Sampling and Analysis of Water to Assess Exposure

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1 INTRODUCTION

An essential pre-requisite of any experiment or programme involving sampling and analysis is a clear description of the objective of the study. Although this statement is so widely recognised that it has almost become a platitude, it is worth repeating because, frequently, insufficient attention is paid to consideration of the objective before experiments are started.

The objective of interest for the purposes of this paper can be readily stated. It is: the determination of the exposure of a given organism, human or other species, to a given chemical from the measurement of the concentration of the chemical in samples of water. This is a simple statement; but in practice, exposure is usually a complex process which has to be carefully considered before the programme of sampling and analysis can start if the objective is to be achieved. While detailed consideration of the term "exposure" and the many factors that influence it lie outside the scope of this paper, it is useful to consider two illustrations of the complexities involved and of the considerations that go into selection of sampling times and procedures and analytical systems.

Example 1: Estimation of human exposure to a chemical present in a water supply.

Water may be sampled from the consumer's tap, but the concentration of chemicals in such samples may depend on, for example, the residence time of the water in the pipe, on the type of pipe material, and on the water flow rate during sampling. In addition to direct consumption, it should be recognised that tap water may be used to prepare hot beverages, during which changes in concentration of a chemical may occur, and for cooking food, to which the chemical may be transferred from the water. The tap water supply may also be used for washing and laundering operations, and these may offer other exposure routes. Finally, in the assessment of exposure, assumptions have to be made about the amount of tap water ingested by individuals, the amount of bottled water consumed, and changes occurring as a result of different forms of domestic water use.

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Example 2: Estimation of the exposure of a fish to a chemical present in river water.

As with the previous example, more than one route of exposure has to be taken into account. Direct uptake, principally through the gills, is likely to be a major route, and the fish will feed on organisms that may themselves have taken up the chemical. Also, for bottom dwelling fish, direct contact with a chemical adsorbed onto sediment may provide another mechanism of exposure. The concentration of chemicals in river water may fluctuate with time and position in the river, as will the suspended particulate load—which may be important if the chemical adsorbs to particulates. The type of fish, its feeding behavior and its age will also influence the relative importance of different exposure routes.

These examples illustrate that the measurement of the concentration of a chemical in water near to, or ingested by, an organism provides only part of the characterisation of an organism's exposure to that chemical. The other factors involved can be complex and frequently are not well understood. One of the attractions of monitoring exposure through direct analysis of biological specimens is that the effect of many of these variables can be ignored, but this and the problems of direct biological monitoring are the subject of other papers from this meeting.

Basically, the determination of exposure by water analysis can be separated into three inter-related problems:

(1) Choosing a representative sample, or a sampling programme that gives an adequate representation for the medium of interest of the fluctuations of chemical concentration in time and space;

(2) Processing and analyzing the sample(s) to define concentrations relevant to organism exposures; and

(3) Fusing the analytical results to produce exposure estimates, taking into account different exposure routes and the bioavailability of the different forms of the chemical.

This paper concentrates on problems (1) and (2); problem (3) is dealt with in another paper in this series. There are several excellent books, monographs and articles that describe in great detail recommended procedures for the sampling and analysis of water (see IHD-WHO, 1978; Suess, 1982; USEPA, 1982; Hunt and Wilson, 1986). These papers generally concentrate on monitoring for compliance with standards. In this paper, we outline these details and concentrate on those aspects most relevant to exposure assessment.

2 WHAT WILL WATER SAMPLES CONTAIN?

Chemicals may be present in many different forms in both treated and natural waters. The identification of the chemical species of interest in the

exposure study is critical, not only from the viewpoint of sample programme design and chemical analysis, but also because of the well known dependence of bioavailability and toxicity upon chemical speciation. An example of this is the extreme toxicity of tributyl tin compounds to molluscs in contrast with the low toxicity of inorganic tin (DOE, 1986). Another illustration is the wide variation in toxicity to rodents shown by the family of polychlorinated aromatics (McKinney *et al.*, 1985).

