ECETOC

Technical Report No. 76

Monitoring and Modelling of Industrial Organic Chemicals, with Particular Reference to Aquatic Risk Assessment

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CONTENTS

SUMMARY

Monitoring and laboratory data have integral roles alongside fate and exposure models in comprehensive risk assessments. The principle in the EU Technical Guidance Documents (EU TGD) for Risk Assessment is that measured data may take precedence over model results but only after they are judged to be of adequate reliability and to be representative of the particular environmental compartments to which they are applied. In practice, laboratory and field data are used to provide parameters for the models, while monitoring data are used to validate models' predictions. Discrepancies between the results of models and monitoring should be investigated in terms of the representativeness of both. Thus, comprehensive risk assessments require the integration of laboratory and monitoring data with the model predictions. However, this interplay is often overlooked. Certainly in the context of the EU risk assessment of existing chemicals, the specific requirements for monitoring data have not been adequately addressed.

Worst-case assumptions in the exposure scenarios and exposure models have led to the belief that monitoring data are unreliable and/or only represent the best case and therefore cannot be representative. There is thus a need to position monitoring data in the context of risk assessment, and specifically 1/ to define and position worst-case and reasonable-worst-case scenarios in a probabilistic exposure and risk assessment; 2/ to recommend a monitoring strategy for collecting new data suitable for use in risk assessment; and 3/ to determine criteria for the acceptability for risk assessment of existing data from typical environmental compartments.

■   It is not a foregone conclusion that PECs based upon measured concentrations will take precedence. It must be clearly demonstrated that the monitoring data are representative of the intended scale, setting, scenario, life stage, etc. If this is the case, the monitoring data may be used to derive environmental concentrations, to validate the exposure model and/or be used for improvement in default emission assumptions.

■   By using monitoring and laboratory data to calibrate fate and exposure models for a particular chemical and environmental compartment, and monitoring data to verify and validate these models, greater confidence can be placed in the resulting risk assessment and conclusions based on it.

■   Whenever possible, existing monitoring data should be used for environmental risk assessment and model validation. However, it is essential that the data set contains appropriate information and is shown to be fit for purpose.

■   There is no one way to do 'good' monitoring. For example, spatial distribution and sampling frequency are key to the quality of a dataset, but the criteria by which these attributes are judged will depend directly on the objectives of the monitoring programme.

■ Monitoring programmes should be designed to meet the specific objectives of the study e.g. assessment of water quality, PEC_{local} or $PEC_{regional}$, either targeted or comprehensive exposure and risk assessment. The monitoring site or sites should be selected accordingly.

■ Monitoring data can be used in a straightforward manner to carry out site-specific or local risk assessment, provided that sufficient information on the chemical and the environment, the release history of the chemical with respect to the monitoring site, and the analytical methods used to determine the concentrations is available.

■ The use of monitoring data for regional risk assessment will be a possibility in the future, when the data necessary to relate the characteristics of a monitoring site to the distribution of site characteristics for the rest of Europe have been identified, collected, accepted and released for general use. These data may include distance from and concentration at release, and environmental characteristics determining residence time of the chemical in that environment.

In addition:

■ An approach should be developed to harmonise monitoring programmes across Europe and ensure appropriate data logging and data access. Ideas of how to harmonise monitoring and incorporate the wealth of data that exists into a database should be investigated.

■ Guidelines should be developed and agreed to ensure ready availability and transparent access of data via standardised procedures. A dedicated data centre whose role is to co-ordinate data acquisition and dissemination may be a cost-effective way of achieving this goal.

■ For future programmes, it is recommended that representative areas and sites be developed to depict specific scenarios for river basins as part of the Proposed Framework for Community Action in the Field of Water Quality. Representative regions should also be developed, and used to define local and regional scenarios for the assessment of substances under the Technical Guidance Documents on Risk Assessment.

This report is not intended to be a comprehensive guide on how to carry out specific monitoring programmes. The general principles and recommendations that should be adopted when planning a monitoring exercise are:

■ use clearly-defined monitoring objectives to determine the sampling strategy which, in turn, should promote an efficient, relevant and cost-effective programme;

■ involve all interested parties from the early planning stages to optimise knowledge and resources and maximise acceptance and communication of the study findings;

■ field trips to select thoroughly- 'characterised' sites;

■ a preliminary study to confirm suitability of sites and applicability/feasibility of analytical methodology;

■ once a site is identified which is consistent with the goals of the monitoring programme, a relevant sampling protocol needs to be developed;

■ both the choice of the site(s) and the monitoring data must be associated with a particular scenario in order to be of use in establishing the realistic risk scenario, the 'reasonable worst case' or 'representative or realistic case';

■ use validated sample preservation, quality assurance and control procedures;

■ organise an appropriate supporting programme so that the results may be placed in context;

■ audit the programme regularly and modify if and as necessary;

■ develop an effectively planned and implemented reporting procedure to deliver the information gathered to all parties interested in the scenario;

■ the ultimate goal of monitoring is to provide information to meet well-defined objectives. The reliability of the information must be checked in the light of these objectives;

■ monitoring results should be summarised in order to draw conclusions about, for instance, the real concentration or the representativeness of the reported numerical values of the total group of samples.

1. INTRODUCTION

Risk represents the likelihood that a hazard will be realised - i.e. that due to exposure an adverse effect may occur in some 'receptor'. Risk assessment is the process that evaluates the likelihood that adverse ecological or human health effects may occur, are occurring, or have occurred as a result of exposure to one or more physical, chemical, or biological agents.

Fundamental to the definition of risk assessment is the recognition that risk requires two elements:

■   the inherent ability of a chemical or material to cause adverse effects;

■   the exposure or interaction of the chemical or material with an ecological component, or with a human population, at sufficient intensity and duration to elicit the adverse effect(s).

The risk assessment process can be a step-wise process in which assessment of potential adverse effects and exposure is integrated and compared with increasing realism. The ratio of the Predicted Environmental Concentration (PEC) to the Predicted No Effect Concentration (PNEC) is used as a measure of this risk.

The assessment of risk can require an in-depth assessment of the intrinsic physico-chemical properties, biodegradability, bioaccumulation potential and toxicity or potential effects of the chemical. In addition, a thorough assessment of the release pathway, environmental fate and distribution of the chemical is required based on exposure measurements and/or mathematical models. In environmental exposure assessment the concentration of a substance in the different environmental compartments is estimated from the amount of the substance released in the production and formulation processes, the use and disposal patterns and the releases resulting from them, the physico-chemical properties of the substance and the properties of the environmental compartments into which the substance is released. The PEC can therefore be calculated from a knowledge of the quantity of the substance that will enter the environment and the distribution and degradation processes occurring in the environment using generic, representative model environments specified in the Technical Guidance Documents (EEC, 1996a,b) for Risk Assessment of New and Existing Chemicals.

An alternative to such calculations is measuring (monitoring) the concentrations in the relevant environmental compartments according to a pre-planned sampling strategy. This is only possible for substances which are released in quantities large enough to be detectable by appropriate analytical methods after dilution in the environment. In those cases where reliable high quality monitoring data are available - with proper statistical and temporal evaluation and adequate spatial representation - they should take precedence over the predicted PECs.

Worst-case assumptions in the exposure scenarios and exposure models have led to the belief that monitoring data may be unreliable and/or only represent the best case and therefore cannot be representative. There is therefore a need to position monitoring data in the context of risk assessment and specifically:

■ to position worst-case and reasonable worst-case risk assessment scenarios in a probablistic risk assessment context;

■ to recommend a monitoring strategy for collecting new data which is suitable for risk assessment;

■ to determine criteria for the acceptability of data already existing in the different environmental compartments for risk assessment purposes.

The overall environmental risk assessment process, data, assumptions and models have been reviewed in detail in several ECETOC reports and documents. Monitoring and modelling are integral parts of risk assessment. The principle in the EU TGD for Risk Assessment (EEC, 1996c) is that measured data may take precedence over model results but only after they are judged of adequate reliability and to be representative of the particular PEC to which they are applied. In practice, laboratory and field data are used to provide parameters for the models, monitoring data are used to validate predicted environmental concentrations and modelling predictions to verify quality and representativeness of monitoring data. Thus, comprehensive risk assessments require the integration of laboratory and monitoring data with the model predictions. However, so far this interplay has not been addressed nor have the specific requirements that one should put on monitoring data.

Unfortunately, because of the structure of European legislation controlling the use and emission of substances, the concept of the PEC is taken in isolation for a given substance and extrapolated to represent the actual 'state of the environment'. Whereas in practice, all physical, chemical, biological and ecological factors should be considered, the risk assessment approach of substances currently only demands the quantification of exposure of the specific substance under consideration. This is unfortunate because, at the local scale, the risk management strategies adopted by companies and local regulators may be extremely useful in quantifying overall risk and potential deleterious effects to local environments. Local and regional ecological monitoring or physical surveys to quantify mixing and dilution characteristics can be extremely useful to help quantify local impact of discharges, and much of this type of work is undertaken routinely in various catchments around the EU.

There is a need to define better the terms *observation, monitoring and surveillance* as used in the TGD since the difference between them is unclear, and to develop guidance on the relationships between generic steady-state model predictions and specific monitoring data. In addition, guidance on monitoring strategies (e.g. sampling, analysis techniques, etc.) needs to be developed for validation of the exposure models and/or for checking if the risk management is working. In addition, monitoring

may not necessarily need to be restricted to absolute measurement of specific substances but could possibly be extended by measurement of certain parameters that can help to refine the risk assessment, for example dispersive or diluting factors.

This has been recognised by the EU and EU member states, and has been discussed with OECD. ECETOC was asked to contribute to a workshop on the subject organised by OECD.

A Task Force was therefore established with the following Terms of Reference:

■   define the terms *observation, monitoring* and *surveillance* as used in the EU Risk Assessment Technical Guidance Document and evaluate how these relate to the risk assessment of substances;

■   evaluate environmental settings adopted by the EU Risk Assessment Scheme and develop guidance on the relationship between monitoring data variable in time and space and the predictions of exposure models;

■   develop guidelines for monitoring strategies resulting in the generation of representative high quality data for use in risk assessment and to establish that any risk management is working;

■   seek collaboration with OECD and other stakeholders for the development of a transparent and consistent guidance document on the use of (existing) data within the risk assessment framework.

2. LEGISLATIVE SETTING AND DEFINITIONS

2.1 LEGISLATIVE BACKGROUND

Since October 31, 1993 all notification of new chemicals to the EU authorities must comply with the 7th. Amendment Directive (92/32/EEC) of the Dangerous Substances 67/548/EEC. This implies that competent authorities are required to conduct a risk assessment for man and the environment for the chemical being notified.   The Commission Directive on Risk Assessment of New Chemicals (93/67/EEC) came into force on October 31st 1993, the same day as the implementation of the 7th Amendment of the Directive.

Similarly, the Existing Substances Council Regulation (793/93/EEC) requires that a risk assessment be carried out according to the principles described in the Commission Regulation on Risk Assessment of Existing Substances (1488/94/EEC). Regulation 793/93/EEC requires that dossiers be submitted on all existing substances listed in EINECS (about 100,000 chemicals). All data pertaining to the ecotoxicological, toxicological and physico-chemical properties of the substance (Harmonised Electronic Data Set - HEDSET) will be included in the International Uniform Chemical Information Database (IUCLID) developed by the European Commission.

In accordance with Regulation 793/93/EEC, the Phase I and Phase II of the HEDSETs for about 2500 high tonnage "existing substances" (those appearing in EINECS and produced or imported at > 1000 tpa) were completed by industry in summer 1995 following two official deadlines (June 4, 1994 and June 5, 1995). These data sets are stored in IUCLID which is located at the European Chemicals Bureau (ECB) Ispra, Italy and are accessible by all regulatory authorities in the EU. A CD-ROM version of all compiled HEDSETs was made available in May 1996 to industry, consumer groups etc. This version contains the submitter's name and all the physico-chemical, ecotoxicity and toxicity data on all submitted chemicals but the agreed confidential data were omitted (e.g. tonnage per manufacturer). The final HEDSET submissions - Phase III - required on all other chemicals which are produced or imported at > 10 tpa were completed by industry by June 4, 1998.

Using IUCLID, the EU and Member States will draw up priority lists of about 50 chemicals/year for risk assessment by the regulatory authorities.   In principle, the submitted data will be used to rank the substances according to their relative risk based on an automated Informal Priority Setting method (IPS model). Prioritised substances will then be evaluated and assessed according to the principles laid down in the 793/93/EEC.

The details of the risk assessment have been captured in the TGD which is intended to provide harmonised guidance to all Member State authorities on the procedures for conducting acceptable risk assessments for man and the environment. The TGD is not legally binding but the intention and

expectation is that European regulators charged with conducting a risk assessment will use these documents for developing their conclusions concerning the potential risks of a chemical.

Since the introduction of risk assessment legislation in the EU, separate guidance documents have been prepared for the evaluation of both New and Existing Chemicals (1993 and 1994, respectively). Because the Risk Assessment Directive of New Substances and Risk Assessment Regulation of Existing Substances were supported by a number of different technical guidance packages which resulted in different risk assessment conclusions, and possibly could lead to different risk management strategies, the Commission agreed to develop a uniform guidance package. This package was finally published in 1996 with the supporting risk assessment computer model EUSES (European Uniform System for Evaluating Substances).

2.2 DEFINITIONS

Monitoring is defined in Chambers English dictionary as:

1.   checking and sometimes adjusting for quality or fidelity,

2.   watching, observing or checking, especially for a special purpose,

3.   keeping track of, regulating, or controlling (as a process for the operation of a machine).

Note that both (1) and (3) involve adjustment, regulation, or control, which fit well with the various types of monitoring information.

Monitoring is long-term, standardised measurement, evaluation, and reporting of specified properties of the environment, in order to define the current state of the environment, and to establish environmental trends. Surveys and surveillance are both used to achieve this objective.

In the TGD, different terms are often used, and some clarification may be needed. The TF recommends the following definitions.

Observation is the practice of seeing and noting;

A *survey* is a sampling programme of finite duration, and for a specific purpose;

Surveillance is a more continuous, specific measurement or observation over an extended period with the goal of measuring status or trends in some aspect of environmental quality;

Environmental monitoring is most often defined as a long-term and standardised measurement, observation, evaluation and reporting of the environment in order to define status and trends.

3. MODELLING OF EXPOSURE IN THE CONTEXT OF THE TGD

3.1 MODELLING OF EXPOSURE

Models that predict the physical/chemical behaviour of chemicals and the fate of chemicals in the environment are used as a part of risk assessment. These models are, however, only a mathematical approximation of the processes that effect the environmental fate of the chemical, and can never be a 100% accurate representation of the chemical's fate in the "real" world. At the screening level of the assessment, the environmental heterogeneity and temporal dynamics found in the "real" world have been substituted by a fixed generic environment, which is used in the prediction of a steady state PEC_{local} and $PEC_{regional}$.

3.2 EU TECHNICAL GUIDANCE DOCUMENTS: RELATIONSHIP BETWEEN PEC_{local} AND $PEC_{regional}$

In environmental exposure assessment the estimation of the concentration of a substance in the different environmental compartments is based on the physico-chemical properties of the substance, the production and emission processes, the use and disposal patterns and the properties of the environmental compartments. The PEC can therefore be calculated based on knowledge of the quantity of the substance that will enter the environment and the distribution and degradation processes occurring in the environment, using generic, representative model environments.

In the release estimation of substances a difference is usually made between chemicals that are emitted through point sources, to which one (or more) specific location(s) can be assigned, and chemicals that enter the environment through diffuse release. This differentiation in release scenario has implications for the calculation of the predicted environmental concentration of a substance in the sense that two spatial scales must be distinguished: a local scale and a regional scale, to which PEC_{local} and $PEC_{regional}$ are allocated.

PEC_{local}

The concentration of chemicals emanating from point sources is normally assessed in a so-called generic local model. In these local models a hypothetical site is defined with average standard conditions. The scale is usually small and the targets (man and species in the ecosystem) are assumed to be exposed in or at the border of the model area. In general, yearly average concentrations or steady-state concentrations are calculated although in some cases time-related concentrations may be obtained, for instance in situations where intermittent releases pertain. In principle, degradation and distribution processes are taken into account in the calculation of PEC_{local}.

However, because of the relatively small spatial scale, the ultimate concentration in a compartment is typically governed by only one or two key processes. Models to calculate the PEC_{local} are available for air, water and soil.

The PEC_{local} for air is used in two different ways:

■   as input for the calculation of the intake of chemicals through inhalation in the assessment of indirect exposure of man through the environment;

■   as input for the calculation of PEC_{local} in soil.

Another input to PEC_{local} in soil is obtained from chemicals contained in sewage sludge which is then applied to agricultural land. The concentration of a chemical in any sewage sludge is determined by the rate and extent of its biodegradation and the partitioning behaviour of the chemical in the wastewater treatment plant (WWTP).

Following discharge into surface water, substances contained in the effluent are subject to further partitioning between aqueous phase, suspended matter and sediment. Concentrations in ground-water are estimated from the concentrations calculated in soil porewater, which has, in turn, been derived from the chemical concentration in applied sewage sludge. Pathways other than those described, like the release to air, surface water and soil from waste disposal sites or release from air to surface waters, could also be of relevance in the risk assessment process. No guidance for taking these pathways into account is available at this time.

The model incorporated in the TGD assumes that the concentration in the surface water ($PEC_{local,water}$) is in principle calculated at 1000 m from the point at which the effluent enters the receiving water. At this distance, the system is assumed to be completely mixed. Degradation in surface water, volatilisation from the water body and sedimentation may occur in practice within the mixing zone, *but are at present neglected in the model*. Sorption to suspended particles is taken into account. The resulting concentration of the dissolved chemical is used for comparison with $PNEC_{water}$. It should be noted here that at present only dilution (by assuming a standard dilution factor of 10) and sorption (by correcting for the fraction of the chemical that is adsorbed to suspended matter) are taken into account. Thus the 1000 m distance is of little relevance in the model. However, consideration of other fate processes as part of a higher tier refinement of the risk assessment process will make the distance parameter relevant because of the time or distance dependencies of these processes.

$PEC_{regional}$

In addition to PEC_{local}, a $PEC_{regional}$ is calculated using a generic regional model. This model is designed to describe the diffusive and/or multiple point continuous release of substances into a larger

region taking into account the further distribution and fate of the chemical upon release.   A second purpose of a regional model is the calculation of a 'background concentration'. As with the local models, a standard environment with average characteristics is defined. Typically, box models are applied in which water, sediment, soil, air, biota and suspended matter are distinguished as separate compartments. The outcome of a regional model is a set of steady-state concentrations of the chemical in all relevant environmental compartments.

The regional standard environment is assumed to be highly industrialised, relatively small but densely populated. The size is 200 x 200 km with 20 million inhabitants. This corresponds to a population density of 500 inhabitants per sq km compared with a European average of 1.3 inhabitants per sq km. It is also assumed that 10% of the European production takes place within this area.

Relationship between different model scales

Since advection, defined as inflow from outside the model or outflow from the model environment, can be very important for the outcome of both regional and local model calculations, the concentration of a chemical at the "border" of the region must be taken into account. This will be defined as the background concentration of a chemical. The background concentrations in a local model are then taken as the concentration calculated by the regional model. For chemicals with many relatively small-point sources these background concentrations may add considerably to the concentration emerging from one local source.

The background concentration in the regional model has to be calculated using a similar box model of a larger scale, i.e. with the size of the European continent. In this continental model, however, there is assumed to be no inflow or outflow across the boundaries. Furthermore it is assumed that all chemical releases enter this continental environment. The resulting steady-state concentrations are then used as trans-boundary or background concentrations in the regional model.

PEC_{local} and $PEC_{regional}$ as defined in the TGDs are not directly related to data which can be obtained from a monitoring exercise. The TGDs suggest that the 90th percentile of concentration data obtained from a local site (air, water, or soil) be considered as a reasonable worst case approximation to PEC_{local}, but that full justification should be given for any monitoring data suggested to be representative of $PEC_{regional}$.

3.3 INTERPLAY BETWEEN MODELS AND DATA

To provide a more accurate exposure assessment, there needs to be a fundamental interplay between modelling, monitoring and laboratory data. This interplay includes the use of monitoring and laboratory data to parameterise and validate the models for the chemical and environment of interest.

