In most environments the changes in concentration with sampling position at a site are important, particularly where point source inputs are found. In lakes, concentrations may change appreciably between the biologically active photic zone and the lake bottom or on either side of the thermocline. This can be quantified by depth sampling, i.e. taking discrete samples at predetermined depths. Other options include depth integrated sampling (DIS) to collect one composite sample for the profile. In rivers it is normally necessary to collect discrete samples across transects from the channel centre at various depths or at a fixed depth[13]. If concentrations in the bulk of the water are needed, care is essential to avoid the surface "microlayer" which often concentrates hydrophobic compounds by their interaction with natural and synthetic surfactants.

(b) *Temporal variability*

When samples are needed to measure discharge loads in rivers or fluxes in lakes, it is important to plan the sampling to cover periods when the concentrations are likely to differ from the baseline values, e.g. during spates or storm periods. In these instances the sampling may be flow-weighted which means that samples are taken after fixed volumes of water have passed the sampling point. Alternatively, samples are often taken by automatic samplers at predetermined time intervals. In both cases the event trigger may be rainfall, water-level or flow-rate. A detailed discussion of the methods available for sampling programmes in situations where the variability is random, cyclic or systematic is available elsewhere[2]. As a guide, when the variability is random, the number of samples, n, needed to achieve a particular precision is:

$$n = (1.96\,\sigma/e)^2 \tag{1}$$

where σ is the standard deviation of the normal distribution of the measured concentrations and e is the tolerable imprecision of the mean concentration. Hence for σ = 10% of the mean and e = 5% of the mean, n is 15 to achieve 95% confidence limits. Alternatively when the natural heterogeneity is larger, rather than collecting numerous samples at a site, the heterogeneity may be estimated from[14]

$$h_e = \{[\Sigma(C_1 - C_2)^2]/n\}^{1/2} \tag{2}$$

where h_e is the variability associated with the heterogeneity of the site, C_1 and C_2 are the concentrations of duplicate samples at the same location at the site with n duplicate samples taken at the sampling location, i.e. river site or lake basin.

METHODOLOGY

Materials

Borosilicate glass containers with PTFE lined tops are normally recommended for sampling organic compounds because: (1) plastics such as polyethylene and polypropylene may leach plasticizers, e.g. phthalate esters, to the sample and lead to interference problems in the subsequent chromatography analysis; (2) many plastics are porous to volatile compounds leading to potential losses during transit and storage; (3) the surface of plastics generally facilitate microbial colonisation and the potential for enhanced biodegradation of some compounds.

Glassware has the added advantage that it is easily inspected and may be baked at a higher temperature than many plastics. Amber bottles are also available for use with compounds that are photolabile.

Most container materials adsorb organic compounds[15,16] and therefore special precautions are necessary to ensure that the internal surfaces of the sampling bottles are extracted with a suitable solvent. Even a 1 litre borosilicate glass bottle adsorbs significant amounts (> 10%) of compounds with a $\text{Log}K_{ow} > 5$[15], e.g. for pesticides at concentrations < 10 ppb. Hence special attention is needed in the construction of any sampling equipment; materials such as borosilicate glass, stainless steel and PTFE are normally recommended. Other materials will need to be evaluated according to their use.

Cleaning

Several methods of cleaning apparatus to minimize contamination of the samples are available. Sample blanks need to be evaluated and if these indicate no contamination or interference in the analytical method, the cleaning methods should be deemed effective. Needless to say, for the trace analysis (< µg/l) of organic compounds such as pesticides in natural waters, the cleaning procedure needs careful planning. In this laboratory 1 litre sample containers and ancillary equipment are soaked overnight in detergent, rinsed thoroughly in distilled water and 30 – 50 ml of chromic acid added to each bottle, shaken, the caps removed and rinsed with distilled water, and the equipment left in contact with chromic acid overnight. The equipment is then thoroughly washed with distilled water and rinsed with hexane or appropriate solvent before use. In the analysis of surfactants, the use of detergents is prohibited. Alternatively, non-volumetric borosilicate glassware may be heated to 400°C for 1 hour although thermally stable compounds such as PCBs may not be eliminated unless the glassware is subsequently rinsed with acetone.

After cleaning, the bottles must be capped and other apparatus sealed as appropriate, e.g. using aluminium foil, and stored in a clean place.