A brief outline of the types of substances found in water samples is useful. At the molecular level, chemical species will exist in true solution—i.e., single molecular or ionic species. These could be organic chemicals or ions such as acetone or acetate ion, or inorganic species such as free metal ions (e.g., Cu^{++}), ion pairs (e.g., $PbCO_3$) or complexes (e.g., $Cu(CH_3CO_2)_2$). At the macromolecular level, rather complex and generally poorly characterised species such as fulvic and humic acids are present, and molecular and ionic species can associate with, or adsorb onto, these macromolecules. Colloidal materials are even less well characterised and are generally larger, although there are no clear cut divisions based on particle size. Colloids can also adsorb both organic and inorganic species. Finally, suspended particulate matter is usually present—consisting of micro-organisms and/or inorganic material which can also adsorb organics and inorganics.

The association between chemicals and macromolecules, colloids and particles varies in strength, and in the degree and rate of reversibility, depending on the precise species involved and, possibly, on the time of contact. For organic chemicals, the associations are usually non-specific, and are governed mainly by the content of organic carbon in the macromolecular or particulate phase and by the octanol/water partition coefficient of the chemical concerned. In contrast, associations of metal ions are more specific, depending on the detailed nature of the macromolecular or particulate material involved and are, therefore, difficult to generalise or to model.

Given the diversity of forms of chemicals in water samples, the selection of the forms that are available for uptake by the organism of interest, the "bioavailable" fraction of the total, is a very important preliminary to any exposure study. In the case of human exposure, a further complication arises because most of the uptake from drinking water is likely to occur in the stomach, where the pH is markedly lower than the pH of the drinking water itself. This consideration brings us to the crux of the distinction between "exposure" and "dose", which is discussed in the Joint Report.

Bioavailability is currently the subject of a great deal of research effort. For divalent metal ions, a consensus has emerged that the concentration of the free metal ion in solution provides the best measure of the bioavailability of metal for aquatic organisms living in the water column (Hunt, 1987; Sunda and Hansen, 1987). However, for sediment dwelling organisms, further research is needed (Hunt, 1987). For persistent and bioaccumulative organics, it also appears that direct uptake from water is most important

for chemicals with low to moderate solubility, but that uptake via food becomes more important for low solubility chemicals (see Oliver and Niimi, 1988).

3 DESIGN OF SAMPLING PROGRAM

A written description of the objective of the programme referred to at the beginning of this paper is essential at this stage. It should provide information in three critical areas:

(1) Definition of the substance to be determined (the determinand);

(2) Definition of what information is required for the determinand, for example, whether the average concentration is required or some other measure; and

(3) Definition of the required accuracy.

With this information in hand, the problem becomes one of obtaining valid, representative information from small samples of water taken from a source in which concentration generally varies in both space and time. Careful consideration of the information required, of the known or predicted behavior of the determinand, and of the known behavior of other chemicals in the water body or source of interest to ensure that information is collected in an optimal manner.

There does not appear to be a text that deals with the particular problems of designing sampling programmemes for exposure assessments in relation to water. However, three texts deal with the characterisation of water quality in general and provide valuable advice; much of what follows is based on these (Hunt and Wilson, 1986; HMSO, 1980; USEPA, 1982).

3.1 DEFINITION OF DETERMINANDS

In view of the discussion above, it is clear that this definition is far from trivial. Often, lack of knowledge about the detailed chemistry and/or restrictions in available analytical methodology limit the possible definitions of determinands to operational classes; e.g., "total filtrable zinc" or "total p,p′-DDT obtained on solvent extraction". Research is needed to give these operational classifications some biological relevance, or to develop more relevant classification systems. In many cases, a wider than desired definition of the determinand is chosen, sometimes from necessity—as with copper, for example. Free cupric ion, Cu^{2+}, is generally recognised to be the toxic form; however, measurement of Cu^{2+} in natural waters is not possible at present (Turner, 1984), so "total filtrable copper" is used instead. While the use of a wider than desired definition errs on the side of safety and is, therefore, defensible in the area of water quality standards, it can give rise to problems even in this area, and is even more problematical for exposure assessments.

3.2 SELECTION OF SAMPLING LOCATION AND TIMES

Most of the discussion under this heading is concerned with the measurement of the average concentration of the determinand over a given period of time. For the estimation of exposure, the time-averaged value is most often required, so problems associated with estimation of a 95 percentile (i.e., concentrations not exceeded for 95 percent of the time) or maximum value (which are sometimes required for monitoring compliance with a standard) will not be covered.