Laboratory and field data are frequently used to provide parameters that are necessary to run fate models and develop structure/activity relationship models (QSARs) that can predict various physical/chemical parameters. QSAR models have been successfully used for non-polar, relatively hydrophobic compounds such as hydrocarbons. However, these models should be carefully evaluated before use for surfactants, ionisable compounds or polymers, since they may have a high degree of uncertainty (ECETOC, 1998). Experimentally derived data are the most reliable source of the physical/chemical parameters for these chemicals. There are many examples of the use of laboratory data to parameterise fate models. For example, Holysh *et al* (1986) used laboratory and field data to parameterise Mackay models (Mackay, 1991) for the surfactant linear alkylbenzene sulphonate (LAS). Laboratory data on a chemical's volatility, biodegradation, and sorption are needed to parameterise wastewater treatment plant models (e.g., Cowan *et al*, 1992). Dilution factors calculated from river and sewage flows are used in models to calculate the distribution of sewered chemicals in the surface waters near Dutch and U.S. wastewater treatment plants (Versteeg *et al*, 1992; Rapaport,1988; Lahlou *et al,* 1996). Many other examples are described in the literature, and also describe the interplay for more complex dynamic flow or chemical load models. Examples of the latter are TOXIWASP (Ambrose *et al,* 1983; Kuo and Hu, 1989), SeauS (Bildstein and Vancon, 1994) and EXDISP (Bruggemann *et al,* 1991).

Models are typically developed for specific chemicals, classes of chemicals or environments. They embody the current understanding of the chemical and the environmental compartment of interest. To ensure accurate predictions, the model results need to be validated by comparing them to monitoring and laboratory data. Each time the model predictions are validated with monitoring and/or laboratory data, confidence in the predictions increases for the environment and class of chemicals considered. This does not mean that the model yields accurate or even reasonably accurate predictions for all environments or all chemical classes unless the validation process has included a wide range of environments and classes of chemicals.

For example, the fate of 'down the drain' chemicals for risk assessments is often predicted by the use of wastewater treatment plant models. Processes that can affect the chemical's fate in these plants are biodegradation, volatilisation and sorption. The relative importance of these processes is affected by the chemical properties of the material of interest. Typically, these models have been validated for a limited set of chemicals only and with limited data - for example, volatile organic compounds, (Card

and Corsi 1992; Namkung and Rittman 1987; Struijs *et al*, 1991), non-polar organic compounds (Clark, 1986) or surfactants (Birch, 1991; Cowan *et al*, 1992). None has been shown to be valid for organic compounds in general. Thus, their application to organic compounds beyond those for which they are validated could lead to inaccurate predictions and inappropriate conclusions from the risk assessment. A validation of these models has just recently been published for LAS (Feijtel *et al*, 1996), and a project is in progress at the University of Wageningen to verify their validity for other substance classes.

Other examples of the use of monitoring and laboratory data to validate models, and use of validated models to provide insights into the important environmental processes are presented in Caprara and Rapaport (1991), Fendinger *et al* (1992), Hennes and Rapaport (1989), Versteeg *et al* (1992) for river models, and Lung *et al* (1990) for estuaries. In each of these cases, the results of the models were compared to monitoring data at specific sites for either anionic surfactants, or a cationic surfactant, di-hardened-tallow-dimethylammonium chloride. These studies identified the fundamental need to include in-stream removal in the models. This is now being tackled with the development of a Geography-referenced Regional Exposure Assessment Tool for European Rivers (GREAT-ER). The objective of the GREAT-ER project is to develop and validate a powerful and accurate aquatic chemical exposure prediction tool for use within the EU environmental risk assessment schemes (Feijtel *et al*, 1997). A new database, model and software system is being developed to calculate the distribution of PECs - both in space and time - of household chemicals in European surface waters, on a river and catchment area level. The system uses a Geographical Information Systems (GIS) for data storage and visualisation, combined with simple mathematical models for prediction of chemical fate. Hydrological databases and models are used to determine flow and dilution data. This refined exposure assessment tool should greatly enhance the accuracy of current local and regional exposure estimation methods. The new exposure assessment methodology will integrate specific environmental information into a geographically-referenced framework, ultimately on a pan-European scale. This research project is carried out on behalf of ECETOC, and sponsored by the Environmental Risk Assessment Steering Committee (ERASM) of the Association Internationale de la Savonnerie, de la Détergence et des Produits d'Entretien (A.I.S.E.) and the Comité Européen de Agents de Surface et Intermédiares Organiques (CESIO) in co-operation with the UK Environment Agency.

Once models have been validated for the class of chemical and specific environment of interest and parameterised using appropriate field and laboratory data, the models can be applied with a certain degree of confidence to:

■   extend these data to larger geographical areas;

■   provide statistical distributions of concentrations;

■   explore the effect of variations in the environmental and chemical properties.

This integration of monitoring data with model predictions in comprehensive risk assessments is illustrated in fate assessments for anionic and cationic surfactants (Fendinger *et al*, 1992; McAvoy *et al,* 1993; Rapaport *et al,* 1992; Versteeg *et al,* 1992).   For example, the river models presented in Caprara and Rapaport (1991), Hennes and Rapaport (1989), Versteeg *et al* (1992), Feijtel (1995), Feijtel *et al* (1997), once validated for representative sites, can be used with an estimated degree of confidence to predict the concentrations of similar chemicals in other rivers worldwide.

By using laboratory and field data to parameterise the fate models for the chemical and environment of interest, and monitoring data to validate these models for specific environments and classes of chemicals, greater confidence can be placed in the resulting risk assessment and conclusions based on it.   Thus, monitoring and laboratory data serve integral roles alongside fate models in comprehensive risk assessments.

3.4 DATA, MODELS AND ENVIRONMENTAL RISK ASSESSMENT

Environmental risk assessment often involves steady-state models, while monitoring data must of necessity relate to the specific place and time of collection, and therefore may be part of a dynamic data-set.   It is therefore necessary to position the measured data in an appropriate context, if the time-and-space-specific data are to be used for steady-state model evaluation or environmental risk assessment purposes. The context and interplay will depend upon the type of model employed.

In the US, site-specific local models are used for risk assessment, while in the EU, local models for sites at which production, formulation, and disposal after use in the community occur are included in the environmental risk assessment programme. As discussed in section 3.1, the EU local scenarios require concentrations at sites 1 km from the point-source of the emission (factory, or sewage treatment plant.) The positioning of monitoring data can be relatively straightforward in these situations (assuming that complete mixing has been obtained), as monitoring data collected at the appropriate location over a representative time period can be directly related to the parameters which are calculated by the model.

European environmental risk assessment also includes the concepts of regional and continental PECs, which are the environmental concentrations predicted by a steady-state model of the Mackay level III type (SIMPLEBOX - [Brandes *et al*, 1996]).   The concept here involves an average over space, being a representative 200 km by 200 km for the regional model and continental Europe for the continental model, as well as the average over time. In addition, for the regional model a "reasonable worst case" is required, which involves increasing the factory and population density, and thus the chemical emission load, to above the European average. Relating these predicted average concentrations to the discrete results of monitoring studies is not straightforward.

The PEC for a region is a somewhat theoretical construct, and there are likely to be very few places where an "average" concentration for the region could occur. One could perhaps take numerous environmental samples over the course of a year or more in locations which are far from point-source emissions but representative of both urban and rural areas throughout the EU. The region selected would necessarily have to be one where the chemical under study is produced, formulated and/or used.   In any case, a good data set should be representative of the entire temporal range of variation in chemical measurements and be associated with a particular scenario in order to be of use in establishing the realistic risk scenario - the 'reasonable worst case'. Measurements of chemical concentration in Member States where the chemical is not utilised would hardly represent a 'reasonable worst case'.

A dataset for a regional PEC should also be representative of the entire spatial range of variation in chemical concentrations, as determined both from emission variations, and from variations in environmental characteristics, such as soil type, river flow rate and volume, or wind velocity. At the present time, the data necessary to determine this representativeness have not been assembled for Europe, although this is being attempted in some areas. For example, digitised soil maps of Europe allow representative soils such as the Eurosoils (Kuhnt and Muntau, 1994) to be identified, as well as "average "and "worst case" soils for several processes (e.g. leaching). The Corinair (EUR 13232 - 12586, 1995) database is collecting the necessary data for the air compartment, and it might be possible to establish "representative" conditions from an analysis of the data contained therein.

Several water quantity and water quality databases exist for Europe, and though coverage is not complete and flow velocity data in particular are very scarce, it should ultimately be possible to determine a set of representative river catchments, for either water quality or flow. From this, it might ultimately be possible to relate monitoring data to standardised conditions, which would reflect the conditions in the "representative" areas. For example, if, over all of Europe, a factor of 10 represented the average and a factor of 3 represented the 95`percentile dilution ratio of effluent from a sewage treatment works by river water, then monitoring data obtained at a site where the dilution was 5:1 (or any other ratio) could immediately be placed in context. Programmes are underway within the European Environment Agency to locate and assemble the data that would enable the definition of a representative environment. The collection and release of these data should actively be encouraged.

The GREAT-ER project (Feijtel *et al*, 1997), will contain data from the model validation areas by 1999, but data from the rest of Europe will need to be obtained before this model can be used fully in a risk assessment context.   The data contained in GREAT-ER will be useful for characterising representativeness for sewage effluent dilution and for river flow, and will provide another means of relating monitoring data obtained at a specific site to concentrations that might be expected in other areas, where different conditions apply.

In summary, monitoring data can be used in a straightforward manner to carry out site-specific and local risk assessment, provided that sufficient information is available concerning the chemical and the environment, the release history of the chemical with respect to the monitoring site, and the analytical methods used to determine the concentrations.

The use of monitoring data for regional risk assessment will be a possibility in the future, when the data necessary to relate the characteristics of a monitoring site to the distribution of site characteristics for the rest of Europe have been identified, collected, accepted and released for general use. These data may include distance from, and concentration at, release, and environmental characteristics determining residence time of the chemical in that environment.

In those cases in which a measured environmental concentration can be associated with the predicted concentration from a risk assessment model, the chosen appropriate statistical summary of the environmental data is chosen as the 'reasonable worst case' (e.g. 90-percentile), and the PEC is estimated to be this concentration value. However, it is still necessary to compare this PEC based on monitoring (measured concentrations) with the PEC estimated by calculation (computer models such as EUSES, 1996; ECIMOS or GREAT-ER). If the two estimates are substantially different, then an explanation must be sought. It is not a foregone conclusion that PECs based upon measured concentrations will take precedence. It must be well demonstrated that the monitoring data are representative of the intended scale, setting, scenario, stage in the chemical's life cycle, etc. If that is the case, it is likely that this comparison could be used for validation of the models and/or improvement in default emission assumptions.

4. MONITORING PRACTICALITIES

4.1 GOALS AND STRATEGY

Environmental monitoring forms an integral part in the development of risk assessments and in the processes of risk management and pollution control. The main value of monitoring is to confirm exposures and/or detect changes in the state and functioning of ecosystems such that timely counteractive measures can be initiated, developed, and evaluated. Sampling is only the first step in the monitoring process, and is followed by analysis, interpretation and evaluation of results, concluding with timely reporting. To be cost-effective, the monitoring must have clearly specified goals and a strategy to achieve those goals.

The most commonly encountered goals of monitoring are to:

■ provide information on the location and intensity of a source;

■ identify state (concentration) and trends in air/water/soil quality;

■ identify the mass flows in the environmental compartments to check consistency in monitoring data;

■ compare measured concentrations with predicted model concentrations for use in risk assessment; check the result of pollution control strategies on environmental quality;

■ verify compliance with regulatory limits for confirmation of effective risk management;

■ provide early warning and detection of pollution.

In practice, data from routine monitoring programmes are sometimes used for purposes additional to those for which the programmes were designed.

Confirmation of exposure levels is important for chemical legislation and control, but is also of particular relevance for validating models. Mass flows in wastewater treatment plants, rivers, soils and other compartments allow the risk assessor to interpret monitoring data and refine exposure models, increasing confidence in their use in risk assessment.

Identification of state and trends in environmental quality is also important for policy and management. The identification of mass flows in rivers and wastewater discharges is of particular importance at the boundaries between countries, districts or water systems. Mass flows are the subject of international negotiations and are an input for mass balances for specific substances. Guidelines on water quality monitoring and assessment of transboundary rivers were recently published by a UN/ECE Task Force

(1996). Testing of compliance with standards (control) is related to water quality objectives for surface water as prescribed in both national and international standards. The early warning monitoring programme to signal pollution due to (accidental) spills by industry and shipping is especially important if that particular river or water system is used for public water supply. Finally, data can also be used for various projects including research.

One objective of monitoring programmes that is closely related to risk assessment, is the measurement of environmental concentrations on which to base PEC values, which are representative of a specific setting. There is considerable interest in using monitoring data for this purpose since the default local emissions, contained within the TGD for EU risk assessment, and on which exposure modelling (PEC estimation) is based, are conservative. In this context , monitoring data may be used in two ways:

■   to estimate total emissions;

■   to estimate directly a PEC based on measured concentrations in the environment.

Total emission estimates are usually made from the concentration of the substance in the emission and the emission's flow, while PEC estimates may be made from concentrations measured directly from samples.

To devise a monitoring strategy, detailed consideration must be given to the type of data to be collected, the planning of how those data will be collected and the limitations of available resources and manpower.   The following practical aspects of conducting a monitoring programme must be considered:

■   data representativeness - are the results fit for the intended purpose ?

■   data quality - what sampling and analysis are appropriate and how is this documented ?

■   design practicalities - what are the generic issues related to planning and co-ordination ?

4.2 REPRESENTATIVENESS OF DATA

It is important that the design criteria of a monitoring programme are selected so that the results of the monitoring represent a well defined environmental concentration. There are two distinct types of representativeness:

■   Sample representativeness relates to the number of samples taken, how far apart they are taken, and how frequently they are taken. The sampling frequency and pattern must be sufficient adequately to represent the concentration at the site selected;

■ Scenario representativeness, relates to the site at which the sampling is done; how representative is it of the setting and scenario intended within the risk assessment framework?

4.2.1 Sample Representativeness - Measuring the "True" Concentration

The idea of measuring a representative concentration is a complex statistical issue (Barcelona, 1988). If the distribution of an environmental concentration of a substance were homogeneous and constant, the problems involved in assuring representativeness could be handled with simple sampling statistics and an evaluation of the random errors (bias) inherent in the equipment and the process of sampling and analysis. A statistical understanding of the resultant data variability leads directly to a calculation of the number of samples needed to report a mean concentration at a level of confidence which meets the objectives of the study (Taylor, 1988; Natrella, 1966).

The environment, however, is both heterogeneous and dynamic and thus the concentration of any particular chemical will vary in space and time as a result of variations in its rates of emission, transport and degradation. Transport is greatly influenced by the state of the particular medium. Some examples of environmental properties which affect transport in different compartments are:

■ air: wind speed and direction, turbulence, precipitation;

■ water: flow rate, turbulence, stratification, depth, dilution volume;

■ soil: percolation rate (porosity, rainfall, surface features), organic matter, moisture.

Environmental factors, such as temperature, UV and redox potential etc, affect degradation rates as will interaction with other chemicals and biota.

The heterogeneity of the environment which influences chemical concentration may be both microscopic (for example differences in soil particles or the differences between particle-bound and soluble concentrations in soil, water or air) and macroscopic (for example major land features). An understanding of the factors influencing the spatial distribution of a chemical may be useful in designing a sampling programme which is reflective of the true variability in the environmental concentration. Microscopic variability may be ignored by taking suitably large or composite samples and, with appropriate mixing and extraction techniques, be represented as the average total concentration. Alternatively, microscopic variability may be investigated with appropriate sub-sampling or separation techniques.

An understanding of the physical and chemical processes influencing macroscopic (spatial) variation in concentration may be used to design a grid pattern of sample points which will allow the data to represent the concentration gradients of the chemical in three-dimensional space. An important

example of spatial variation in environmental concentrations is the "mixing zone" down-stream or down-wind from an emission source. The chemical concentration in the neat effluent or emission will be diluted in the receiving medium of water or air, through mixing and diffusion. In the EU risk assessment scheme, the concentration representing the local scenario is taken as that region where the effluent or emission is estimated to have completely mixed with the receiving medium. In practice however, there will be a gradient of concentrations influenced by local conditions. This issue of mixing zones will be more fully discussed in the section dealing with water monitoring (section 6.1).

Similar considerations apply to the way in which concentrations of a chemical vary with time. Certainly daily and seasonal environmental conditions influence these. Temporal variability is highly influenced by the emission characteristics for the chemical. If the chemical is entering the environment from a point source, the frequency and duration of the emission are directly correlated with the environmental concentrations. Rather than random sampling, a knowledge of the times and duration of the emission will allow sampling intervals to reflect temporal variation in emissions. This approach is far more cost-effective than random sampling over an extended period of a year or more.

The most useful monitoring data are those which capture all of these sources of spatial and temporal variability. The data may then, with proper statistical analysis, be used to estimate probability distributions of the chemical in space and time. Such probability distributions may be used to choose locations for subsequent sampling programmes and, in risk assessment, to estimate the likelihood of reaching a particular concentration at specific locations and times. Knowing the intended use of the data, together with the necessary statistical treatment of the data, is important to planning a representative monitoring programme (Flatman *et al*, 1988; Borgman and Quimby, 1988; Journel, 1988).

4.2.2 Scenario Representativeness - Generalising the Concentration to other Sites

If the data from a site monitoring study are to be extrapolated to cover sites of a similar nature, the monitoring site should be shown to be representative for the selected exposure scenario.

For risk assessment, the PEC may be determined by modelling or measurement. The PEC must represent a reasonable worst case estimate of the concentration for a specific setting and scenario. The reliability of the measured data must be established and also how representative are the data of the general emission situation. Two area scales are defined, local and regional which are discussed in more detail in section 3.2.

■   the PEC_{local} is the concentration, after mixing, of the chemical in a generic local environment. The local environment is a hypothetical site having standard environmental characteristics;

■   the $PEC_{regional}$ covers a wider area and takes into account the further fate and distribution of the chemical after release and at steady state. The $PEC_{regional}$ takes into account all point and diffuse sources of the chemical. In addition, some chemicals occur naturally and will contribute to the $PEC_{regional}$ and the $PEC_{local.}$ Since the region defined in the TGD is fictitious and is not represented by any one area within the EU it is difficult to envisage a representative monitoring scheme to validate this regional exposure scenario.

Values of PEC_{local} are determined for all those stages in the 'life cycle' of a chemical where it is most likely to be emitted from point-sources to a local environment. For example, the production of a specific chemical may give rise to a release of some fraction of it to wastewater and subsequently to a river. A measurement of the concentration of the chemical in the river below the effluent out-fall and after mixing could be used as the $PEC_{local, water}$. To represent the PEC for production, the out-fall would clearly have to be from a production facility. Moreover, to be representative for the production process in general, it must be known that the production facility is typical with regard to the production levels, processes employed, emission levels encountered and size of receiving water. In addition, more general information on the local environment, industrial usage, population level, etc. is useful in selecting typical sites. Therefore, if the data are to be used for risk assessment, attention to such details is necessary in order to select a representative site for monitoring.

4.3 DATA QUALITY

Before representative monitoring data (see section 4.2) are included in a risk assessment, their quality must be assessed. The quality issues relate to the technical aspects of both sampling (sample integrity) and analysis. Quality control objectives (Keith, 1992) ought to be defined in the planning phase of the study.

4.3.1 Sample Integrity

Since it is impossible to measure concentrations in the total environment the objective of sampling is to collect a sample small enough to be handled, transported and analysed conveniently but which still accurately reflects that part of the environment sampled i.e. the sample is truly representative. Not only should the sample be representative of the environment but no change should occur during sample handling.

■   Sample handling and storage
    Avoid contamination, physical loss, degradation and mis-identification of samples (Mascarinec and Moody, 1988). Sampling equipment needs to be appropriately cleaned between samples to avoid cross-contamination. If possible, sampling times or locations should be planned so that sample progression is from higher to lower expected concentrations. Sample volume should be

kept to a minimum related to the needs of the analytical procedure but be sufficient to allow for replicate or repeat analyses if necessary. Careful packing for transport is necessary to avoid breakage, leakage or loss of samples during shipping.

■   Sample preservation

The main approaches used to preserve samples are, pH adjustment, addition of chemicals and refrigeration. In the case of the very readily biodegradable chemicals it is essential to ensure that preservative is added to the sample container prior to the sample being collected. Failure to do so will result in significant loses of parent material. The samples should be extracted or otherwise prepared for analysis as soon as practicable. Storage of samples under the wrong conditions can result in considerable changes in the analyte concentration. Refrigeration or cooling from the point of collection until analysis is usually advisable even when other preservation techniques are employed.