Sampling

In general the sample bottle must not be rinsed with the sample water prior to filling. It is better to ensure that the bottle is clean and free of contaminants before use. Many organic compounds adsorb to glass and pre-rinsing will produce an erroneously high result if the internal surface of the container is extracted as part of the analyses. For more water soluble compounds this is not likely to be important if the suspended solids concentration is low[15]. Rinsing usually introduces suspended material that attaches to the

inner container wall and this may remain intact during the subsequent filling. It could be argued that pre-rinsing saturates adsorption sites on the inner surface of the container and as long as the container wall is not extracted with solvent, the measured concentrations will correspond to the bulk water values. However, this is not usually recommended because of the uncertainties introduced by desorption/adsorption with changing temperature and uncertainties in the sorption kinetics to the container walls.

The wide range of physical and chemical properties of organic compounds found in surface waters make generalisations difficult. However some basic comments are possible:

(1) For samples in a pipeline, e.g. distribution system or groundwater borehole, it is usual to flush the pipe prior to taking the sample to avoid sampling water that has changed after long periods of standing, e.g. changes can occur because of biodegradation in biofilms or volatilization (1).

(2) For discrete spot samples (dip samples), a weighted bottle should be immersed at a suitable location and retrieved. For rivers this is normally mid-channel at a depth of 0.5 – 1 m. Depth samplers permit discrete samples to be taken at pre-determined depths. A sealed sampler that is open and sealed at an appropriate depth is preferable to an open sampler that is closed at the appropriate depth. This avoids pre-adsorption of the target compounds on the inside of the container at shallower depths prior to sealing the sampler. With a sealed sampler it is important to be able to extract the container walls whereas with a open sampler extraction of the container wall may lead to erroneous results. In this situation, particularly operating in field conditions, a pragmatic approach is to flush the sampler and transfer the contents to a glass bottle on site without pre-rinsing the bottle. This avoids the difficulty of extracting the field sampler but requires that the sample container be extracted during the analysis.

(3) The use of autosamplers is particularly difficult at present for the more hydrophobic compounds. Commercially available equipment is not generally designed for sampling trace concentrations or representative sampling of suspended solids The design and orientation of the sample intake with respect to the water flow is particularly important in this respect. It is necessary to strive for so called iso-kinetic conditions when the sample intake faces into the flowing water and the intake velocity matches the water velocity. This condition permits the entrainment of suspended solids at the same concentration as in the natural water. Sampling errors of *ca* 30% in the suspended solids concentration have been reported for relative flow rates of 0.5, i.e. river velocity/intake velocity.

On-line sampling

The successful application of solid adsorbents for the extraction of trace organic compounds dissolved in water[17], creates opportunities for the automation of the extraction at the sampling site. This method involves passing a known volume of water directly from the water-body through a suitable solid-phase-extraction (SPE) column at the sampling site. This largely eliminates the problems associated with losses of analyte onto surfaces of containers. The method has been used successfully to collect samples containing pyrethroids[18] from ponds and no doubt will find other applications, particularly when *in-situ* sampling on a regular basis is needed. An added advantage is that the SPE samples can be stabilised by storage at -20°C until they are eluted with a suitable solvent or further processed. The main problems with the application of the method to flowing waters are associated with sampling the suspended solids and

ensuring that the sample is representative. On-line filtration of the suspended solids for subsequent liquid extraction is probably essential for many compounds in natural waters. The overall benefits probably rely on some degree of automation of the collection system.

CONCLUSION

It is important for the sampling strategy and subsequent analytical methodology to consider the composition of the water in terms of the dissolved organic compounds and trace organic fractions associated with colloids and suspended solids. An assessment of the temporal and spatial variability at the sampling site is crucial to any measurement but this often necessitates extensive investigation for individual sites. Most of the problems associated with sampling organic compounds relate to the low concentrations of the analytes such as pesticides in natural waters and the precautions necessary to avoid contamination of the sample and losses through degradation between sampling and analysis and adsorption of the compounds to sampling equipment. Lipophilic compounds are generally strongly adsorbed to many types of surface whereas water soluble compounds, with low octanol-water coefficients, are less difficult to handle. In some situations on-line automatic sampling through the use of solid-phase adsorbents may be feasable in the near future.

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