3.2.1 Sampling Locations

The sampling location is usually clear from the programme objective, as is the case in quality monitoring (IHD-WHO, 1978; Suess, 1982; Hunt and Wilson, 1986). However, in assessing exposure, additional account may have to be taken of known point or diffuse sources of the chemical of interest. Once the locations have been broadly identified, a number of general factors should be noted (HMSO, 1980; Hunt and Wilson, 1986).

First, it is normally recommended that, unless the objectives dictate otherwise, samples should not be taken at the boundaries of a water body (e.g., at the surface or bottom of lakes and rivers or near to the banks), because such samples may be unrepresentative of the main body of water.

Second, there is the difficulty of dealing with incompletely mixed waters. Basically, the waters may be unmixed (e.g., thermal stratification of lakes, the stratification of fresh and salt waters in estuaries) or they may be in the process of mixing (downstream of an effluent discharge to a river, for example), although there is no clear-cut distinction between these cases. In the former situations, it is necessary to sample at several locations and to combine the results with other information on the unmixed waters to derive the values required. When mixing is in progress, it is normally best to find, by exploratory studies, a location where mixing across the section is complete, and to sample there. If such a location cannot be found or used, several samples must be taken and some averaging applied, using other knowledge of the water body, to obtain a representative value.

Particular problems attend the representative sampling of suspended particulate matter in water bodies, and of substances which float on the surface, such as oil. In the case of oil films, it is not meaningful to seek a sample representative of the body of water as a whole; but in the case of suspended matter (and of substances associated with it), two approaches have been identified:

(1) To exploit features of the system (e.g., weirs in rivers) which induce turbulence and hence, a more uniform distribution of suspended matter; and

(2) To use more than one sampling location chosen so that an estimate of the average concentration can be obtained.

In assessing the exposure of consumers to substances in drinking water, other factors need to be considered. A distinction can be made between substances unlikely to change within a distribution system (Type 1) and those likely to change (Type 2) (WHO, 1984). For Type 1 materials, it is sufficient to sample water entering distribution; while for Type 2 materials, sampling at the consumer's tap is necessary. For a new and previously unstudied chemical, sampling at the tap is obviously most sensible. The selection of taps for sampling is not straightforward; if systematic variations are not suspected then random sampling should be employed; however, if systematic effects are expected they should be taken into account in designing the sampling programme (Hunt and Wilson, 1986).

For Type 2 materials, the timing and manner of sample collection can be critically important because the concentrations will depend on the residence time of the water in the distribution and/or plumbing systems. One practical example concerns lead in domestic plumbing (WHO, 1984; Hunt and Wilson, 1986). Samples taken after overnight stagnation give high lead concentrations, whereas samples taken after prolonged flushing give low values. Neither is a good measure of exposure, and in this case random daytime sampling probably gives the best value.

3.2.2 Sampling Times

Continuous monitoring obviously provides the ideal way of coping with temporal variations in concentration, but it is not technically possible for most determinands of interest. Transient high concentrations of chemicals may be important in determining environmental effects; however, it is difficult to design sampling programmes to catch such transients unless they can be associated with some other readily identifiable event—for example, discharge of a given effluent. When estimates of average concentrations are required, account has to be taken of possible random and systematic changes in concentration with time.

In cases where random fluctuations in concentration occur, the variations often follow normal or log-normal distributions, though other forms may also occur (Ellis and Lacey, 1980). For normally-distributed fluctuations, the time of sampling is relatively unimportant and the number of samples required is determined by the required confidence limit of the mean and by the magnitude of the random variations (Ellis and Lacey, 1980; Hunt and Wilson, 1986). When systematic variations occur, the sampling frequency chosen should not be an exact multiple of the frequency of any cyclic systematic variation; otherwise, the mean will be biased.

If a measure other than the mean is required, for example a 95th percentile, the number of samples required is much higher to provide an equivalent measure of confidence. Some of the statistical considerations

have recently been summarised (Ellis and Miller, 1984) though not in relation to exposure assessment.

3.3 REQUIRED ACCURACY OF ANALYTICAL RESULTS

The accuracy required of individual analytical results is an important issue which should be discussed with analysts and data users at an early stage of project planning.* It is determined by the tolerable inaccuracy of the numerical results of the overall programme, and by the nature of the sampling programme and by the magnitude of natural variations in concentration. Lack of prior knowledge of the latter may preclude precise estimation of ideal requirements, but this should not discourage the appraisal of needs and a clear statement of requirements, so that suitable analytical systems can be selected. More stringent requirements mean greater cost, and needlessly stringent requirements must, therefore, be avoided; however, results of inadequate accuracy may render the entire programme valueless.