■   Sample identification

Sample containers should be prepared and labelled in advance. Each sample should be identified by its specific location (grid reference), date (and time, if needed) and should be initialled, at the time of collection, by the individual who collected it. Labels should be affixed in such a manner that weather or storage conditions will not remove the label or deface the writing. On arrival at the analytical laboratory, the samples should be inspected and an inventory made to ensure that the correct sample number and identification, as specified by the sampling protocol, have been delivered. Any peculiarities such as broken containers, leakage, unexpected visual appearance, etc. should be noted on the inventory.

Sample containers need to be composed of materials which will not influence subsequent analyses through leakage, absorption or contamination of the sample. Whenever possible containers ought to be unbreakable.

Each of the steps in the sampling regime is a potential source of error which can influence the concentration finally measured. Since the aim is to measure the actual concentration as accurately as possible, all of these sources of error must be minimised (see Figure 1).

These sampling issues are best addressed through a quality control programme.

Figure 1: Potential Sources of Error
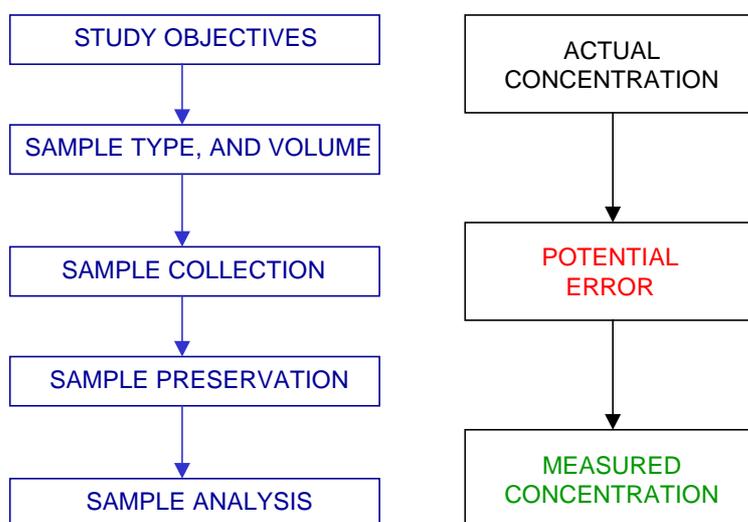
4.3.2 Sample Analysis

The limitations of the analytical methodology also affect the quality of the data generated from a monitoring programme. The three major quality features of any analytical method are *selectivity, sensitivity* and *reproducibility.* The selectivity of the analysis should be such that all of the target analyte and only the target analyte is measured and that other related chemicals or contaminants do not interfere with the response. Thus, a chromatographic method is preferred. The method should be sufficiently sensitive to measure the chemical concentrations expected to be found. The method must have sufficient reproducibility to limit the number of replicate samples but still provide information on the actual variability in chemical concentration between the samples. The appropriate validated methods for environmental analysis should be used.

To provide convincing evidence that the analytical scheme is accurate and precise, methods should be used and reported that standardise the assay and correct for background and losses. The detection limit of the analytical scheme must be appropriate to the expected concentrations encountered in the field since the detection limit may contribute significantly to the final calculated concentration if a large proportion of the samples analysed are at or below the detection limit of the assay (see Appendix D). Whatever the published or expected sensitivity and reproducibility of the method, it is necessary to demonstrate sensitivity and reproducibility in the specific laboratory and samples in the monitoring study.

The measures used to assess the quality of the data should include:

■ laboratory blanks (instrument, reagent, matrix, etc.) and field blanks (matrix-match, equipment, etc.) to assess laboratory and field contamination;

■   laboratory standard additions (at concentrations applicable to the sample matrix) to assess the recovery or efficiency of the analytical methodology;

■   field standard additions (spiked blanks or samples) to assess the preservation technique, stability of the samples, etc;

■   replicate field samples to assess overall variability in sampling and analysis;

■   replicate analysis of the same sample to assess variation in analytical procedure.

Inter-laboratory analysis (or repeat, "blind" analysis in the same laboratory) of spiked and unspiked samples (i.e. sample sub-divided in the field) may also serve as a check on reproducibility. For all types of locations it is important to collect samples which can be checked in the laboratory for the presence of any materials which cause interference with the analytical determination, recovery of standard additions and minimum levels of detection. For frequent analyses, it is useful to have a continuing check on reproducibility through the use of quality control (QC) charts (Lewis, 1988; Black, 1988). In QC charting, the mean analytical response to the specific chemical and its associated variability is calculated and charted. If the standards fall outside the expected range of normal variability for a particular day's analysis, this fact is immediately apparent and may be investigated.

4.3.3 Quality Control and Quality Assurance

Many of the problems associated with bias and systematic errors encountered during sampling and analysis may be assessed by a variety of internal quality control measures. These measures were discussed in Sections 4.3.1. and 4.3.2. The study plan should include the quality control and quality assurance procedures to be used. All methods and steps undertaken in the programme require trained, skilled personnel. Minimum requirements for the test laboratory are listed in EN 45001 or ISO Guide 25 (1990) standards. Standard operating procedures, conformance with the protocol, and clear and timely record keeping are necessary. These issues may be addressed with a quality assurance inspection or audit of the written records, of the work in progress, and of the final report.

4.3.4 Reporting

Data generated by monitoring programmes are being used increasingly to evaluate the environmental impact of chemicals. Since monitoring programmes may have many different objectives, which ultimately affect study design, it is essential that the data be used and reported correctly and transparently.

Procedures used for sampling, sample handling and analysis all need to be reported so that the data may be adequately evaluated. The limitations of the method as regards background interference, recovery, and detection limits must be clearly stated. The details of the procedures employed to check

the selectivity, sensitivity and reproducibility of the analytical method need to be reported. To allow an adequate evaluation of the results for use in risk assessment, additional information on the characteristics of the sample and the site need to be described (see section 4.4.1).

Anomalous high or low sample results are often due to error in sample handling, labelling, etc. If these are encountered within the data set it may be appropriate to re-analyse the samples or to disregard the result. The criteria for re-analysis or data deletion ought to be established prior to sample collection, either in the protocol or by written standard operating procedure. The reported results need to indicate the number of samples analysed for each particular time and location and, whether data were omitted to indicate this within the report. Any statistical procedures employed to summarise the data need to be clearly described and the individual data points ought to be available.

The need for the use of appropriate statistics to summarise the data is obvious. When a detailed monitoring programme is properly conducted, large numbers of data points are produced encompassing differing locations and times of sampling and blanks, spikes, standards and quality control samples. The limits of detection and confidence in the result must be assessed and reported. As a minimum, sufficient statistics ought to be conducted to quantify the sensitivity and reproducibility of the assay and to represent the statistical distribution of the data. For samples from multiple locations or different times, a simple mean value omits much of the valuable quantitative information on the variability of the concentration in space and time. Such data should be inspected or assessed statistically for the possible presence of time trends, either monotonic or cyclical. For use in risk assessment, a mean value is insufficient for a PEC since the TGDs define the reasonable worst case as the 90th percentile concentration.

4.4 GENERIC DESIGN PRACTICALITIES

There are a number of practical considerations when designing a monitoring programme which are generic regardless of the compartment being monitored. Some of these design considerations relate to quality and representativeness of the data and have been discussed in sections 4.2 and 4.3. Designing a monitoring study to determine $PEC_{regional}$ is very difficult (section 4.2.2), and consequently most of the ensuing discussion relates to monitoring to determine the PEC_{local}. The topics considered are practical, and concern the specifics of study design and implementation.

The objectives of the study need to be well defined as these will determine the site selection, the sampling strategy (duration, type and numbers of samples), the data requirements, etc. Execution of the plan requires co-operation of those on site, adequate training of personnel, and a host of other technical details.

The human and financial resources needed to carry out a monitoring programme can be significant. To ensure these resources are effectively utilised it is important that the relevant parties (e.g. landowners, police, media etc.), whose knowledge and practical experience can be used and whose endorsements are necessary for the acceptance of the study, are identified and involved at all stages of the project. Attention should be given to identifying and involving regulatory authorities, local officials, laboratories, and academia. Following initial discussions with interested parties, which should establish a commitment to the study, a management team should be set up. Their team role is to agree to a project protocol which clearly states the aims and objectives, identifies individual responsibilities and allocates resources. Figure 2 illustrates some of the key stages in designing a monitoring programme.

Figure 2: Stages in Planning and Execution of a Monitoring Programme
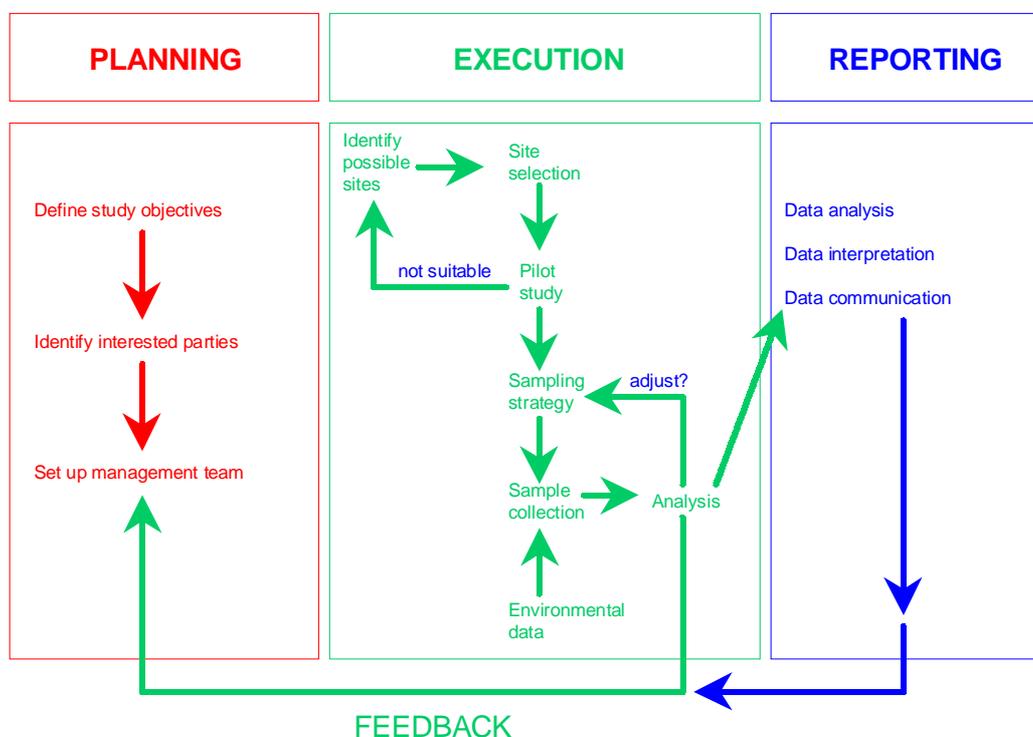
As discussed earlier, monitoring programmes may have any one of a number of objectives, including confirmation of regulatory compliance, trend analysis, warning of a pollution event, establishment of the concentration of a particular chemical for purposes of risk assessment or risk management. Defining the objectives of the study allows one to define the site or sites which will be needed to meet these objectives. The site and sampling pattern need to be chosen such that they will adequately represent the setting and location which are intended by the study objectives.

4.4.1 Site Selection

Selection of an appropriate site for a monitoring study is one of the most important considerations. For risk assessment, if the study objective is to identify the PEC for a specific life stage of a chemical, e.g. production, then a site needs to be selected which is representative of that "scenario". Such aspects of the site as the annual throughput, manufacturing process, emission rates and routes, wastewater treatment and the local environmental conditions need to be typical for the manufacturing of that chemical. It must be possible to record, with the necessary provision, the environmental conditions and parameters at the site.

In addition to representativeness, there are other considerations with regard to site selection:

■   the site must be accessible. If the study objectives require numerous samples over a range of distances from the emission source or over an extended time period, then the intended locations for sampling must continue to be readily accessible. Evaluation of the site for these sorts of details is most readily accomplished through site visits;

■   weather conditions (ice cover, storms, floods, etc.) which would affect sampling or change the characteristics of the environment need to be anticipated;

■   the safety of sampling personnel;

■   the site should also be secure from interference in sampling, from vandalism, or from theft of sampling equipment.

Such pragmatic details can mean the difference between success and failure in completion of the study.

The history of the site is also important. Prior activities on the site may lead to background chemical interference in the analyses or unexpected physical obstructions to sampling. Site history should also include some idea of the stability of the local environment surrounding the site. Have there been changes in surrounding land or water due to human activities or catastrophic weather or geological events (e.g. changes in river flow, flooding, mud slides, new construction, etc.)? If past history indicates changes in either the site use or local environment, consideration needs to be given to the possibility that the site may not remain as intended over the future course of the monitoring programme. In some cases, site geology should be evaluated to assess the background concentration of naturally occurring substances and the possible influence of the geology on water chemistry and thus bioavailability.

The state of the environment surrounding the site may also be impacted by other nearby activities. If neighbouring facilities or communities contribute to emissions of the chemical being studied their

influence must be taken into account when considering site representativeness. Furthermore, the influence of these neighbouring emission sources must be accounted for by collection of adequate background samples (e.g. upwind or upstream).

Site visits and a pre-study sampling exercises are very valuable in evaluating these site selection considerations.

4.4.2 Pre-Study

Suitability of the site and sampling locations which can be easily identified should be confirmed in the pre-study. If necessary they should be marked by reference to local fixed features so that comparable samples can be taken over a period of time. The feasibility of protocol details such as sample preservation and transport should be evaluated. Samples from the pilot study should be evaluated for interferences and unanticipated analytical problems.

Another useful purpose of a pre-study is to gather data for final selection of representative sample locations. For air this would mean noting prevailing wind conditions and emission sources in order to determine appropriate locations for sampling devices. For river water samples, this might entail describing flow patterns in order to establish the distance downstream of the mixing zone, movements of plumes, etc. For soil monitoring, samples may need to be collected to determine soil chemistry, soil type and prior history. Finally, during the pre-study, the nature of, reasons for and value of the programme may be explained to all concerned. This serves to establish an involvement and 'ownership' of the project.

Site visits are also a good way to get local knowledge and history of the site which may not necessarily be officially documented. Another important function of a site visit is to confirm that the local facility or facilities are stable and operating normally, and that no development work or change in facility design, operating conditions or equipment is scheduled over the proposed study period. Consult site records of all events that may have affected facility operation, do not rely solely on memory (or honesty) of the operator, and confirm that such records will be kept during the period of the monitoring study.

4.4.3 Sampling Programme

After establishing a suitable site, a programme for sampling and recording environmental conditions should be developed.

The number of samples collected for analysis must be sufficient to meet the intended use of the data. There are many types of sampling situations some of which can be satisfied by a simple sampling regime whereas others may require sophisticated sampling techniques. If the objective is to have a

"spot check" on compliance, a single sample may do. Should the objective be to investigate trends, for example in air or water quality for a region or a catchment over a number of years, then obviously a large number of samples will need to be taken. Protocols for the sampling regime (time, place, type and frequency) and the training of the sampling staff should be such that it can guarantee that these criteria are fulfilled and the same locations are sampled.

There are a number of issues which need to be addressed when deciding whether to use grab or composite samples. Both have their limitations and the appropriate technique should be used. Due regard should be given to the resource implications of using either of these two methods. The manpower and equipment needed to carry out a composite sampling programme are considerably more than those required for grab sampling The statistical validity of spot versus composite samples is an area of continuing debate and study (FWR, 1994). If both the flow rate and concentration of determinand vary significantly then flow proportional composite samples would currently be recommended. They are however of no value for identifying transient peaks in concentration of a determinand.

Samples may be taken over a long duration or numerous individual samples composited in order to smooth out short-term variation in concentrations. This compositing of samples also reduces the number (and cost) of sample analyses. For rivers and effluents, flow- or time-related samples should be considered. For soil, chemical concentrations tend to vary less with time, but owing to localised differences in soil properties soil concentrations of chemicals often show more variability with sample location. Again, this variability may be averaged by taking more samples or by compositing a number of samples taken over a larger area. If the objective of the study is to obtain a representative concentration for a specific sample site, then such compositing of samples may be more cost effective than analysing numerous samples and then compositing the data through calculating an average. Compositing samples does not however provide data on the extent of variability.

For risk assessment in the EU, as defined within the TGD, there are implicit expectations regarding the degree to which temporal and spatial variability are quantified within a monitoring study. It is expected that seasonal variations in chemical production, dilution water flows, etc. are measured. Thus a monitoring programme for establishing data would need to have sampling intervals planned to correspond to those temporal changes. Good records should be kept such that unreasonable concentrations caused by abnormal situations such as spills, atypical weather conditions, etc. should not be included. Sufficient flexibility needs to be built into the sampling strategy to avoid these situations.

Spatial variability also needs to be considered. The sampling programmes needed to account for this variability are particular to the environmental medium.

A number of other practical considerations need to be kept in mind. Sample size may be limited by the sampling equipment used and sample containers available. Sample number may be limited by sample size, storage capacity, analytical capacity, etc. At times, sampling may be affected by practical feasibility. The skill and training of the sampling staff are important to obtaining the samples planned in the protocol. So is the extent of available resources. Sampling times or locations need to be planned to allow the staff sufficient time to store the sample properly and take the next sample at the expected time. Unforeseen on-site conditions such as accidents or weather conditions may cause deviation from planned activities.

4.4.4 Sample Handling and Analysis

See Section 4.3.1.

4.4.5 Communication of Results

It is important to include in the study design a supporting programme designed to obtain the necessary data and/or information to allow the correct interpretation and positioning of the data set obtained. It is also important to include within the study design a plan for how, and to whom, the data are to be reported, and how appropriate data relating to risk, uncertainty, costs, and benefits are to be communicated.

4.4.6 Summary Table

The major areas to consider when designing of monitoring programmes to collect chemical concentration data to be used for risk assessment are summarised in Table 1. The Table focuses attention on generic areas of importance for the design of monitoring studies but not on the issues specific to different environmental compartments, which are addressed in Chapter 6.

The information which is important in characterising measured chemical concentrations is subdivided into six categories:

1. technical details of how the sample was collected, preserved and analysed;

2. degree of quality assurance and quality control employed in arriving at a final environmental concentration;

3. location in space and time of the sample(s);

4. condition and characteristics of the sample and the environment from which it came;

5. local manufacturing facilities, the characteristics of the facility;

6. data handling, how many analyses does a concentration represent and how were the numbers composited?

Categories 1, 2 and 6 pertain to the data quality issues in sampling and analysis, while categories 3 to 5 relate to issues necessary or useful in establishing the representativeness of the samples and of the site (geographically and within a particular risk assessment scenario.)

Close adherence to the principles specified in Table 1 should ensure that the resulting monitoring programme generates results which will be both siutable and acceptable for use in environmental risk assessments.

Table 1: Considerations for the Design of New Monitoring Programmes

Specific type of information needed to meet objectives of the monitoring programme

1. Technical Aspects of Sampling
   a. Select appropriate sample size, (i.e. volume, weight, etc.)
   b. Select appropriate sampling techniques: apparatus (type and materials), duration, transfer methods
   c. Select appropriate containers (size, composition, type, labelling, cleaning procedures, closures), replication, methods to avoid (cross)contamination
   d. Select appropriate sample preservation, cooling, transport - storage times and conditions
   e. Select sub-sampling techniques: methods to avoid volatile losses, methods to remove sorbed or precipitated chemical from container surfaces, separation of suspended particulates, mixing, homogenisation etc

2. Technical Aspects of Analysis
   a. Describe techniques for sample preparation, concentration or extraction
   b. Describe approach used to correct for losses during the analytical scheme (recoveries of laboratory and field spikes at appropriate concentrations)
   c. Describe techniques to evaluate and account for background interference or contamination
   d. Select or develop selective chemical analysis with appropriate sensitivity and reproducibility
   e. Quote method detection limit and assure that it is low enough for intended purpose
   f. Specify method and frequency of calibration/standardisation of the analysis

3. Quality Control and Quality Assurance
   a. Establish procedures for tracking and documenting sample integrity, transfers, etc.(e.g. inventories, chain of custody, etc.)
   b. Establish procedures to assure consistent sampling and analysis methods (protocol, standard operating procedures, personnel training, etc.)
   c. Establish procedures to associate final analytical result with original sample (sample coding and unique sample i.d.s, data sheets, transfer forms, etc.)
   d. Establish procedures to track and document analytical reliability (e.g. QC charting, sample re-analysis, blind performance samples, etc.)
   e. Establish criteria for re-analysis or omission of "'outliers'.
   g. Define monitoring or auditing responsibilities for supervisory or independent QA checks on conformity of sampling and analysis with the protocol requirements

4. Sample Location in Time and Space
   a. Select sampling duration, frequency and times (of day, month, year) - is there a sampling window?
   b. Select sample sizes and decide on compositing or not
   c. For composite samples, select locations or sample intervals to be combined - for aqueous samples flow or time composites?
   d. Consider influence of season and weather on sample representativeness
   e. Sample location (macro): Select catchment, country, geographic location (e.g. latitude/longitude), distance from source(s), etc.
   f. Sample location (micro): Select sampling locations relative to source and surface of environmental compartment and relative to other samples taken (i.e. distance, direction, time interval). Positively identify site for future sampling

Table 1: Considerations for the Design of New Monitoring Programmes

5. Sample Characteristics
(Sample characteristics depend upon specific compartment being sampled and are treated separately)

6. Environment Characteristics
(Environment characteristics generally differ with specific compartment but a few are generic)
a. For the specific purpose (scenario) for which the data are intended the following are appropriate:
    i. Distance from industrial effluents of the same chemical
    ii. Population (urban, sub-urban, rural)
    iii. Climate and weather (temperature variations, rainfall, etc.)
    iv. Physical characteristics (topography, distance inland, etc.)
b. Presence and location of other sources of pollution in the region of the sampling site
c. Data on the site history regarding physical characteristics and pollution

7. Local Source or Site Characteristics
a. Site selected is representative of the emission source (point source or diffuse source)
b. Site is representative of intended life stages of chemical (production, processing, storage, etc.)
c. Site is typical of the industry in annual production or throughput of the chemical
d. Site selected is using typical processes for the industrial step
e. Site selected uses similar waste disposal and wastewater treatment practices to those which are representative of the industry
f. Site selected has a stable operational schedule; the time frame for releases of the chemical are known and not likely to change. no changes in schedule, new
   equipment, or processes changes are likely to occur over the time frame of the study

8. Reporting
a. Details of sampling scheme, sample locations and time intervals, sample sizes and numbers, local environment and sample characteristics
b. Available data on site representativeness including direction and magnitude of source and site characteristics regarding industrial activities, tonnage throughput, etc.
c. Details of the sample handling and tracking procedures. Give results of background or procedure blank analyses
d. Details of the sample preparation procedures including mixing. sub-sampling, extractions or concentration, dilution of extracts, etc.
e. Details of analytical methods and data on selectivity and background interferences. Results of blank/background analyses, sample analytical result
f. Data on the sensitivity and reproducibility of the sample handling and analysis, including results for spikes, QC samples, QC charting, etc.
g. Statistical summary of the data: number, distribution, mode, mean, std. dev., 90th %-ile, etc.
h. Description of the value used to incorporate non-detects in the mean and the actual number of non-detects
i. Discussion of the relevance of the data, how concentration compare with background (upstream) data, historical data, data from other similar monitoring studies, etc.

5. USE OF EXISTING DATA FOR ENVIRONMENTAL RISK ASSESSMENT AND MODEL VALIDATION

5.1 EXISTING DATA

Whether or not it will be possible to use a given set of existing data for certain aspects of environmental risk assessment and/or model validation will depend upon several different considerations. These include considerations involving the chemical, the environment, the release of the chemical, and the accuracy of the data requirements for the specific risk assessment or modelling application. One of the conclusions in the executive summary in the recent report on monitoring water quality in the future (Villars, 1995) is the deficiency in the information gained as a result of the lack of harmony of monitoring programmes within Europe. The same conclusion holds for other environmental compartments. Furthermore it has often been forgotten or overlooked that the ultimate goal of monitoring is to provide information, not data. In the past many monitoring programmes have been characterised by the 'data rich, information poor' syndrome.

It is only natural to want to obtain as much useful information from a data set as possible, but there is inherent danger in trying to use the data for inappropriate reasons. To address this problem we have proposed **three** quality levels for existing data (Table 2). Further details on the criteria can be found in the relevant section in the report.

Table 2: Minimum Information to Justify Use of Existing Data

Criteria	Highest Quality Data	Support for Exposure Assessment (data interpretation difficult)	Not for Use in Exposure Assessment (but may be useful for other purposes)
What has been analysed?	✓	✓	✓
Analytical method	✓	✓	
Minimum level of detection	✓	✓	
Blank concentration	✓		
Recovery	✓		
Accuracy	✓		
Reproducibility	✓		
Sample collection	✓		
One shot or mean		✓	
Location	✓	✓	✓
Date dd/mm/yy	✓	Minimum is knowledge of year	✓
Time	✓		
Compartment characteristics	✓		
Sampling frequency and pattern	✓	✓	✓
Proximity of discharge points	✓	✓	
Discharge emission pattern and volume	✓		
Flow and dilution or application rate	✓	✓	
Explanation of value assigned to non-detects if used in a mean	✓	✓	

To be classified as highest quality data (Table 2) for use in risk assessment, the most important factors to be addressed are the analytical quality control (AQC) and the representativeness of the sample. Clearly at concentrations approaching the limit of detection of an analytical method, percentage errors will be greater than at higher concentrations. AQC activities are the basis for establishing some checks on the analytical performance, and whilst they are now widely used, they have not been employed in the majority of environmental monitoring programmes until very recently.

The criteria relate to either quality or representativeness. For highest quality data it is important to have information on:

■ What has been analysed? Precisely what has been analysed should be clear. Details of the sample preparation including for example whether the analysis was of the dissolved fraction, the suspended matter (i.e. adsorbed fraction) or the total (aqueous and adsorbed) should be given. How was the sample collected, preserved and stored, including material that sample collection and storage containers were made of what measures were taken to avoid contamination. The chemical speciation in the environment under investigation must be easily determined from the information given. Therefore more information will be required for some chemicals than for others.

■ The analytical method, including sample extraction, clean-up and end analysis (e.g. specific GC/MS or HPLC/MS or non-specific e.g. colorimetric) should be given in detail or the scientific publication, ISO/DIN method or standard operating procedure should be referenced;

■ The minimum level of detection and details of possible interfering substances should be quoted;

■ Concentrations in systems blanks should be given to support the minimum level of detection;

■ Recovery of laboratory and field standard additions (spikes) should be quoted;

■ Accuracy. The relationship between the measured concentration and the minimum level of detection should be given;

■ Reproducibility. The degree of confidence and standard deviation in the results from repeat analyses should be given.

The following criteria for sample representativeness are considered to be important:

■ Monitoring location. Details of the monitoring location should be given (i.e. geographical coordinates, grid references). The monitoring site should be shown to be representative of the location and scenario chosen. The type of site will determine the homogeneity of the samples and therefore the need for replication and frequency of sampling. It is also important to know if any changes (product regulation, risk reduction measures, new production plants, increased capacity etc.) have occurred at the site since the sample was collected. The type of location will also

determine the homogeneity of the samples and therefore the need for replication or frequency of sampling.

■   Proximity of discharges. For the aqueous environment detailed information on the distance from and location of other sources, flow and dilution are needed. For soils the application rate is important.

■   Discharge emission pattern. Is there a constant and continuous discharge or is the chemical under study released as a discontinous emission showing variations in both volume and/or concentration with time? Peak emissions are characterised by relatively large discharges over short periods, and the time between peaks can vary greatly. Block emissions are characterised by reasonably constant flow over a certain time followed by regular intervals with low or zero emission.

■   Sampling frequency and pattern. The temporal and spatial representativeness needs to address seasonal variation and whether or not the samples are time averaged or extremes.

■   Date of sampling. The time, day, month and year may all be important depending upon the release pattern of the chemical. For some modelling and trend analysis the year of sampling will be the minimum requirement.

If some of the above information is lacking, use of the data in risk assessment will be more difficult and therefore expert judgement will be required to evaluate fitness for use.

In many instances it will be recommended to use the most recent data but there is also benefit from looking at trends.

It is recognised that by applying these selection criteria, many existing data will be deemed unsuitable for risk assessment but they will however prove to be of value for other purposes. The differences in data quality will therefore have an impact on the use to which those data should be put.

In the absence of detailed information on the geographical spread and temporal extent and frequency of monitoring data, it is not possible to prescribe data analysis techniques that would be appropriate for all substances. It should be possible however to use techniques such as:

■   cusum (cumulative sum) analysis;

■   non-parametric approaches.

Non-parametric statistical methods are likely to prove particularly important if the substances either exhibit non-parametric variability or have a significant proportion of values below the limits of detection (WRc, 1989). WRc also has statistical techniques to help cope with the potentially false signals arising

from temporal changes in limits of detection. Additionally they adapt the balance of the data analyses in response to such factors as the frequency of data and the number of monitoring sites for specific substances. Thus, for example, if a particular substance were monitored at a large number of sites, detailed trend analysis would be performed for just a representative sub-set of those sites to determine the most appropriate statistical technique. The information gained from such a preliminary analysis would then be exploited in defining a more abbreviated form of trend analysis that could be conducted on the full set of sites.

Criteria for harmonised statistical methods for the detection of temporal trends and for determining their statistical significance have been reviewed by the Advisory Committee on the Marine Environment (ICES, 1997).

As discussed in Chapter 3, due consideration should be given to whether existing monitoring data pertain to a local site only or whether enough additional information is available to position the data for use in the TGD regional risk assessment scheme. As the $PEC_{regional}$ is a rather theoretical construct, it will probably be impossible to identify an average site for monitoring purposes. It may however prove possible to derive a $PEC_{regional}$ by taking numerous data over the course of a year or more in locations which are distant from point source emissions but representative of both urban and rural areas throughout the region (e.g. a basin or country etc).

5.2 ISSUES TO CONSIDER WHEN INTEGRATING DATA IN EXPOSURE MODELS

Are existing monitoring data good enough to be used in current exposure models? The answer to this depends upon the analytical accuracy of the monitoring data *per se*, the amount of information accompanying the data and whether or not this information is sufficient to determine that the data are appropriate for the process being modelled. These data will cover:

■ the chemical – how much was initially released, where it was released and what form it was in at release and in the environment;

■ the environment.

The amount of information required is almost always specific to the type of model, and to the chemical under consideration. Some indications of the type of questions which should be asked, and the types of information required to decide if a certain dataset is indeed appropriate, are indicated in the following sections.

5.2.1 The Chemical - Speciation

The chemical speciation in the environment in which the concentration is reported must clearly be determinable from the information given. Thus, more information will be required for some chemicals than for others. For example, if a chemical ionises or perhaps hydrolyses at a given pH, then data on the pH of the environment will need to be specified. For other chemicals, this information may not be necessary.

5.2.2 The Environment

A chemical may undergo processes in the environment, such as adsorption or biodegradation, of which the mechanism may depend on the environmental conditions. Thus, for many organic chemicals, the amount of organic carbon present in soil or sediment will influence adsorption. Additionally, ionic organics may adsorb to charged soil constituents, if these are present at the pH of the soil. If biodegradation of the compound takes place, then the existence of aerobic, anoxic, or anaerobic environmental conditions, and perhaps the fraction of time that each prevailed both before and during the monitoring study, will be necessary to understand the monitoring result, and to correctly position it in either a risk assessment or a specific modelling context.

The specific chemical under investigation and the processes to which it will be subjected in the environment will determine the minimum parameter set, or the minimum number of environmental properties for which information must be given in order for the data to be useful for risk assessment or model validation.

5.2.3 The Chemical - Release Data

The history of chemical release or deposition at the monitoring site must be known, in order to position the monitoring data correctly, or to determine the appropriateness of the dataset for the modelling or environmental risk assessment purpose. Information is needed concerning the total load emitted and also the spatial and temporal emission pattern. Important factors are the distance of the monitoring site from the source, the strength of the source, and, for non-continuous emission, the full historical release pattern, including the time between monitoring and the last application or release. Background concentrations may also be important, and knowledge of both the distribution of sources and previous emission patterns may be necessary to establish a background level, especially for sites with high historic deposition levels.

The release history of the site will then determine whether or not the monitoring data are suitable for the specific application, as, for example, monitoring data from a site dominated by the run-off of a specific chemical from a historical disposal site would not be relevant for relating current chemical emissions to

environmental concentrations, but would have some relevance if the total environmental load determination were the object of the modelling or risk assessment exercise.

5.2.4 Model Considerations

The analytical accuracy of an existing dataset may not determine *a priori* whether or not the dataset is useful for risk assessment or model validation purposes. The type of model used, and the accuracy to which the model predictions are either possible or desired must also be considered. It is probably most cost-effective to accept that all existing environmental monitoring datasets which satisfy the minimum parameter constraints and release history constraints given above, and which meet minimum analytical standards and report concentration data most of which are above the level of detection, have some degree of use for environmental risk assessment and model validation purposes. The degree of usefulness of the dataset should be specified in the context of the model itself. However, it must be established that the model is valid for the conditions that pertain to the dataset, before the data can be used to validate the model.

As an example, consider a Mackay model (Mackay, 1991; Cowan *et al*, 1995) for the distribution of a chemical between different environmental compartments, as currently recommended for screening level risk assessment in Europe. Models of this type generally predict average environmental concentrations to within an order of magnitude, if release is into the compartment in which the component is measured. They are less accurate for predictions for the other environmental compartments (Cowan *et al,* 1995). Consider a chemical continuously released into air, where the annual release amount is known, and found in air, soil and water, the steady-state concentrations in air, soil, and water can be predicted.

Assume that :

1. a site-specific environmental database exists, for which one can verify from site history that all release of the chemical is from a suitable source – i.e. that no accidental release of the chemical has taken place within a time-span which would influence the monitoring results. (This time-span could range from minutes to perhaps centuries, as for a non-biodegradable, highly adsorptive compound accidentally discharged to a static medium such as soil);

2. the chemical releases over a suitable period are known. This gives the required chemical loading input data for the model (note that, in this example, all release is into one compartment – air);

3. the model is capable of predicting concentrations in air, soil and water.

If,

■ the predicted concentrations in one compartment, perhaps soil, are several orders of magnitude below the limits of detection;

But,

■   the soil monitoring data of a suitable standard exist - i.e. one can be certain that the chemical measured came from the soil, and not from the laboratory apparatus used in the analysis - and that these data are predominantly above the limits of detection.

Then,

■   the model, which predicts much lower concentrations is invalid or

■   the model is inapplicable - i.e. the processes which led to the measurable chemical concentrations are not considered by the model.

If one can be certain that the latter case does not apply, then the dataset can be used to invalidate the model, because the model prediction for one compartment, soil, will be invalid.

For another example, start again with the Mackay model described above and follow steps 1 and 2 as before. Now assume that:

3.   for another compartment, perhaps water, a series of monthly grab sample data covering several years exists, and this dataset can be described by a distribution function of a given shape, with mean, standard deviation, maximum, minimum, etc.

Then,

■   model validation will be determined by comparing the model prediction with the mean or range or some agreed statistical measure of the measured data. Bearing in mind the estimated model uncertainty of greater than an order of magnitude, it is likely that the dataset will lie within the model prediction range. In this case the model prediction uncertainty will dominate the exercise - i.e. that the relationship between the mean and the standard deviation of the measured data, or the quality of the measured dataset, will be largely irrelevant. Almost any dataset not dominated by analytical error would be sufficient - and would indicate the validity of the model, within the stated predictive error.

If the compartment above had been the compartment of release, or if a model claiming much improved accuracy, perhaps a detailed site-specific model, had been employed, then the improved accuracy of the model would require a correspondingly greater accuracy in the dataset.

As a final example start again with the Mackay model described above and follows steps 1 and 2 as before. This time assume that:

3.   instead of a highly detailed aqueous dataset, the data consist of a concentration value for a single soil grab sample, which could potentially differ by an order of magnitude from a similar sample taken a metre away;

Then

■   this would not be accurate enough for a detailed site-specific model;

■   and might be questionable for the Mackay model.

The conclusion must be that the uncertainty in the model employed, and the uncertainty analysis of the dataset, must both be considered to ensure that the dataset is useful for modelling and environmental risk assessment.

It is possible that a modeller, in order to validate a model, will need accurate data which is difficult or impossible to obtain in the real world. For example, consider a model which predicts the removal of a biodegradable, sorptive compound in a river. There are two processes, biodegradation and sorption, which will occur simultaneously, as well as different sorptive media and many potential biodegrading microorganisms in the system. In most cases the experimental error of the most accurate measurements will not allow discrimination between the results predicted for different types of biodegradation kinetics in these complex circumstances.

In this case the modeller must consider the predictions of the biodegradation kinetics model, for which validation is needed and of other possible models, in the context of the experimental uncertainty of the monitoring results. This will indicate whether any difference predicted will be determinable from experimental results – and thus whether or not the experimental support for the model is possible.

It is important to recognise that in the strictest sense it may not be appropriate to use monitoring data for model validation - though monitoring data which can be shown to be appropriate can be used to invalidate a model. This arises because it is quite possible to get the right PECs with the wrong model, particularly when substantial averaging or cancellation of errors takes place in the model calculations (Haughs *et al*, 1996). Indeed, the difficulties of validating models such as EUSES are identified by Jager (1995), who concludes that validation should only be undertaken on a module by module basis, and that careful experimental design is needed to address the specific components of the model in question.

5.2.5   Conclusions

In summary, existing data should be used, whenever possible, for environmental risk assessment and model validation purposes. However, it is essential that the dataset contains sufficient information concerning the chemical and the environment, the release history of the chemical with respect to the

monitoring site, and the analytical methods used to determine the concentrations. The definition of sufficiency may vary with the specific chemical, and will also vary with the application - i.e. the type of environmental risk assessment or model validation under consideration. Essentially, the data must be shown to be fit for the purpose for which they are intended to be used.

6. WATER AND SEDIMENT MONITORING

The following discussion describes particular issues relating to collection of data from the aquatic environment.   The intention is to be illustrative rather than comprehensive for all possible chemicals and/or scenarios.   There are numerous procedures and guidelines on the design and execution of environmental monitoring programmes (for example, Bartram and Ballance, 1996; U.S. EPA, 1982; UN/ECE, 1996; Berg, 1982; HMSO, 1986; Groot and Villars, 1995) which should be referred to for greater detail.

6.1 MIXING ZONES

A discussion about mixing zones is a more general topic related to the risk assessment approach. However, it has distinct implications for monitoring at a local level.

In the past there has been much confusion and debate over the definition of a 'mixing zone' and what it really represents, particularly for larger water bodies. However, it is an important concept for local risk assessment and there is a need to address its meaning in the context of risk assessment, particularly with respect to larger rivers, estuaries and open seas.

The TGD suggests that a suitable definition for the mixing zone for river systems is 1 km downstream from a discharge point. This may or may not be a reasonable assumption (depending on the size of the river), since the assumption is that after this distance any substance in the water is uniformly mixed over the width and depth of the river.   In practice, each river is different and the distance to complete mixing can be quite variable. Clearly, if a monitoring programme is intended to represent a scenario of complete mixing, it will be necessary to establish whether this has occurred, which may require monitoring at various depths and across the width of the watercourse at different distances downstream and under various conditions of flow. The PEC_{local} in risk assessment relates primarily to the end of the mixing zone, rather than a fixed, arbitrary, distance from the discharge.   As a first step, an estimate of the mixing length can be obtained by using predictive models such as RIVMODEL (ECETOC, 1994).

In an estuary, the effective dilution is determined more by the tidal regime and local mixing characteristics than by the freshwater flow. When a substance is released it will travel both up and down stream and may be characterised either by a long, thin effluent plume, or perhaps by one that is shorter and wider. Often, this may also only affect the side of the estuary where the discharge is located. Moreover, the effective dilution is frequently much greater than 10 at much shorter distances from the outfall and taking a distance of 1 km may be quite inappropriate.

The OSPARCOM guidelines, for example, take an (arbitrary) 500 m from the outfall and assume a dilution factor of 1000 at this distance for typical produced water discharges from offshore oil platforms. This contrasts strongly with the TGD value of 10 for typical European rivers. Currently there does not appear to be any guidance for estuaries. Intuitively, somewhere between the two would appear to be reasonable.