The required accuracy should be stated in the following way (Hunt and Wilson, 1986): "the total error should not exceed c in concentration units or p percent of the concentration whichever is greater." It is often convenient to set c to the lowest concentration of interest and p to 20.

3.4 SAMPLING METHODS

The practical and logistical problems of sampling are well covered in several tests (see for example IHD-WHO, 1978; Suess, 1982; Hunt and Wilson, 1986), and discussions are not repeated here.

4 SAMPLE TREATMENT AND STORAGE

If immediate analysis of the sample is not possible—and it seldom is, except for some rather simple determinands—sample storage and transport will have to be planned. During storage and transport, it is necessary to protect the sample against three possible changes:

(1) Material being lost from the sample (e.g., by adsorption or volatilisation);

(2) Material being added to the sample (contamination); and

(3) Material changing its character within the sample (chemical or biological reactions).

Detailed discussion of these problems is provided by Hunt and Wilson (1986), and several other publications also detail recommended containers and storage conditions (APHA, 1980; HMSO; 1980; Suess; 1982; USEPA,

* Analysts and statisticians should both be involved, together with representatives of any other relevant disciplines, at the beginning of programme planning.

1982). The recommendations tend to relate to three areas: precautions prior to sampling, precautions during or immediately following sampling, and precautions during transport and storage. Essential details are noted below; for more complete information the reader is referred to the four references noted above.

4.1 PRIOR TO SAMPLING

Selection of sample containers and stoppers can be critical. Bottle caps must fit tightly, and the bottles have to be well-cleaned and stoppered before they leave the laboratory. Glass bottles are usually preferred for organic determinands, and polyethylene or PTFE for inorganics. The choice of sampling equipment and preservation agents also needs careful consideration, and tests may be necessary to ensure that these are not a source of contamination.

4.2 POST SAMPLING

If sample filtration is to be undertaken, it is best performed immediately following sampling to avoid redistribution of determinand between solution and particulate phases. In practice, however, this is sometimes impossible, because of problems with contamination, in which case filtration should be undertaken as soon as practically possible after sample collection. Sample preservation is often required (e.g., the addition of acid to control heavy metal adsorption and the addition of biocide to hinder biodegradation of organics). Sample bottles should normally be completely filled to restrict oxygen access and to prevent re-distribution of contaminants between the liquid and vapor phase within the bottles.

4.3 TRANSPORT AND STORAGE

The chances of chemical or biological changes occurring need to be minimised by storing the samples in the dark or at least out of direct sunlight, and preferably refrigerated. Care should be taken during transit to avoid contamination; oil and petroleum hydrocarbons and heavy metal contamination are all real risks.

Upon receipt in the laboratory, recording of the sample should occur, and the sample should be stored in a dark refrigerator until required for analysis. If the determinand is well known, there should already be some information on sample stability; otherwise some tests may need to be undertaken to determine how long the sample can be stored without deterioration.

The sample containers should, of course, be clearly labelled. Field blanks are essential to provide a check on sample contamination prior to analysis.

5 PROCESSING OF SAMPLES FOR ANALYSIS

5.1 SUB-SAMPLING

This is a straightforward matter except when particulate material is present or when adsorption of the chemical on the container walls has occurred. In the former case representative sub-samples are not easily obtained: at the very least, vigorous shaking is necessary, and some check on sub-sampling bias may be required. In the latter case, sub-sampling is not really possible, and the best solution is to avoid adsorption in the first place by appropriate choice of sample container or by the addition of a preservative reagent. However, if adsorption has occurred or is suspected the whole sample should be used, and the container should be rinsed out with an appropriate solvent to remove adsorbed chemical.

5.2 COMPOSITING

To obtain a reasonable measure of the mean, it may be necessary to take many different samples at different times and locations. This can cause considerable analytical problems, particularly when the samples should be analyzed as soon as possible after collection. One way of dealing with this is to combine the samples and to determine the mean from the composite. The precautions and limitations of this approach are detailed elsewhere (HMSO, 1980; Hunt and Wilson, 1986).