The reason that this discussion has been included is because it is important to understand precisely the purpose of any proposed monitoring programme. Should estuarine monitoring be undertaken at 1000 m downstream where concentration levels may be too low and too variable to monitor accurately and effectively, or should the definition of the mixing zone for estuaries be modified to allow for local monitoring strategies that are likely to be more successful, but that only give information at 100 m (for example) from the discharge?

Up to 100 m from an outfall it is also much easier to establish local ecological effects of any discharged effluent using standard techniques for quantifying species abundance and diversity. This information can be extremely valuable for quantifying local impact. Further afield, such techniques frequently fail to detect any significant differences between healthy communities and those that might be affected by discharges. Changes in a community can, however, have causes other than pollution. Surely the risk assessment should allow, and indeed welcome, the use of such techniques to help understand the risk of discharging substances in the environment? Again, this would require a discussion of the appropriate distances at which to monitor and raises the question of defining a relevant mixing zone or 'impact zone' for estuaries.

If such considerations are given this will help to define guidelines on the type of monitoring and location of monitoring points that can be used in local risk assessments.

6.2 SITE SELECTION

Most of the considerations for site selection are generic in nature and have been covered in Section 4.1. However, there are some considerations that are specific to monitoring the aquatic compartment.

It is important to understand fully the nature of the receiving water body. Sampling programmes will become complex where wide variations caused by extreme changes in temperature, flow patterns or intermittent discharges occur. The most important factors to be considered when choosing a river site are the flow characteristics. Flow characteristics which will influence the degree of dilution and mixing include the total flow rate (volume/time), the current velocity, the depth, and the degree of turbulence caused by irregular channel or bottom features. The direction of flow may be changeable. In particular, details of tidal limits, locks, navigational use or recreational use and major confluences should be known. The flow rate may vary considerably and be more dependent on the amount of

navigational use (number of locking operations, for example,) than upon prevailing weather conditions. Similarly, any abstraction or discharge points can affect significantly river flows and all such features should be identified and the relevant abstraction or discharge volumes obtained, plus any potential variability due to batch discharges etc.

Weather conditions which will interfere with a sampling schedule such as flooding or ice need to be considered.   It is likely that water and sediment samples will need to be taken by boat so that dangerous currents or obstructive conditions such as dams, low bridges, etc. need to be considered.

6.3 SAMPLE LOCATIONS AND INTERVALS

The spatial distribution and sampling frequency will depend directly on the objectives of the monitoring programme

In surface waters a targeted approach is usually required, which takes account of prior information about where and when a chemical might be found. This is normally the most cost-effective approach. The sampling locations and frequency must represent the anticipated spatial and temporal variability in river flows and discharge volumes or concentrations. The discussion on mixing zones in the previous section is also relevant and it may be necessary to target effluent plumes to facilitate a proper interpretation of the results.   Sampling locations outside mixing zones, particularly in large water bodies such as estuaries and open seas, may yield concentrations that are simply too low to measure or require expensive 'accumulative' sampling techniques.

For rivers, a number of features regarding sampling location and frequency are common to many monitoring programmes. A background (upstream) concentration should be measured at a site shown not to be contaminated with the discharge. Effluent samples at the discharge point are normally required and a number of points downstream, depending on the scale and objectives of the monitoring programme. As well as the chemical monitoring data it is normally essential to record the discharge and river flows during the sampling period.

The spatial distribution of sampling points depends largely on the homogeneity of the actual distribution of a chemical, which can be affected by many different factors.   Stratification in the receiving water will affect the concentration at different depths so that the depth of sampling is an important variable. Differences in temperature or density between the effluent and receiving water will also influence the distance the effluent plume will travel downstream before it is well mixed. The use of mathematical models, from simple flow models to complex computer models, can be extremely useful for estimating the flow-mixing properties and choosing appropriate sampling locations.

The temporal variability of concentrations will often determine whether sampling should be continuous or discrete. However, this may also depend upon available resources and the constraints of the analytical method. Continuous measurements of a property such as conductivity can give a complete and continuous picture of all changes over time. Usually, discrete samples are taken at specific time intervals. These samples may be taken for a long duration through pumping a large sample volume or through the use of some chemical extraction procedure (ion exchange resin, non-polar sorbent, etc.). Alternatively smaller single samples may be taken at a specific instance in time (grab sample). Often large dilution factors are found in water analysis so that the chemical must be extracted and/or concentrated to reach detectable amounts, depending upon the constraints of the analysis. In these instances, large sample volumes are required or smaller samples may be composited.

Sampling of bed sediment is usually limited to the surface layer of the bottom of the river or other water body. Normally it is the horizontal spatial distribution that is of interest, but for some longer term studies the concentration profile of a chemical with depth in the sediment can provide useful information on the history of contaminant deposition. However, the accuracy of such determination depends very much on the sampling method deployed and the conditions of formation of the sediment and its stability.

Much more detailed information, advice and guidance on water monitoring is given in the papers by Berg, (1982), Plumb, (1981) and Greenberg *et al* (1985), WRc (1989), Kristensen, (1996), Kristensen and Bogestrand, (1996), Nixon *et al* (1996).

6.4 USEFUL SUPPLEMENTARY DATA

Numerous aspects of the sample, beyond its size and the concentration of the chemical, provide useful data in determining sample representativeness or in interpretation of the chemical concentrations in the context of risk assessment.

One of the most important aspects of water sampling is the flow rate. A number of devices are available which can be used at the time of water sampling to measure concurrently the flow.

Some characteristics of the sample may be measured in the laboratory. Many of these parameters relate to the bioavailability of the chemical to cause toxicity in aquatic species. Sediment adsorbed chemical is not likely to be fully bioavailable, nor produce the same toxic effect as chemicals in free solution. Similarly, dissolved organic carbon will affect the bioavailability of chemicals. The toxicity of metal ions and of ionisable species are greatly affected by the pH and by the presence of other ionic species such as calcium and magnesium. In the case of these types of substances, the chemical species measured, oxidation state, etc. needs to be appropriate to the toxic effect to which it is compared and not measured as total chemical. For water, useful support analyses include suspended

sediment concentration, dissolved organic carbon concentration, alkalinity, hardness, etc. depending upon the specific chemical interactions of the chemical of interest. Analogous data in sediment are particle size distribution, organic carbon content and ion exchange capacity.

Other sample characteristics may provide information on the type of environment that was sampled and how much it may have been impacted by pollution. Data on salinity, temperature, hardness, buffering capacity, etc. help define the general water quality. Data on the dissolved organic carbon and biochemical oxygen demand may be used to evaluate the extent of pollution. Direct measures of contaminants such as ammonia, heavy metals, cyanides, or specific pollutant chemicals are also useful in putting the data into the risk assessment context. Finally, ancillary data on the presence of micro-organisms, higher organisms, coloured matter, surface films, etc. may also be valuable indicators of the type of water or sediment sampled.

Table 3 summarises some of the main considerations for monitoring programmes which relate specifically to surface waters and sediment.

6.5 SPECIFIC CONSIDERATIONS FOR MARINE ENVIRONMENTS

Monitoring in estuaries, coastal waters and open seas requires some specific considerations which are not always appropriate to address in river systems. There are many factors that distinguish marine systems from freshwater, but in terms of monitoring the environment and the implications for risk assessment two, in particular, demand consideration:

■   much larger volumes of water result in higher dilution;

■   coastal systems are normally influenced by the tide.

The first point above is particularly important with respect to detection levels. Quite simply, if concentrations are very low it may be difficult to measure them, even with advanced analytical techniques, and the volumes of water available for dilution are often such that levels may fall below detection limits within a short distance from a discharge point. A 2 km^2 area around an oil platform in the North Sea, for example, will contain six hundred million cubic metres of sea water (= 6×10^{11} litres). Moreover, the nature of turbulent mixing in the North Sea, together with the elliptical motion of the tidal currents, means that any discharged effluent will normally cover an area much larger than this within a very short space of time.

If such low concentrations are to be measured, it is necessary to apply the right sampling technique. There are, for example, water samplers which can concentrate several hundred litres of sea water on a filter and adsorption resin. This, however, makes sampling relatively time consuming and expensive.

The implications of this are that it may be extremely difficult to measure anything at a remote distance from any discharge location (at least in the water phase), and for most substances it will be necessary to undertake monitoring close to outfall locations in order to detect and quantify the amount entering the environment. Thus local monitoring may be the only realistic option for some substances.

An exception to this might be for high volume discharges of substances which are persistent in the environment. Such substances, released over time, may build up to detectable concentrations at more remote locations. The adsorption characteristics however, and potential for bioaccumulation will also provide important indicators in such cases on which compartment (water, sediment or biota) should be monitored to look for elevated concentrations on a regional scale.

The second point concerns tidal effects. Many tidal phenomena are extremely complex and the potential list of specific considerations for risk assessment of the marine environment is large. However, in terms of monitoring the main factor is that the tide goes in and out. Thus a substance discharged at one moment may be travelling north with the tidal current, whereas in six hours time it may be travelling south. Over the space of a few hours therefore, given the dilution characteristics outlined above, the concentration at any one location close to the discharge point may vary over several orders of magnitude, depending on which direction the tide happens to be flowing. Hence any local monitoring of the tidal environment will need to be targeted to take into account the direction of the tide, in order to be able find detectable levels.

There is another important consideration for tidal and other time varying exposure scenarios in that different organisms will 'experience' different exposure times. Risk assessment of environmental discharges is normally based on PEC/PNEC ratios. As a result, application of a PNEC based on regular acute toxicity tests and accepted safety factors will over-estimate the risk, because the real life exposure dose (time × concentration) is much lower than the corresponding dose from a laboratory experiment at a fixed concentration of the actual chemical. Monitoring should therefore be designed to give time variable concentration fields, or exposure doses in the actual area. Alternatively, or additionally, monitoring of body burdens of the discharged compounds in biota can be performed. Such data can be used alongside models which predict the dilution, exposure, effect and environmental risk on a local and regional scale.

Much the same sort of considerations must be given to estuaries as to the open sea. Both are characterised by tidal regimes and much larger volumes of water available for dilution. Estuaries tend to be much wider towards the sea, and discharges on one side of an estuary may not have any impact on the opposite bank, depending on wind speed and direction etc. Thus any 'local' monitoring must often be targeted in the same way as in the open sea, also taking into account the turning of the tide, in order to detect measurable concentrations. This also raises the concept of mixing zones, which is discussed in a previous section.

Table 3: Considerations for the Design of Water and Sediment Monitoring Programmes

Specific type of information needed to meet the objective of the programme

1. Technical Aspects of Sampling
   (See Table 1)

2. Technical Aspects of Analysis
   (Once a representative homogeneous sample has been obtained, the details of analysis are generic regardless of the compartment or medium being analysed. However, a few are more specific to water and sediment)

   a. Techniques for concentration or extraction from dilute aqueous solutions
   b. For water, will the concentration measured be the total (water and suspended solids) or that of the water only?
   c. For sediment, will the concentration be reported on a dry or wet weight basis?

3. Quality Control and Quality Assurance
   (Quality control aspects of studies are generic and not dependent upon the medium – see Table 1)

4. Sample Location in Time and Space
   a. Select sample locations: distance up and down stream, control sites, transects, distance apart, distance from river bank, proximity to obstructions or structures causing water flow changes, depth, etc. For bottom sediment select depth from which the sediment the sample will be taken
   b. Select sample frequency and duration: continuous or discrete, automated or manual, time intervals between samples
   c. Decide on compositing (flow or time related) samples from different locations or different time periods
   d. Select season, days of weeks, time of day for sampling

5. Sample Characterisation
   a. For water, decide on measurements of the following:
      i. Temperature
      ii. Suspended solids content and dissolved organic carbon content
      iii. Water chemistry (hardness, salinity, alkalinity, pH, other depending on concerns)
      iv. Indicators of pollution (dissolved oxygen, oxygen demand (BOD/COD), H_2S etc.
      v. Inorganic contaminants (nitrate, nitrite, ammonia, sulphate, phosphate, metals etc.)
      vi. Organic indicator of pollution (specific contaminants)

Table 3: Considerations for the Design of Water and Sediment Monitoring Programmes

b. For sediment, decide on measurements of the following:
  I.   Temperature and pH
  ii. Total organic carbon content
  iii. Physical properties (granularity, density, ion exchange properties)
  iv. Characteristics of overlying water (as in 5a. above)

6. Environment Characteristics
  a. Select the water-body which meets the study objectives with respect to:
    i.   Type (lake, canal, river, estuary, coastal or open sea)
    ii. Flow at time of sampling (current speed, flow volume, tidal range, phase of the lunar cycle, spring tide, neap tide, high water, low water, none)
    iii. Size (width, depth, volume)
    iv. Ancillary information (abundance and diversity of aquatic and benthic biota, bottom characteristics, shoreline biota, etc.)
  b. Take the following characteristics into account when selecting a site:
    i.   Distance downstream from WWTPs and industrial effluents of the same chemical
    ii. Land usage (residential, industrial, mixed-use, agricultural, natural)
    iii. Representative water traffic (major port, barge transport, pleasure boats, none)
    iv. Water quality (polluted, un-impacted, eutrophic, oligotrophic etc.)

7. Local Source or Site Characteristics
  (Local site characteristics and representativeness are generic considerations and not dependent upon the medium. However, a few are specific for water.)

  a. Does all aqueous effluent undergo wastewater treatment (storm water runoff, cooling water, etc.) and what is the type, flow rate, etc. of the WWTP or is it discharged untreated?
  b. Is the chemical process used wet or dry?
  c. Is the process used typical of the industry or unique to this manufacturer or location?

8. Reporting
  (Reporting aspects of studies are generic and not dependent upon the medium)

However, there are some important differences between estuaries and open seas which may have implications for monitoring :

■ the estuarine environment is much more compact than the open sea and often contains a much wider diversity and abundance of wildlife;

■ the tidal effect is such that substances may remain in the estuary and potentially accumulate for several tidal cycles (perhaps hundreds), depending on the degradation characteristics of the substance, and the location of the discharge in terms of distance from the sea;

■ many industrial sites are located on estuaries;

■ there are often several discharges from different industrial and domestic wastewater sites in one estuary, each discharging different types of effluent.

All the above points recognise that estuaries are potentially more vulnerable environments than the open sea but they are also naturally robust and capable of withstanding extremes such as wetting/drying, fresh/saline waters and freezing/baking. Monitoring activities should be tailored to take this into account, and will vary from estuary to estuary depending on the local geomorphology and ecology.

6.6 SAMPLING TECHNIQUES

6.6.1 Sediment Sampling

Oslo and Paris Commission (OSPAR) guidelines for environmental monitoring in the vicinity of offshore petroleum installations (OSPAR, 1990) should be referred to for detailed advice on sediment sampling.

Generally an undisturbed surface sample of the sediments is collected. The guidelines specify the minimum volume and surface area for a sample to be accepted for biological (taxonomic) and chemical analysis. Five replicate biology and three replicate chemistry samples are required from each sampling site. Sampling is performed both along local transects around each platform depending on water current situation, and regional grids covering a larger area. Sampling frequency and the number of sampling sites is set by the national government in co-operation with the industry.

A number of different grab samplers have been recommended and utilised during the 25 year period of offshore environmental monitoring in the North Sea. The two most frequently applied grab types today are the box-corer and the Van Veen grab.

The box-corer

This grab gives an excellent, undisturbed surface sample, and has been frequently used in monitoring surveys. Many types of box-corer grabs are available, designed to give different sample sizes for different sediment types. In general, however, the box-corer only operates well in relatively soft sediments like clay and silt.

The Van Veen grab

The Van Veen grab was originally designed for sampling of biological samples, and may give problems if used to collect samples with undisturbed surfaces. This is because the water is not allowed to flow through the sampler as it is lowered towards the seabed, resulting in the formation of a shock wave in front of the grab. The Van Veen grab is however excellent for retrieving sediment samples under most circumstances, and is extensively applied in offshore sampling surveys.

The Shipek grab

This grab was especially designed for extremely hard sediments, and is mainly applied for chemical sampling, because of the limited sample volume collected. In some situations, the Shipek grab has been used to sample for biological analysis, by combining several grab samples to make one sample replicate.

6.6.2 Water Sampling

Direct water sampling

Solvent extraction of water samples may be carried out either on site or back in the onshore laboratory. Unless filtration of the water is included in the sampling procedure, this technique will provide the total concentration of the target compound in the water phase. Typical sample volumes are between 1-10 L, resulting in relatively high limits of detection for the target compounds. Extraction of large water volumes is relatively time-consuming and labour intensive.

Large volume extraction

Extraction of large water volumes in the field can improve detection limits and reduce the amount of work involved. The analysis will represent the total fraction of the pollutants present. Such techniques may be sensitive to vigorous movement of a ship, and bad weather can be a problem.

Solid phase extraction (SPE) is an alternative approach. Extraction discs/filters and cartridges coated with a suitable adsorbent can be used to extract trace compounds from large water volumes, and thus concentrate the target compounds in the monitoring. Normally, these techniques will give the total fraction of the pollutant present, and are comparable to the techniques described above. Combining the extraction disc or cartridge with a pre-filtering step can provide additional information about the particle adsorbed and water dissolved fractions. An exception to this rule is the solid phase micro extraction (SPME) method, which measures only the dissolved fraction of the analyte in the water column (see Appendix E).

Extraction through adsorbents can also be performed by deploying sampling devices which are designed to pump large water volumes through combined filter and adsorption resins, in the desired distance from the source and water depth.

Living organisms (see Chapter 7)

In many cases, the most interesting and relevant information is connected to the bioavailability of the discharged pollutants. Deployment of mussels in cages has frequently been applied for offshore monitoring. The concentration of target compounds in the mussel reflects the total available fraction present in the water column. A number of limitations are connected to this method. Only compounds with a certain accumulation potential can be monitored, and metabolism in the mussel may cause problems for the interpretation of the results. The mussels have to be present in the environment for a relatively long time, and may thus not reflect a realistic exposure situation. The mussel method has, nevertheless proven to be extremely powerful for monitoring of low concentrations of lipophilic compounds even in relatively rough environments. A large number of field studies employing different organisms for determination of presence, uptake of effect of various chemical compounds can be found in the literature.

Semi-permeable membrane devices (SPMD) (see Appendix E)

SPMDs were originally designed as an alternative to blue mussels (*Mytilus edulis*). Being a synthetic, non-living lipid membrane, improvements are obtained in precision and accuracy of the system. Whether direct comparison to blue mussels is possible is still a matter of debate. Many results suggest that SPMDs are only suitable to measure the water-soluble fraction of the bioaccumulated compounds. The blue mussels method is however proving to be both sensitive and reliable.

Direct sampling of living organisms.

Often, sampling and analysis of organisms living as natural inhabitants in the actual area may prove appropriate. For monitoring in open sea, sampling of fish or plankton are frequently applied techniques.

Again, understanding of the exposure regime and history of the organisms are important criteria for achieving valuable information. International accepted standards for such sampling and analysis are available, and should be followed (ICES, 1987).

Sampler type	Sample type									
	Total	Dissolved	Adsorbed	Bioavailable	Sensitivity	Reliability	Time Needed	Cost	Local	Regional
Direct water sampling and analysis	++	++ 1)	++ 1)	-	-	+	+	+	+	-
Liquid/liquid solvent extraction	++	++ 1)	++ 1)	-	+	-	-	+	+	+
Solid phase extraction	++	-	-	-	-	-	-	-	+	-
In situ large volume extraction	++	++	++	-	+	-	+	+	+	+
Semi-permeable membrane device (SPMD)	-	++	-	+	+	+	-	-	+	+
Solid phase micro extraction (SPME)	-	++	-	-	-	+	++	+	+	-
Blue mussels	-	-	-	+	++	+	-	-	+	+

+ represents strength of a sampling method within a certain area, while - indicates that the method has weaknesses in this area.

The terms total, dissolved, adsorbed and bioavailable indicate the state of which the pollutant is present in the water column. In particular, bioavailable means the fraction of the pollutant which can be accumulated in living organisms.

Sensitivity reflects the ability of the method to reach low detection limits of the target compounds. This is also reflected by the columns for local and regional.

Cost: a positive indication in this column indicates that sampling and analysis can be performed at relatively low costs.

1) Requires pre-filtering

7. BIOTA AS SAMPLERS FOR CHEMICAL MONITORING

Lliving organisms ('biota') are frequently used as sampling devices for environmental monitoring of chemicals with a potential for uptake and accumulation in tissue. The potential for uptake and bioaccumulation is controlled by:

■   rate of biodegradation/catabolism in organisms;

■   the potential to be retained by lipophilic material present in biota.

Such sampling may be designed by collecting species which are naturally present in a certain area, or by placing homogenous selections of certain species in fixed positions in the area of interest. These methods are applied for monitoring both sediments and the water column.

In general, using biota as samplers for chemical monitoring of lipophilic compounds provides a number of advantages compared to conventional water and sediment sampling, especially with respect to sampling at large distances from a discharge source or on a regional scale. The benefits include:

■   a more convenient approach than extracting huge amounts of water in the laboratory directly or by means of an artificial extracting material like XAD-resin or polyurethane;

■   a closer relation with risk assessment, because the body burden may be related to toxic endpoints.

There are, however, also certain clear limitations and disadvantages connected to this approach, which it is important to keep in mind when designing a monitoring study. Depending on the choice of target compound and species, sensitivity can be significantly improved by biota sampling. On the other hand information gained from such sampling and the subsequent analysis may be specific for the species in use, and thus of limited value with respect to general applicability for the monitoring area. Factors like feeding habits, metabolism, movement and fat content of the applied monitoring organisms may influence the results dramatically. Using such data for environmental risk assessment is therefore a challenging task, and requires model tools that contain more comprehensive approaches to risk calculation than the traditional PEC/PNEC approach. The introduction of time-variable exposure doses and NOECs related to body burden are vital parameters for a successful risk assessment based on such monitoring results.

A few examples of applying biota as monitoring tools are given below.

Fish

The concentration of certain chemical compounds in fish may be of particular interest both from an environmental and a commercial viewpoint. In the North Sea a number of fish monitoring surveys have been performed during the past decade. Monitoring of persistent organic pollutants (POPs) in fish has been proposed by OSPAR and analysis of PAH in fish is included in the guidelines for environmental monitoring of the petroleum activity in the Norwegian sector of the North Sea issued by the Norwegian State Pollution Control Agency (SFT).   The experience with these analyses so far is that fish, because of their high metabolic activity and mobility, are not especially well suited for such monitoring purposes. On the other hand, significant increased levels of petroleum-related hydrocarbons have been detected in fish from certain areas and such findings clearly defend the establishment of systematic monitoring programmes.

Because many fish migrate randomly within large areas, the application of fish species for monitoring discharges from point sources is difficult, if not impossible. Collecting free-living specimens will mainly serve regional monitoring programmes, where multiple discharge sources are present. Another approach to the application of fish as monitoring "samplers" is to cage a number of individuals of the same species at a fixed point with respect to the location of a discharge source or a defined monitoring area.

Mussels

Mussels (*Mytilus edulis)* are frequently employed in environmental monitoring studies, and are, because of their low metabolism and strong resistance towards rapid environmental changes, very well suited for this purpose. A number of monitoring surveys employing mussels have been carried out both in open sea, and in coastal zones (Goldberg *et al*, 1978). Using mussels as sampling devices for chemical analysis of lipophilic compounds provides the analyst with an extremely sensitive tool for determining low concentrations of the target compound in the water phase. However, caution must be taken when evaluating the results from mussel monitoring, since the results obtained can not be transformed directly into the representations of any particular fraction of the chemical in the water phase (i.e. dissolved, adsorbed, metabolised).   On the assumption that the substance is not metabolised, then the amount of that substance that has accumulated in the mussels reflects a total bioavailable fraction in the monitoring area.   Because of the characteristic and specific biological properties of the test animals however, these results cannot be directly extrapolated to other species. Furthermore, the presence or absence of a substance in mussels cannot be taken as evidence of general absence in biota since the rate of metabolism can vary from species to species. Providing knowledge of the metabolism in known, then results from mussel monitoring may reflect a "worst case" bioavailable fraction of the target substance for a number of species, and may thus be applied in risk assessment calculations.

Marine mammals and birds

These organisms generally occupy the higher trophic levels, such as predators, and bioaccumulation is mostly via biomagnification from food. The half-life in these organisms is generally greater than for other aquatic organisms due to their different physiological systems. Although the metabolic conversion rate of persistent contaminants is generally higher than in fishes, the overall elimination rate from the mammalian and avian organism appears to be lower than in other aquatic organisms. The measurement of concentrations in bird's eggs can also be useful. The concentration in an egg may however depend on whether it is the first or last laid. Although they may not necessarily be typical, tissue analysis of marine mammals and birds, found dead, may provide a lot of information on background contamination of the environment. In this connection realistic risk assessment models including time-variable exposure and body-burden based risk and effect assessment will become more important.

Human adipose tissue, human milk fat, blood lipids

Sampling and analysing of these biological materials provides information on the background exposure of man to persistent lipophilic substances. As part of US-EPA efforts to assess the potential exposure of humans to these compounds, human adipose tissues were collected through the EPA's National Human Adipose Tissue Survey (NHATS) repository for analysis (Stanley *et al,* 1991). In the scope of her thesis, Krüger (1988), studied the presence of persistent organohalogens in freshwater fish and human milk fat. The results of these surveys provide information on the actual body burden of these materials. In connection with data on toxicity studies with information on body residues the ratio between NOEL and actual tissue level (margin of safety) is indicative of the extent of the health hazard of individual substances.

Usefulness of sediment and biota monitoring: interpretation of data

When chemicals degrade slowly in the environment and have a relatively high log k_{ow}, they accumulate until the input to and elimination from the environment are in balance. The chemicals present in air, water, soil and sediment may end up in biota. The half-life in sediment and biota for these compounds is mostly months to years. Sampling sediment and biota once or twice a year and analysing the samples may therefore provide a good indication of the contamination of these environmental compartments.

Fine particles and colloids will also end up in the sediment, but may not be found in biota. In addition, it is possible to find contamination of the sediment with organic compounds which have such a low solubility and have such a large molar volume that bioconcentration and biomagnification do not, or

hardly, occur. In the following, some examples of bioaccumulating and inert substances will be discussed.

Watanabe *et al* (1987) studied the occurrence of polychlorinated and polybrominated aromatic compounds in the Japanese marine environment (see Table 5).

Table 5: Concentrations of PCBs and polybrominated aromatics in the marine environment

Osaka area	PCB content (ppb)	Tetrabromo-diphenyl ether (ppb)	Decabromo-diphenyl ether (ppb)
River sediment dry weight	1000 - 7700	<2 – 31	33 –375
Estuary sediment dry weight	410 - 4400	<2	<5 – 20
Mussels wet weight	85 - 479	1.6 - 14.6	<0.5 - 1.4
Fish wet weight	21 - 135	~ 0.1	<0.5

According to de Boer (1995) there is a close correlation between organohalogen contaminants in sediment and in the liver of yellow eel or cod, if sampled at the same location. This was essentially true for PCBs and tetrabromodiphenylether. However, the table above demonstrates that the biota will not always be the site of maximum accumulation even when log $k_{o/w}$ is high. Decabromodiphenylether does not follow this finding, probably due to the superlipophilic character of this compound with the corresponding extremely low water solubility or due to the molecular volume, which hinders the permeation of biological membranes. From experimental bioaccumulation studies with compounds like the structurally-related decabromobiphenyl, it was observed that these types of compounds do not bioaccumulate at all (Chemicals Inspection & Testing Institute Japan, 1992). So comparison of the levels in sediment and in biota does not provide information on the bioaccumulation potential of organohalogens. The tendency to bioaccumulation decreases with increasing halogenation of organic aromatics, although these compounds can be detected at considerable levels in the sediment of the aquatic environment.

In addition, analysing biota for environmental contaminants like PCBs provides interesting information on the metabolic capacity of organisms in the food chain. Kannan *et al* (1995) showed that the presence of vicinal H-atoms in PCBs makes them more susceptible to metabolic degradation in biota and this enhancement of biodegradation was higher with increasing trophic level. The concentrations (on lipid basis) of PCBs with vicinal H-atoms in both aromatic rings was comparable along the food chain from diatom through to porpoise, but for PCBs without vicinal H-atoms the levels were 10 to 20 times higher in porpoises than in diatoms.

So the absence of bioaccumulation of lipophilic compounds through the food chain may have the following causes:

■   their molecular volume is too high to pass biological membranes (Opperhuizen *et al*, 1985);

■   their solubility is too low to enable absorption;

■   their catabolism prevents bioaccumulation.

8. CONCLUSIONS AND RECOMMENDATIONS

■ to be valid for use in risk assessment, the most important factors to be addressed when reviewing monitoring data, or planning new programmes, are the quality of the data and the representativeness of the sample(s).

■ it is not a foregone conclusion that PECs based upon measured concentrations will take precedence. It must be clearly demonstrated that the monitoring data are representative of the intended scale, setting, scenario, life stage, etc. If this is the case, the monitoring data may be used to derive environmental concentrations, to validate the exposure model and/or be used for improvement in default emission assumptions.

■ monitoring and laboratory data have integral roles alongside fate and exposure models in comprehensive risk assessments.

■ by using monitoring and laboratory data to calibrate fate and exposure models for a particular chemical and environmental compartment, and monitoring data to verify and validate these models, greater confidence can be placed in the resulting risk assessment and conclusions based on it.

■ there is no one way to do 'good' monitoring. For example, spatial distribution and sampling frequency are key to the quality of a dataset, but the criteria by which these attributes are judged will depend directly on the objectives of the monitoring programme.

■ monitoring programmes should be designed to meet the specific objectives of the study e.g. assessment of water quality, PEC_{local} or $PEC_{regional}$, either targeted or comprehensive exposure and risk assessment. The monitoring site or sites should be selected accordingly.

■ once a site is identified which is consistent with the goals of the monitoring programme, a sampling protocol, which is also consistent, needs to be developed.

■ monitoring data can be used in a straightforward manner to carry out site-specific or local risk assessment, provided that sufficient information on the chemical and the environment, the release history of the chemical with respect to the monitoring site and the analytical methods used to determine the concentrations is available.

■ whenever possible, existing monitoring data should be used for environmental risk assessment and model validation. However, it is essential that the data set contains appropriate information and is shown to be fit for purpose.

■ the use of monitoring data for regional risk assessment will be a possibility in the future, when the data necessary to relate the characteristics of a monitoring site to the distribution of site characteristics for the rest of Europe have been identified, collected, accepted and released for general use. These data

may include distance from, and concentration at, release, and environmental characteristics determining residence time of the chemical in that environment.

When designing new monitoring programmes the following points are recommended:

■ use clearly-defined monitoring objectives to determine the sampling strategy which, in turn, should promote an efficient, relevant and cost-effective programme;

■ involve all interested parties from the early planning stages to optimise knowledge and resources and maximise acceptance and communication of the study;

■ field trips to select thoroughly 'characterised' sites;

■ a preliminary study to confirm suitability of sites and applicability/feasibility of analytical methodology;

■ once a site is identified which is consistent with the goals of the monitoring programme, a relevant sampling protocol needs to be developed;

■ both the choice of the site(s) and the monitoring data must be associated with a particular scenario in order to be of use in establishing the realistic risk scenario, the 'reasonable worst case' or 'representative or realistic case';

■ use validated sample preservation, quality assurance and control procedures;

■ organise an appropriate supporting programme so that the results may be placed in context;

■ audit the programme regularly and modify if and as necessary;

■ develop an effectively planned and implemented reporting procedure to deliver the information gathered to all parties interested in the scenario;

■ the ultimate goal of monitoring is to provide information to meet well-defined objectives. The reliability of the information must be checked in the light of these objectives;

■ monitoring results should be summarised in order to draw conclusions about, for instance, the real concentration or the representativeness of the reported numerical values of the total group of samples.

In addition:

■ an effort should be made to harmonise monitoring programmes across Europe and ensure appropriate data logging and data access. Ideas of how to harmonise monitoring and incorporate the wealth of data that exists into a database should be investigated.

■ guidelines should be developed and agreed to ensure ready availability and transparent access of data via standardised procedures. A dedicated data centre whose role is to co-ordinate data acquisition and dissemination may be a cost-effective way of achieving this goal;

■ for future programmes, it is recommended that representative areas and sites be developed to represent specific scenarios for river basins as part of the Proposed Framework for Community Action in the Field of Water Quality. Representative regions should also be developed, and used to define local and regional scenarios for the assessment of substances under the Technical Guidance Documents on Risk Assessment.

■ if the monitoring data and model predictions are substantially different, then an explanation should be sought.

GLOSSARY

Advection	Physical transport or movement of a substance with its medium (air, water, sediment).
Assessment (as distinct from analysis)	The combination of analysis with policy-related activities such as identification of issues and comparison of risks and benefits (as in risk assessment and impact assessment)*
Background Concentration	The concentration of a chemical in a medium prior to the action under consideration or the concentration that would have occurred in the absence of the prior action*. For some chemicals geogenic sources will contribute to the background concentration.
Bioavailability	The ability of a substance to interact with the biosystem of an organism. Systemic bioavailability will depend on the chemical or physical reactivity of the substance and its ability to be absorbed through the gastrointestinal tract, respiratory surface or skin. It may be locally bioavailable at all these sites. *
Blank	Is used interchangeably with the term "control". *
Catchment	The area from which rainfall flows into a river. (ODEng.)
COD	Chemical Oxygen Demand – The amount of oxygen consumed by a specified oxidising agent during chemical oxidation of the matter present in a sample.
Co-kriging	See kriging
Compliance	In accordance with legislative or regulatory requirements. *
Composite Sample	Two or more samples or sub-samples mixed together in appropriate proportions (based on either time-related or flow-related measurements)
Control	A treatment in a study that duplicates all the conditions of the exposure treatments but contains no test material. The control is used to determine the absence of substance under basic study conditions
DOC	Dissolved organic carbon.
DOM	Dissolved organic matter.
ECIMOS	ECETOC integrated modelling system for use in risk assessment
EINECS	European Inventory of Existing Commercial Chemical Substances: a list of all chemicals either separately or as components in preparations supplied to a person in an EC Member State at any time between 1 January 1971 and 18 September 1981.
EMEP Network	Protocol on long-term financing of the Co-operative Programme for Monitoring and Evaluation of the long-range transmission of air pollutants in Europe.
Emission	Release of a substance from a source, including discharges into the wider environment. *

Environmental Compartments	Subdivisions of the environment which may be considered as separate boxes, and which are in contact with each other. A simple model would separate the environment into air, water, and soil, with biota, sediment (bottom and suspended), layering of water bodies, and many other refinements being allowed if data to support their inclusion are available. Concept from Mackay (1991).
Existing Chemicals	Chemicals listed in the EINECS (EU legislation). See also EINECS.
Exposure	1) Concentration, amount or intensity of a particular physical or chemical agent or environmental agent that reaches the target population, organism, organ, tissue or cell, usually expressed in (numerical) terms of substance concentration, duration, and frequency (for chemical agents and microorganisms) or intensity (for physical agents such as radiation), and
	2) process by which a substance becomes available for absorption by the target population, organism, organ, tissue or cell by any given route. *
Exposure Scenarios	Descriptive pathways which describe the specific release pattern of a chemical into the environment, and the specific properties of that environment which will influence the fate of the chemical within it.
Fate	Disposition of a material in various environmental compartments (e.g. soil or sediment, water, air, biota) as a result of transport, partitioning, transformation, and degradation. *
Hazard	The set of inherent properties of a substance or mixture which makes it capable of causing adverse effects in man or to the environment when a particular level of exposure occurs. c.f risk. *
HPVC	High production volume chemical. See also EINECS.
IUCLID	Programme developed by the European Chemicals Bureau to facilitate access to and query of data on Existing substances. Currently contains data on HPVC chemicals. See also EINECS.
Kriging/Co-kriging	Kriging is a method of analysing data taking advantage of the fact that the measurements taken are correlated, i.e. they follow a pattern. By analysing the observed data, one can estimate the pattern of distribution of the endpoint and make a more accurate prediction of its concentration at a point one has not sampled. In *co-kriging* one also measures other variables at each location which are related to the endpoint in some known way and use those patterns of distribution to further refine the estimate of the desired endpoint. For example, if the analyte of interest tends to aggregate in specific soil types, knowing the pattern of soil types in the region will give additional information to use in estimating the unknown.
Local Scale	A specific concept in EU Environmental Risk Assessment, which defines a specific or local release site. Further details may be found in the TGDs.
Measurement Error	Error that results from an inaccuracy and impression in the measurement of parameter values. *
Mixing Zones	Sections of water downstream of a discharge, with in which the discharge and the receiving water have not yet been fully mixed.

Model	A formal representation of some component of the world or a mathematical function with parameters which can be adjusted so that the function closely describes a set of empirical data. A *mathematical* or *mechanistic* model is usually based on biological, chemical or physical mechanisms, and its parameters have real world interpretations. By contrast, *statistical* or *empirical* models are curve-fitted to data where the mathematical function used is selected for its numerical properties. Extrapolation from mechanistic models (eg. Pharmacokinetic equations) usually carries higher confidence than extrapolation using empirical models (e.g. the logistic extrapolation models). A model that can describe the temporal change of a system variable under the influence of an arbitrary "external force" is called a *dynamic* model. To turn a *mass balance* model into a dynamic model, theories are needed to relate the internal processes to the state of the system, expressed eg. in terms of concentrations. The elements required to build dynamic models are called *process* models. *
Model Error	The element of uncertainty associated with the discrepancy between the model and the real world. *
Monitoring	Long-term, standardised measurement, evaluation, and reporting of specified properties of the environment, in order to define the current state of the environment, and to establish environmental trends. Surveys and surveillance are both used to achieve this objective.
Monitoring Strategies	Approaches used to achieve the objectives of a monitoring exercise within the constraints of available resource and manpower.
New Chemicals	In the EU, those produced since 18th September 1981. They are not listed on the EINECS.
Observation	The practice of seeing and noting
Parameterise	The allocation of values to the variables.
Parameter Uncertainty	The element of uncertainty associated with estimating model parameters. It may arise from measurement or extrapolation. *
PEC	Predicted Environmental Concentration. The concentration of a chemical in the environment, predicted on the basis of available information on certain of its properties, its use and discharge patterns and the quantities involved. *
PEC_{local}	In the EU TGDs, the PEC predicted for the vicinity of a point source eg, a production or formulation site, or for a wastewater treatment plant.
$PEC_{regional}$	In the EU TGDs, the PEC averaged over a standard European region of 200km x 200km, with twice the average European population density and production capacity.
PNEC	Predicted No Effect Concentration: environmental concentration which is regarded as a level below which the balance of probability is that an unacceptable effect will not occur.
Probablistic	The characterisation of a property by a distribution function (incorporating distribution shape, standard deviation, mean, median, and other statistical descriptors) rather than by a single value.

Reasonable Worst Case	Reasonably unfavourable but not unrealistic situation. Combining the most adverse environmental circumstances and worst-case release parameters necessarily results in an unrealistic over all worst-case estimation, which is extremely unlikely to occur. *
Receiving Water	Surface water (e.g. in a stream, river or lake) that has received a discharged waste, or is about to receive such a waste (e.g. just upstream or up-current from the discharge point). *
Reproducibility	Measure of the extent to which different laboratories obtain the same result with the same reference test compound. *
Risk	The probability of an adverse effect on man or the environment resulting from a given exposure to a chemical or mixture. It is the likelihood of a harmful effect or effects occurring due to exposure to a risk factor (usually some chemical, physical or biological agent). Risk is usually expressed as the probability of an adverse effect occurring, ie. the expected ratio between the number of individuals that would experience an adverse effect in a given time and the total number of individuals exposed to the risk factor. *
Risk Management	A decision making process that entails the consideration of political, social, economic and engineering information together with risk-related information in order to develop, analyse and compare the regulatory options and select the appropriate regulatory response to a potential health or environmental hazard. *
Sampling Strategy	A plan, consistent with manpower and analytical constraints, for collecting a sufficient number of discrete samples from a site, and combining these in such a way that the combined sample will be representative of the property of interest at the site.
Speciation	Determination of the exact chemical form or compound in which an element occurs in a sample, for example whether arsenic occurs in the form of trivalent or pentavalent ions or as part of an organic molecule, and the quantitative distribution of the different chemical forms that may coexist. *
Spot or Grab Sample	A discrete sample.
Steady-state	The non-equilibrium state of a system in which matter flows in and out at equal rates so that all of the components remain at constant concentrations (dynamic equilibrium). In a chemical reaction, a component is in a steady-state if the rate at which the component is being synthesised (produced) is equal to the rate at which it is being degraded (used). In multimedia exposure models and bioaccumulation models it is the state at which the competing rates of input/uptake and output/ elimination are equal. An apparent steady-state is reached when the concentration of a chemical remains essentially constant over time. Bioconcentration factors are usually measured at steady-state. *
Stochastic	Due to, pertaining to or arising from chance and, hence, involving probability and obeying the laws of probability. The term stochastic indicates that the occurrence of effects so named, would be random. *
Surveillance	Measurement of environmental characteristics over an extended period of time to determine status or trends in some aspects of environmental quality. *

Survey	A sampling programme of a finite duration and for a specific purpose.
TGD	EU Technical Guidance Document in support of risk assessment for new and existing chemicals.
TOC	Total organic carbon, often expressed as mg/l in water or kg OC/kg solid. The organic matter content of soil and sediment is often determined by measurement of organic carbon. Typically, about half of all natural organic matter consists of carbon (OC $\approx$ 0.6 x OM). *
Validation (of a physically based model)	The process of establishing that the predictions of a model agree with the results of an experiment, and that the agreement is not fortuitous, but the result of the correctness and the applicability of the theories which are intended to capture the natural processes which the model intends to predict.
Validity (of a physically based model)	A property of a model which requires that it be 1) useful, 2) able to capture natural processes, 3) able to reproduce natural patterns.
Verification	Compare predicted with measured values, and test assumptions and internal logic of the model. This includes 1/ scientific verification that the model includes all major and salient process; 2/ the processes are formulated correctly; and 3/ the model suitably describes observed phenomena for the use intended.
Worst-case Assumptions	The most adverse environmental circumstances, or the highest possible release parameters. Combining these necessarily results in an unrealistic over all worst-case estimation, which is extremely unlikely to occur.