5.3 EXTRACTION/CONCENTRATION/CLEAN-UP

The necessity for, and choice of, appropriate methods for these operations depend critically on the nature of the sample and the determinand. Decisions made at this stage are crucial to the precise specification of chemical species involved in the exposure. For example, if an acid digestion is employed for determination of a heavy metal, many different (but possibly not all) chemical forms of the metal in the sample will be converted into a single form. In general, not enough is known about the effect of the extraction and concentration steps on the species of chemical measured. For many well-known chemicals, there are standard methods of analysis which include descriptions of sample preservation and handling procedures, but for novel compounds new procedures have to be developed and validated.

For organic chemicals, extraction is usually accomplished by one of the following techniques:

(1) Extraction into an organic solvent that is not miscible with water, sometimes after pH adjustment of the sample;

(2) Evaporation of the water by vacuum evaporation or freeze drying, and extraction of the residue with organic solvent;

(3) Adsorption of organics from the sample onto a resin or other

adsorbent and subsequent desorption into an organic solvent; and

(4) Gas stripping, with adsorption of volatiles and subsequent extraction with organic solvent or direct headspace sampling.

With the exception of direct headspace sampling, which allows direct analysis, usually by gas chromatography, the other options all produce a final extract in organic solvent. This can be concentrated by controlled evaporation of organic solvent using standard procedures. Further clean-up of samples is not usually required for water samples.

Many inorganic determinands are analyzed directly without sample processing. For trace inorganics, concentration using ion exchange resins or complexing agents and solvent extraction are sometimes employed; however, these techniques are usually applied after the sample has been digested with acid or given some other treatment to convert all the species in the sample into a single form. This processing contrasts strongly with the procedures for organics, where individual species are separated and determined. One common exception for inorganics is organometals, which are often processed and determined as distinct species.

As in other areas of investigation designed to assess average concentrations, a key problem in exposure assessment can be how to deal with analytical results below the detection limit. There is no scientific or mathematical solution to this problem and obviously the best strategy is to minimise it by choosing an analytical system with a limit of detection lower than the concentration in the great majority of samples. Sample concentration is an obvious way of improving the detection limit; clearly such an approach also increases the risk of introducing bias from contamination and interferences.

6 ANALYSIS

6.1 INORGANICS

A wide range of analytical techniques are applied to the determination of inorganic substances in water, suspended matter, and sediment (Hunt and Wilson, 1986). Some of the more widely used techniques applicable to trace element exposure assessments, and some more recent developments, are presented below.

Atomic absorption spectrometry (AAS) is probably the most widely-used technique for such determinands. The conventional flame mode is often applicable, but increasing use is made of the superior detection power of cold-vapor AAS (for mercury), hydride-generation AAS (for metalloids, such as arsenic and selenium), and graphite furnace AAS (for a wide range of trace elements). The flame technique is relatively free from serious interferences, but this is not so for the other methods. The flame and graphite furnace techniques have widely different limits of detection but both respond similarly to different dissolved forms. In contrast, the hydride

and cold vapor techniques are more sensitive with respect to the form of the element, and this selectivity is exploited in speciation measurements. Direct application of AAS to saline waters is not normally possible, whereas anodic stripping voltammetry (ASV) has been used for the direct analysis of sea and estuary waters, for the determination of such elements as Cd, Cu, Pb and Zn.

Inductively-coupled plasma optical emission spectrometry (ICPOES) is a useful technique for the simultaneous determination of large numbers of elements in fresh waters, although its detection power is very poor for Hg and the 'hydride' elements (As, Se, Sb). However, cold-vapor and hydride-generation techniques may be applied to improve detection limits.

Recently, inductively-coupled plasma mass spectrometry (ICPMS) has become commercially available. It shows promise for water analysis, with rapid, near-simultaneous multi-element capability and very low detection limits rivalling those of graphite furnace AAS. The prospect of directly coupled HPLC-ICPMS is an intriguing development for studying trace element speciation.

6.2 ORGANICS

Two widely employed separation techniques for organics include high pressure (or performance) liquid chromatography (HPLC) and gas chromatography (GC). These techniques are largely complementary and cover most chemicals of interest in water analysis, although other techniques such as TLC are used on occasions (see, for example, Hunt and Wilson, 1986). With the advent of capillary GC and microbore HPLC columns, it seems that adequate resolving power is currently available for most analyses; deficiencies usually relate to the mode of detection: can it detect low enough concentrations and can the molecules be identified?