 * From Van Leeuwen, C.J. and Hermens, J. (1996).

APPENDIX A. SOIL AND GROUND-WATER MONITORING

A.1 ENVIRONMENTAL MONITORING IN SOIL

A significant difference between soil and the other environmental compartments is that it is generally much less mobile. Mixing processes occur more slowly than for other compartments and spatially variable deposition, compounded by variability in soil parameters such as texture and organic content, results in heterogeneous patterns of contamination. Consequently, the concentration in a single soil grab sample may differ greatly from a sample taken close by.

In addition to spatial heterogeneity, a monitoring programme must take account of temporal variability. This will be affected by such factors as degradation, partitioning (which may lead to reduced bioavailability) and evaporation. Understanding of the science underlying these factors is rudimentary and it is difficult to simulate to make predictions relating to temporal changes in soil concentrations. However, in general, the residence time in terrestrial compartments is much longer and the half-life for degradation is considered to be less of a determinand of accumulation in soil than for the air or water compartment (Shimp *et al,* 1990).   Monitoring may be an empirical solution to this lack of understanding, and the monitoring strategy clearly needs to take temporal changes into account.

In the context of risk assessment, the $PEC_{regional}$ for soil will be determined primarily by aerial deposition. A PEC_{local} may result from aerial deposition, either from a point-source such as a production site or a line-source such as a road, but it may also include direct additions. Such terrestrial additions may be intentional (such as sludge application or pesticide application) or unintentional, (such as through flooding or runoff from roads etc). Given limited resources and an expectation that the PEC_{local} will be greater than the $PEC_{regional}$ it is to be expected that the objective of most monitoring programmes will be to determine the PEC_{local}, and the focus of the rest of this section will be on the requirements of such a programme.

Before establishing a monitoring programme the following preliminary steps are recommended (ISO10381-1, ISO 10381-4, ISO 10381-5):

■   Establish intrinsic properties (biodegradability, physico-chemical properties such as water solubility and adsorption coefficient that determine mobility, abiotic degradability, etc) of the chemical to be monitored in order to estimate transport and fate mechanisms using multimedia Mackay models. This will give information on whether soil is a potential environmental sink and will indicate whether ground-water contamination should be considered.

■ Establish production and use pattern considering the whole life cycle of the product in order to determine possible routes of entry into the soil. Having considered routes of exposure, it will be possible to identify those areas most likely to be contaminated.

■ Establish the history of the potentially contaminated areas by, for example, using old site maps to identify 'hot spots' or interviewing (retired) workers or operators. The occurrence of extensive flooding should also be considered as it can result in significant, and potentially multiple, contamination events. These data will enable identification of specific sites with a high probability of contamination.

Sampling programme

International Standard ISO 10381, Parts 1-6, provides detailed information and guidance on soil sampling, although Parts 1-5 are in draft version. Some important points have been used in the preparation of this document, and are referenced in each section. The British Standards Institution has issued a draft for development covering the same subject (BSI, 1988).

Table 6: Specific Considerations for the Design of Soil Monitoring Programmes

1. **Technical Aspects of Sampling and Analysis**
    See section 4.1 and Table 1

2. **Site characteristics**
    a. history of agricultural and industrial management of the area, e.g. previous sludge applications, ploughing, flooding, prior contamination (radiochemical, chemical or biological)
    b. location (map reference, relation to potential point/line source)
    c. vegetation covering the sampled soil
    d. barriers (buildings, forests, etc.)

3. **Quality Control and Quality Assurance**
    See section 4.3.3 and Table 1

4. **Soil characterisation data useful for risk assessment**
    a. particle size characterisation (% clay, silt, and sand)
    b. % organic carbon
    c. cation exchange capacity
    d. pH (water and/or KCl and/or $CaCl_2$)
    e. moisture holding capacity
    f. exchangeable cation content
    g. clay speciation
    h. iron/aluminium hydroxy-oxide content
    i. rainfall – volume and pH

5. **Reporting**
    See section 4.4.5 and Table 1

Site Selection:

Selection of sampling sites should be based, as discussed previously, on the expected route by which

contaminant reaches the soil taking account of aerial deposition, intentional and unintentional terrestrial inputs (Section 4.4.1).

Several scenarios are possible:

a)   entry via aerial deposition

- can lead to a $PEC_{regional}$ e.g. POP deposition, forms of nitrogen and sulphur
- can lead to a PEC_{local} e.g. emission from production site

b)   direct entry

- sludge amendment, tyre wear run-off etc. leading to a PEC_{local}
- extensive flooding leading to a $PEC_{regional}$

c)   intended entry e.g. pesticides etc. leading to a PEC_{local}

Location of sampling:

Samples (usually not less than 500g) may be taken on grid systems, along transects or at single points (ISO 10381-1, HMSO, 1986). Grid systems may be non-systematic (irregular) or systematic. The advantages and disadvantages of the different systems are discussed in ISO 10381-1. Clearly the choice of system will depend on whether the objective is a spot check, a qualitative pre-study or an extensive quantitative study including statistical analysis. Which method is chosen and why should be fully documented.

The number of samples will also depend on the objective of the sampling strategy. For example when monitoring soil concentrations around a point source, samples may be taken along transects taking account of the prevailing wind direction and sufficient samples would be needed to demonstrate the reduction in contamination with distance from the source. By comparison, use of a grid system would be more appropriate for monitoring soil concentrations after sludge application. In such a scenario, the choice of site would be made after discussions with the authorities responsible for sludge application to determine sites where the history of sludge application (e.g. number of applications and/or time since the last application, Holt *et al,* 1989) will produce a worst case PEC_{local}. A regular grid pattern of sampling would then be appropriate with repeated sampling between applications to establish the potential for losses by degradation, leaching (c.f. ground-water monitoring), and uptake by plants.

Position of Sampling:

If possible samples should be taken in open fields without vegetation or disturbance of air movements/deposition by surrounding buildings. When this is not possible, surface litter should be removed (ISO 10381-6).

Contaminants may or may not be most concentrated at the surface, depending on the site history and physicochemical properties. However, the recommended sample depth is < 10 cm for aerial deposition and plough depth (i.e. 0-30 cm) for sludge amended soil sampling.

If the contaminant in question is expected to leach, sampling should be sufficiently deep to ensure the mobility of the contaminant has been taken into account.

Sampling methods

There are essentially two approaches to soil sampling (ISO 13081-2, Barnard, 1995):

■   the excavation method using a shovel;

■   the probe method using an auger.

During soil sampling the problems of sample disturbance and contamination are of concern (ISO 13081-2). Whilst removing a soil sample, the release of compressive forces and motion may cause modification of the soil structure leading to alteration of constituents, such as volatile compounds which are partitioned in the free volume of soils.

The advantage of the probe method consists of less disturbance of the sample as well as the site. In the probe method most of the disturbance can be expected when the material is extruded from the core or auger.

Table 7: Soil sampling tools

Type	Material
Hand tools	
Shovel	Iron, stainless steel
Scoop	Polyethylene
Trier	Stainless steel
Bucker auger	Steel, hardened high carbon steel tips
Core	Hardened stainless steel, PETG tubes
Sludge sampler	Stainless steel
Power tools	
Backhoe	Hardened steel
Flight auger	Steel, hardened tungstencarbon steel tips

Single samples versus composite samples (ISO 13081-1)

Single samples may be collected to assess the horizontal or vertical distribution of a chemical. This will allow the determination of spatial variability and spatial mapping by using kriging or co-kriging techniques (Stein and Finke, 1994; Franssen *et al,* 1997). Composite samples should be prepared in cases where the average spatial concentration of a chemical in a defined area or horizon is to be determined. The reason for choosing either one method should be documented.

A.2 ENVIRONMENTAL MONITORING IN GROUND-WATER

The quality of a ground-water monitoring programme should be assessed in terms of its ability to represent conditions in the three spatial dimensions and also over time. Samples need to be taken over a complete hydrologic cycle, which will usually be one year. However account must also be made of the weather during the sampling year compared to average conditions. The minimum is to take at least four samples over the year but it is preferable that six or more be taken.

Selection of appropriate sampling sites requires a phased approach (Figure 3, after Nielsen, 1991). Initially, the hydrogeology of the site should be characterised and a conceptual hydrogeological model developed. The model should take account of the site lithology including the extent of hydrogeologic units, the units hydraulic conductivity and porosity and the hydraulic gradients. The model is used to develop a flow-net which takes account of the boundaries of different aquifers and should be related to potential sources of contamination.

Sampling wells are placed in relation to the ground-water flow net and sources of contamination ensuring that both background (upgradient) and downgradient wells are included. Where the underlying hydrogeology is simple it may be sufficient to have one upgradient well and three downgradient wells, but usually more extensive well networks will be needed (Nielsen 1991).

The sampling strategy must take account of sampling depth as well as the position of the wells. Ground-water sampling devices permit permeation of water into the sampling device at specific depths determined by a 'screen'. The depth screened for an individual sample should be as small as practicable. It is preferable to take a series of samples that together build up a depth contamination profile than to use a deeper screen which will average the contamination over a greater depth. The depth profile should cross the zone of diffusivity, taking account of seasonal variations and also geologic zones with different hydraulic conductivity. It is necessary that the upgradient samples are taken from the same stratigraphic horizons as the downgradient samples.

The development of techniques for ground-water sampling should take into account two main characteristics which are common to all ground-waters and which make it different from other natural water systems (Smith *et al*, 1988):

■   only substances soluble in the ground-water are mobile in the aquifer (no transport of chemicals by particulates): ground-water cannot contain any particulate matter;

■   ground-water is nearly oxygen-free.

To be representative of the water in the aquifer, it is of particular importance that ground-water samples are not exposed to air before and/or during the analysis.

The most common devices to obtain ground-water samples are hand bailers, syringes or pumps.

The risk of an alteration of the sample during the collection procedure can be reduced (but not eliminated) through an appropriate design of the monitoring well and pumping selection. Purging prior to sample collection is frequently recommended (Garrett, 1988). For example, the US-EPA recommends three well water volumes for purging a well before sampling and the sampling should occur as soon as possible after purging. However, this can lead to draw-down of water from depths other than the sampling depth and therefore produce an unrepresentative sample. Therefore, purging of wells to equilibrium conditions of pH, Eh and conductivity is not advised prior to sampling. Slow purging of a sample volume equivalent to the volume of the well at the screened depth is preferable. The sample must be taken slowly (e.g. using peristaltic pumps) to maximise its representativeness.

Finally, it is necessary to ensure that the sampling protocol is appropriate to the contaminant of concern. Particular attention may be necessary to ensure that the oxygen concentration in the ground-water is maintained in the stored sample and that the sample is stored in the dark to minimise photolysis. Other conditions applicable to sample storage and analysis are as for other environmental compartments. ISO 5667-11 (1993), NRA (1992), Nielsen, (1991) and Koreimann *et al* (1996) for example, give detailed guidance on ground-water sampling.

Figure 3. Summary of ground-water monitoring system design process (Nielsen, 1991)

DATA ANALYSIS

Conceptual Model

Geology/Hydrogeology
- Surface geology (topography and typical depth of overburden)
- Lithology and thickness of aquifer
- Type of geologic formation (local stratigraphy and structure)
- Recharge/discharge areas
- Aquifer (confining units) permeability and porosity

Flownet Construction

Ground-water flow directions
- Piezometric and/or potentiometric heads
- Relative hydrologic heads between the units
- Three-dimensional flow directions using flow lines and equipotentials
- Interconnection of aquifers

Plot Facility Features

Facility features
- Base map features
- Cross-sections with lithology
- Facility base grades established and compared with flow paths

DESIGN

Select Target Monitoring Zones

Target Monitoring Zones
- Uppermost aquifer established
- All reasonable flow paths identified

Locate Background Wells

Ambient Water Quality System
- Upgradient design - simple geology and heads
- Background design - complex geology and heads
- Number should have statistical basis

Locate Downgradient Wells

Basis for Design
- Geology and permeable zones
- Flow net analysis
- Target monitoring zones
- Facility waste boundaries

Verify Locations

Do the Locations Selected Meet Criteria?
- Between waste areas and down gradient receptors

WELL IMPLEMENTATION

Install Detection Monitoring Wells

Field Installation of Monitoring Wells
- Update conceptual hydrogeologic model
- Document installation

Test System

Test and Operate System
- Performance test all wells
- Use operation and maintenance procedures
- Clear and decommission incorrectly placed wells

APPENDIX B. AIR MONITORING

Chemical sites may cause local air pollution. Depending on the properties of the chemical it is sometimes necessary to evaluate air quality over a larger area - regional or even continental level. Air pollution may be caused either by gaseous or particulate pollutants. In many cases gaseous pollutants may adsorb in aerosols or their chemical composition may change by reacting with other air pollutants. Substances emitted to air may undergo either wet or dry deposition. Water soluble chemicals may be deposited via rain water whilst others, like POPs, may adsorb on particulates and then be deposited on the ground. Deposition monitoring is one practical way to evaluate airborne contaminant routes to the environment. This pathway of pollutant transfer to water bodies, agricultural land or arable land may be an important exposure route for animals and humans.

Consequently, a regulatory limit, generally based on an annual average, is set to limit the deposition to soils and crops. Measurement of the annual average may be carried out by analysis of random air samples over the year at a fixed distance (downwind in the prevailing wind direction) from the source, where the maximum annual average is expected. Of course, measurement of the annual deposition or a representative period of the year may provide the same information.

Many of the emissions leading to air pollution are point-sources e.g. chimney or any kind of stack. There may be any number of this kind of emissions at any one site. Fugitive sources are also typical for industrial emissions of volatile organic compounds (VOC).

Some chemicals can cause odour problems in the vicinity of the emission source. Thermal decomposition of organic chemicals during processing may also result in odorous emissions. Many odorous substances are difficult to monitor because they are present at very low concentrations and yet may still be causing a nuisance. For that reason human experience is usually used to evaluate environmental nuisance caused by odours.

In order to prevent short-term effects like smell or irritation of the respiratory tract or contact damage to vegetation, air quality standards are based on keeping maximum emission levels below a no-effect level or a hardly effective level. In practice this means that a 90%- or 95%-value of the distribution of measured emission levels, averaged mostly over 1 hour, should not be exceeded. Analysis of random samples of air over a year at a fixed point downwind, where the maximum is expected, may provide the required information for compliance with short-term air limits at that specific site. The Technical Guidance Documents in support of Commission Directive 93/67/EEC and of Commission regulation (EC) 1488/94 do not consider short-term limits.

Air quality is usually measured by monitoring networks. Ambient air monitoring does not give full information on individual exposure. People spend a significant portion of most days inside buildings

(home, schools or workplaces) but air quality is usually measured outdoors. The ideal goal would be, if possible, to monitor inhaled air.

In some cases there is a need to monitor particulate matter in the air. The very small aerosol fraction (diameter <10 µm) may be transported in the air like gases. Dust emissions usually cause problems only in the vicinity of the source.

Sampling and Analysis

VOCs are one of the most important group of air pollutants for the chemicals industry because they may cause elevated ozone concentration in the ground level while reacting with nitrogen oxides in sun light, or they may cause odours in the vicinity of the source.

Usually ambient VOC concentrations are very low, generally at the low ppb level. Typical methods used for VOC sampling are passive stainless steel canisters (mainly in United States), inert bags (made of Tedlar®), activated carbon tubes or sorbent tubes (Woolfenden, 1997). Automated gas chromatography equipment has been developed for VOC sampling and direct analysis. Commercial kits are available for BTEX (benzene, toluene, ethyl benzene and xylenes) analysis and the U.S. EPA has published sampling methods for canister and adsorbent tube sampling (Anonymous 1997a, 1997b).

Some of the features and limitations of the major methods for VOC sampling and analysis are given in Table 8.

Table 8: VOC sampling and analysis methods

Conventional methods	small concentrations	very volatile hydrocarbon	BTEX	automatic sampling	Automatic analysis	need of pump	effect of the humidity	costs	validation
Suitability and Limitations									
Activated carbon tubes	(+)	-	+	-	(+)	+	+	low	+
Sorbent tubes	+	-	+	(+)	+	+ and -	(+)	moderate	+
Canister	+	+	+	+	+	(+)	-	high	+
New Methods									
DOAS	-	-	+	+	+		+	high	-
Automated VOC analyser	+	+	+	+	+		-	high	+
BTEX analyser	+	-	+	+	+		-	moderate	+

+ suitable ; (+) some limitations; - not suitable
DOAS Different Optical Absorption Spectroscopy
BTEX benzene, toluene, ethyl benzene and xylenes

For aromatic compounds passive sampling is a practical method for obtaining information on long-period average concentrations (Anonymous, 1994). For styrene, where odour is usually the most essential issue for air quality, short-period sampling with pumps or automated analysers is suitable.

Traditionally particulates have been monitored by using high-volume samplers that collect aerosols on glass-fibre filters. In some instruments, an adsorbent material e.g. polyurethane is placed behind the filter to collect chemicals that may otherwise volatilise from the filter during the sampling period. Some organic chemicals may react with other air pollutants during the sampling period which may cause incorrect results.

High-volume samplers have been developed to sample fine particulates (<10 μm diameter) which may be inhaled. In recent years more effort has been put into sampling techniques for ultra-fine particulates that are small enough to reach the lung alveoli.

Particulates are typically monitored at fixed sites near to inhabited areas such as houses or schools. The EU has set threshold limit values for total suspended particulates. The simplest data from particulate sampling are mass concentrations. Specific analysis on the solvent extractable material on the filter may be carried out if there is a need to know the chemical composition of a sample.

POPs are important because they are resistant to degradation and have the potential to accumulate in the environment. They are characterised by low water solubility and high lipid solubility. Many of them are transported via air (Wania and Mackay, 1996). They are rarely monitored near a local source but if they are, then the methods used are similar to those already detailed for particulates or deposition. POPs are usually monitored via international programmes on a regional or continental level because of the important role played by long-range transportation in moving these compounds from source to other regions.

Deposition monitoring usually means monitoring of wet deposition. Total deposition is very expensive to monitor. Wet deposition includes the water soluble fraction and coarse particulate. Sampling is done by a simple (and cheap) sampler, which looks like a typical plastic hand bucket. There are also some more sophisticated models available. Deposition samples may be analysed like a normal water sample however some filtering is usually needed.

Site Selection

For ambient air monitoring sampling sites are usually located close to the places where people are living or staying. Usually several sampling sites are needed (Council Directive 96/62/EC, 1996). Meteorological information that is representative for local conditions (high buildings and topography, coastal area etc.) is required. Any sampling site must be located far enough from other emission

sources to reduce their influence to a minimum. The site should be classified as an industrial, residential or traffic area, rural or urban. All possible sources causing air pollution must be listed. Other relevant information includes name of the site, location (city and map co-ordinates), sampling period (date of starting), sampling method and in the case of instruments, detailed information on each of them. Sample history is included if the laboratory is following standards like EN 45001.