Mass spectrometry (MS) is an extremely valuable detection method and the development of directly coupled capillary GC-MS has been of critical importance in the field of water analysis. Several HPLC-MS interfaces are currently available and in use, although this hybrid technique has yet to make the same impact on water analysis as GC-MS. More selective detection for HPLC can be achieved using off-line HPLC-MS (Crathorne *et al.*, 1984); however, its application is laborious and expensive. Electrochemical detection for HPLC also provides improved selectivity over the more conventional spectrophotometric detectors. One significant problem with organic environmental analysis is the desire to measure concentrations of mixtures of chemicals (e.g., polycyclicaromatic hydrocarbons and polychlorobiphenyls each of which is frequently cited in environmental regulations and is a complex mixture of many chemicals and isomers). Some insight into these problems is provided by Alford-Stevens (1987) who discusses the problems of defining a limit of detection; similar problems occur with

quantification and comparison of results from different laboratories and studies.

The more routine use of supercritical fluid chromatography-MS (for example, Kalinoski *et al.*, 1987) and triple-quad MS-MS (Betowski *et al.*, 1987) can be expected to both extend the range of organic chemicals that can be studied and to increase the specificity of the analyses. It also seems likely that immunoassays will be used more widely (Vanderlaan *et al.*, 1988).

6.3 ANALYTICAL QUALITY CONTROL

It is now widely recognised that reliance on standard methods of analysis is not sufficient to ensure adequate accuracy and comparability of results. It is also necessary to ensure that the methods are applied correctly. That is as important for exposure assessments as for compliance monitoring. The approach known as Analytical Quality Control (AQC) (Wilson, 1979; Hunt and Wilson, 1986) meets this need. It has been widely applied to water analyses of different types (see Analytical Quality Control (Harmonised Monitoring) Committee 1983, 1984 and Gardner *et al.*, 1986) and has been adopted by WHO for the Global Environmental Monitoring Scheme.

7 PRESENTATION OF RESULTS OF EXPOSURE ASSESSMENT

Much of this subject lies outside the scope of this paper; yet one aspect that deserves mention is the units used to describe findings. It has become convention to use mass, mass per unit volume, or mass per unit mass in reporting environmental concentrations and exposure or dose levels, and in discussing toxicological or environmental effects. It may be too late to attempt to change this widespread practice; however, it is worth pointing out that for well-characterised chemicals, molar units, not mass units, are the logical and sensible units to employ.

Toxicants have effects which depend on the number of molecules of toxicant, not on the mass of toxicant. This distinction assumes particular importance when effects of different chemicals are being compared—as, for example, in structure/activity analysis; it is also important in making decisions about which chemicals to select for study when an arbitrary concentration of, say, 1 $\mu g\ l^{-1}$ may be selected. While we do not wish to condone such arbitrary values, it should be recognised that 1 $\mu g\ l^{-1}$ may represent 10 to 100 times more of one chemical than another. A similar argument applies when analytical detection limits are being compared. In our view, it is only appropriate to use mass per unit volume statements of concentration when either the quantification in the analysis is approximate, based possibly on analytical standards of other chemicals, or where the sample processing or

the analytical procedure is such that the forms of chemical in the sample cannot be determined, as in the case, for example, of the oxidation of organic compounds to measure the TOC (total organic carbon). Where standards of the determinand have been used and the determinand is well characterised, molar concentration units should be used to provide a more rational and logical use and comparison of environmental data for chemicals.

8 CONCLUSIONS

The problems involved with the design and implementation of a programme of water sampling and analysis to assess the exposure of an organism or group of organisms are similar to those involved in water quality monitoring exercises. Once the objective of the exposure study is clearly stated, many of the techniques already developed and widely used for sampling, sample storage, processing and analysis can be deployed to conduct the study. The major current problem concerning inorganic determinands is the identification and subsequent measurement of the most relevant (bioavailable) species of the element of concern. For organic determinands, a similar problem exists at least as far as aquatic biota are concerned. For example, in assessing the exposure of fish in rivers, what importance should be attached to sediment-bound chemicals? In addition, a further problem with organics is frequently the absence of a reliable analytical method likely to provide a sufficiently low detection limit.

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