Monitoring Programmes

Background information on air quality is usually obtained from national or European level monitoring programmes. Most countries have local air quality monitoring networks and on a European level practical information is available from the EMEP network (Protocol on Long-Term Financing of the Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe). EMEP collects information on SO_2, NO_x, NH_3, CO, VOCs and precipitation.

Data Interpretation

Usually mean, average and median concentrations are essential for air quality assessment. Percentiles e.g. 95 - 99 % are also calculated. A very practical tool for presenting air quality information is to show variations in substance concentration in air together with meteorological conditions e.g. concentration of measured VOCs as a function of wind direction. If possible air quality data should be compared to national air quality guidelines.

Table   9:   Considerations for Design of New Air Monitoring Programmes

1. Technical Aspects of Sampling

    a. height of sampling point (air inlet) above the ground surface
    b. meteorological data collection
    (see also Table 1)

2. Technical Aspects of Analysis
    (see Table 1)

3. Quality Control and Quality Assurance
    (see section 4.3.3 and Table 1)

4. Spatial and Temporal Location
    a. operational details – time since shut down etc.
    b. consider influence of local meteorology on sample/site representativeness
    (see also Table 1)

5. Sample Characteristics
    (see Table 1)

6. Environment Characteristics
    a. type of zone (urban, sub urban, rural, industrial)
    b. characterisation of the zone (residential, commercial, industrial, agricultural, natural, mixed)
    c. population
    d. street type in case of traffic station
    e. traffic volume in case of traffic station

7. Local Source or Site Characteristics
    a. main emission sources
    b. description of prevailing meteorological conditions
    c. presence and location of other sources of pollution in the region of the sampling site

8 . Reporting
    a. name and address of the organisation responsible for air quality monitoring
    b. title and name of the responsible person
    c. comparison of data with threshold limit values and air quality guideline values
    d. emissions (annual, variation, incidents)
    (see also Table 1)

APPENDIX C. WASTEWATER TREATMENT WORKS MONITORING

Defining the aims and objectives of the study establishes the precision and accuracy required. These in turn will determine the complexity of the study, the length, the analytical methods and therefore the cost of the study.

For example the design of a study to determine the mean daily concentration of a compound in a sewage influent would be noticeably different from one whose goals were to determine the diel variation in the influent, works removal efficiency or daily load to the receiving water.

Historically the vast majority of routine effluent sampling has been conducted within a 'sampling window' very much narrower than the full 168 hour week. Almost invariably samples have been restricted to weekdays and their time-span has been 09.00 to 17.00 at best (often in practice much less). It follows that existing grab sampling programmes will reflect whatever biases happened to have been introduced at each works by the particular sampling window used there.

The criteria imposed for site selection will vary with the aims of the programme. However the general principle is to have a detailed understanding of the site so that the data generated can be readily interpreted and positioned. Inevitably there will be a number of features about the site which will be essential to achieve to study aims and these will differ according to these aims. The characteristics and operating conditions of the works should be established to confirm that the site is representative for the study in question (Holt and Comber, 1996).

Some of the key factors that need to be understood are:

- sewage works treatment type eg, activated sludge, trickling filter, oxidation ditch, caroussel, rotating disc, anaerobic digester etc;

- sewage works size (e.g. plant capacity, population served, population equivalents, tonnes BOD_5 or COD/day etc.);

- percentages of trade and domestic waste in the raw sewage;

- sewage works performance (BOD_5 removal, nitrified effluent etc.);

- geographical location (as a crude surrogate for temperature and other climatic effects).

- the hydraulics (i.e. flow pattern, sludge retention time (SRT), hydraulic retention time (HRT), sludge wastage, solids recycling, liquid recycling etc);

- tertiary treatment.

A schematic of the works can be useful to establish many of the above factors.

■ confirm that the works is operating normally, that the details match project protocol and that no development work is scheduled over the proposed study period.

■ confirm analytical feasibility - it is vital that there are no compounds present in the samples that will interfere with the specific analytical method to be applied;

■ establish an involvement and 'ownership' of the project with site operatives. The nature, reasons for and value of the programme should be explained to all concerned. It is a practical way to get local knowledge and history of the site which may not necessarily be officially documented.

Information should be collected to establish baseline data for the proposed study and identify the normal inputs including types of trade effluent treated. Certain trade effluents can have a significant influence on the works or can interfere with the analytical procedure making the data invalid.

In addition data interpretation will be simpler and the data validity greater if it is possible to avoid or identify abnormal loads to the system. For example, septic tank waste is often delivered by tankers to STP and discharged into the influent channels. This may or may not be a significant load in terms of volume or BOD_5 to the works, may or may not be added to the influent before the flow detectors and may or may not be a daily event. One of the key parameters essential to understanding works performance is biochemical oxygen demand (BOD_5). There are however no suitable methods available to guarantee preservation of samples prior to determination and this should be considered when BOD_5 data for 24-hour, flow-related composite samples for sewage influents, effluents and river waters are analysed. Even spot (grab) samples should preferably be collected in cooled containers (4°C) and analysed as soon as possible.

It is important, in order to be able to correctly interpret and position any data, to include in the study protocol a supporting programme designed to measure works performance and water quality, unless this is the objective of the monitoring study. Matthijs *et al* (1997) have recommended that boron can be used as an effective tracer for understanding the hydraulics of WWTPs since it is not removed at any stage of the treatment process.

The timing, duration and location of the study should be defined by the objectives and practical feasibility of the study. It is advisable to avoid sustained periods of heavy rainfall if at all possible since storm events generally result in very different operational conditions at the works. In addition to the obvious problems associated with flow and dilution, heavy rainfall can result in premature operation of combined sewer overflows or storm overflows discharging directly to the receiving water. Heavy rainfall can affect the primary settlers leading to an increase in solids in the aeration tank and final effluent. Furthermore the increased flow to the works may, when the storm overflow tanks are full, result in the

discharge of untreated sewage into the receiving water. The operational procedures for discharge from the storm tanks (i.e. direct release to river or after treatment via for example aeration tanks) need to be understood. The siting of the storm overflows may also affect predicted values. The specific considerations to be taken into account when designing monitoring programmes in STWs are listed in Table 10.

Table 10: Considerations for the Design of Monitoring Programmes at Wastewater Treatment Works

1. **Technical Aspects of Sampling**
   (see Table 1)

2. **Technical Aspects of Analysis**
   (see Table 1)

3. **Quality Control and Quality Assurance**
   (see Table 1)

4. **Sample Location in Time and Space**
   a. Select which compartments of the works are to be monitored (primary settler, secondary settler, raw or settled sewage final effluent etc)
   b. Select time of sample (grab, flow or time related composite)
   (see Table 1 for other considerations)

5. **Sample Characteristics**
   a. Temperature
   b. Suspended solids
   (see Table 1 for other considerations)

6. **Environment Characteristics**
   (see Table 1)

7. **Site characteristics**
   a. Historical data from works (flow, removal efficiency)
   b. Location (map reference) and schematic of works, including tank volumes/capacities
   c. Type of primary treatment
   d. Types of secondary treatment - i.e. biological, activated sludge, trickling filter, rotating disc, anaerobic digester, etc.
   e. Types of tertiary treatment
   f. Operating conditions (flow, HRT, SRT sludge wastage, BOD_5 and COD removals)
   g. Population served
   h. Industrial/trade input (including percent and type of industrial waste)
   i. For industrial biotreaters establish works production schedule
   j. Abnormal loads
   k. Confirm works operating 'normally' e.g. no development planned during study
   l. Support programme of water quality

8. **Reporting**
   (see Table 1)

Samples collected during a monitoring exercise at a sewage treatment works are subject to rather different problems than samples of fresh water or seawater, namely :-

■ high biomass (microbial) activity;

■ a complex chemical cocktail.

The high biomass in influents and samples of sludges in particular makes preservation a key issue and therefore it is imperative to have validated the efficacy of the preservative. Even a few minutes without preservation can result in significant errors in the concentration detected.

It is worth re-emphasising that a high level of quality assurance for both sampling and analysis (see section 4.3.3) is required during any environmental monitoring programme at wastewater treatment works because of problems associated with sample stability (primarily biodegradation), contamination of equipment and the very sensitive extraction and analytical methodologies involved. Furthermore, because of the many different factors that can influence the performance of a works it is also very important to keep clear comprehensive records of all events occurring during the exercise.

APPENDIX D. SUMMARY STATISTICS FOR MONITORING DATA CONTAINING NON-DETECTS

The results of environmental monitoring studies often comprise a relatively small number of sample measurements, many of which have results which are below some defined reporting limit, together with a very small number of high concentrations (Shumway *et al*, 1989). The non-reported values are generally described as being below the "detection limit" and the data set containing these values is referred to by statisticians as "censored data" (Lambert *et al*, 1991). Detection limits are intended to describe how well an analytical protocol discriminates low detection of signal response from background interference (Lambert *et al*, 1991). The term "detection limit " has many different meanings and definitions in use by analytical chemists. Often the chemical may be detected and positively identified but not reliably enough to report numerical values. As a result, these "less than" values are often reported as below the "reporting limit" or "limit of quantitation" or "determination limit". The difficulties caused by the differences in definition of detection limits has led statisticians and data analysts to define a new limit for censored data sets called the "minimum reliably detected concentration" which is based on a statistical analysis of the measurement process and 90th percentile of the "probability of detection" curve (Lambert *et al*, 1991).

It is almost always necessary to summarise the results of a series of environmental measurements in order to arrive at some conclusion regarding the concentration. For instance, what the real concentration is or how typical the reported numerical values are of the total group of samples. A number of summary statistics (mean, standard deviation, median, inter quartile range) are used to represent the typical or central value and the variability around this value. Monitoring data, in addition to containing numerous non-detects are often highly skewed, that is not normally distributed, so that application of statistical summaries to the data can lead to quite different results depending upon how the statistics are derived (Helsel, 1990). The mean and standard deviation are strongly affected by the low values and by the few outlying high values and can be quite sensitive to the deletion or addition of a single point. For strongly skewed data, the mean may be exceeded by less than 25% of the measured values Similarly, the standard deviation is inflated by outliers, implying a larger variability than that shown by the majority of the data set. Often, alternate measures of the central value and variability of these data sets are more appropriate. The median and interquartile range (IQR) are not strongly affected by a few outlying values. The mean of the logarithms of the data ("geometric mean", "log transformed" data) are also techniques used to lessen the bias caused by outlying values (Helsel, 1990; Shumway *et al*, 1989).

Another way to deal with such a data set is to delete or insert data. It is evident that using a zero value for non-detects would result in a low bias in the mean or median. Similarly, the use of the detection limit (L) in place of the missing values leads to a high bias. Other simple substitution methods have been suggested such as the use of half the detection limit (L/2) or dividing the limits by the square root

of two (L/√2) (Hornung and Reed, 1990). These methods are simple and widely used but have no theoretical basis (Helsel, 1990). The existence of software which allows for the statistical estimation of the missing values makes these simple substitution techniques indefensible (Helsel, 1990; Newman and Green, 1995).

The other methods used for summary statistics on censored data sets have been classified as "distributional" and "robust" methods. Software (UnCensor©) is available which allows the convenient selection and use of both types of method, depending on the nature of the dataset (Newman and Green, 1995).

In general, since these methods are based upon extrapolation and data distribution, they are only useful for datasets in which most of the results are above the detection limit. As a general rule, reporting summary statistics such as mean and standard deviation is not warranted for datasets with greater then 50% of their values below the detection limit (Helsel, 1990; Hornung and Reed, 1990). If it is necessary to use such data, a better description would be to report the percentage of the samples below the detection limit and the range of the remaining samples (Hornung and Reed, 1990). Furthermore, it is not appropriate to combine data with greatly differing detection limits, particularly if they contain a high proportion of non-detects.

In the special case of the use of censored data for risk assessment, the TGDs require the use of the 90th percentile values as an estimate of the reasonable worst case PEC. This value is easily calculated and relatively unbiased by non-detects if more than 10% of the data are above the detection limit. When most or all of the data in a dataset are below the detection limit, the TGDs recommend using the detection limit as the PEC. From the foregoing, this would appear to result in a high bias and a better empirical approach would be to divide the detection limit by 2. In instances where multiple datasets are available with differing detection limits and where fewer than 10% of the data are above the detection limit, the detection limit from the most sensitive test ought to be used for estimating the PEC. The background for all of the methods described above is an attempt to estimate the distribution of those data which are below the detection limit. The best available analytical techniques are likely to provide a better estimate of these data than an older dataset with a considerably higher limit of detection. If one dataset found no detectable chemical "x" at a limit of 1 mg/L and a later, more sensitive monitoring result of the same setting found no detectable chemical x at a limit of 0.01 mg/L, then the PEC ought to be based on the latter value. The older dataset is only useful where the chemical was detected above the rather high detection limit.

UnCensor© Example:

A surfactant monitoring programme was conducted in France, U.K., Germany and Saarland.   The goal of the monitoring programme was to determine environmental concentrations of this surfactant following its introduction into new detergent formulations.

About 50% of all observations (N=108) were at or below the detection limit (0.3 ug/l). Conventional data analysis methods such as deletion or substitution will produce biased mean values and standard deviations, which may lead to erroneous conclusions.

The data set was analysed with the software program UnCensor developed by the University of Georgia. UnCensor offers a viable possibility to improve our analysis of these censored data sets.

The UnCensor analysis, illustrated in Figure 4,   indicates that calculated mean and standard deviations with different conventional methods may either over- or underestimate. These variations around the mean values may range up to a factor of four.

Figure 4: Comparison of Mean Surfactant Concentrations Using Different Statistical Approaches

Conventional Methods - Substitution with 0 ■ Regression Order Statistics-log Normal
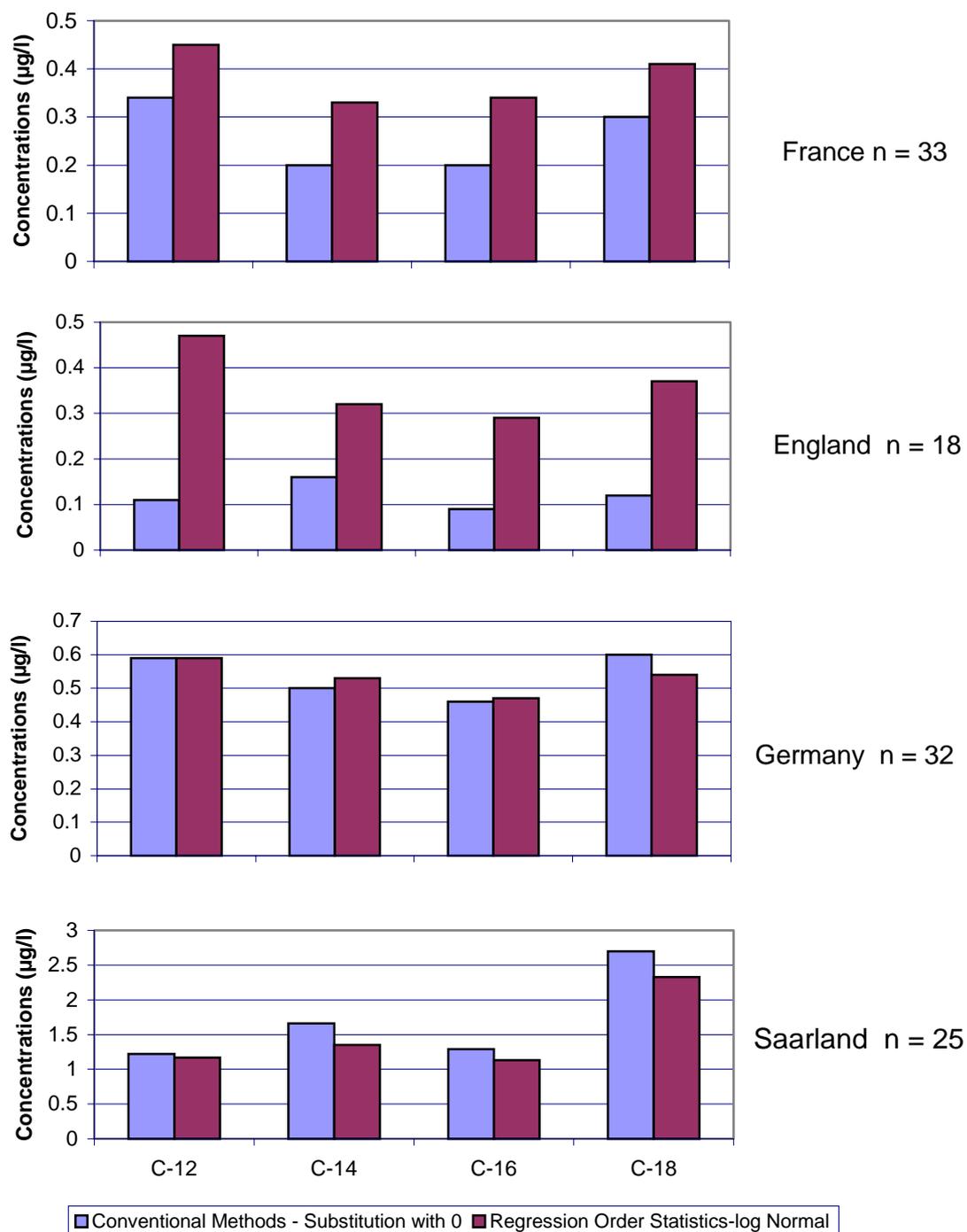
APPENDIX E.   SOLID-PHASE EXTRACTION FOR ESTIMATION OF BIOAVAILABILITY AND TOTAL BODY RESIDUES

Mussels (*Mytilus edulis)* and other bivalve molluscs have been used as indicator organisms due to their ability to accumulate trace levels of certain pollutants from the water column. In the Mussel Watch concept (Goldberg *et al*, 1978), pollutant levels and their changes with time in mussels taken from a given coastal marine zone, provided a basis for monitoring coastal water quality. More recently, mussels have been used for measuring hydrocarbons in the water column by placing cultured mussels of the same age, size and history in cages at sampling sites, often in combination with membrane-based techniques (Herve *et al*, 1991, 1995; Prest *et al*, 1995b; Peven *et al*, 1996; Hofelt and Shea, 1997).

Semi-permeable membrane devices (SPMDs) were originally designed as an alternative to the blue mussel and have received a great deal of attention in recent years. A number of approaches in the design of SPMDs have been reported. Sødergren, (1987) reported on the use of solvent-filled dialysis bags to simulate uptake of pollutants by aquatic organisms. Herve *et al,* (1991) compared the use of hexane-filled dialysis membranes and mussels to measure the uptake of organochlorines from lake water and Johnson (1991) also reported on the use of hexane-filled dialysis bags for water monitoring. Membrane-based pasive samplers were described by Huckins *et al* (1990, 1993) who used a low-density polyethylene lay-flat tubing, filled with either natural lipids or the model lipid triolein. Cellulose dialysis membranes containing micellar receiving solvent (Pekol and Cox, 1995) and polyethylene tubes filled with isooctane (Peterson *et al*, 1995) have also been proposed as possible techniques (Sabaliunas and Sødergren, 1997).

Using these SPMD techniques, a wide range of nonpolar to moderately polar contaminants including PAHs (Lebo *et al,* 1992, Huckins *et al,* 1993), organochlorine pesticides (Ellis *et al,* 1995, Herve *et al,* 1995 Prest *et al,* 1995a,b), polychlorinated biphenyls (Prest *et al,* 1995a,b), dioxins-dibenzofurans (Prest *et al,* 1992) and chlorophenols-anisoles-veratroles (Ellis *et al,* 1995, Herve *et al,* 1995) have been sampled successfully.

Measurement of the bioavailable fraction

For many compounds, transport through biological membranes requires that the compound is dissolved in the surrounding water. The bioavailable fraction is then equal to the water soluble fraction of the compound. The bioavailability of organic compounds in the aqueous environment may be reduced as a result of any one, or combination of a number of, processes: adsorption to suspended solids, adsorption to sediments, adsorption to macromolecules (e.g. humic acids), formation of colloidal suspensions, chelation, compelxation and ionisation (Spacie *et al*, 1995).

Bioavailability is one of the most important factors that influence the uptake and bioaccumulation of organic compounds in aquatic organisms (Gobas and Zang, 1992).

Several methods are available to measure concentrations of dissolved (or bioavailable) substances. Dialysis membranes, head space analysis, solubility enhancement and liquid chromatography on solid phase cartridges are used to separate the dissolved from the bound or associated fraction. Sødergren (1987), and Huckins *et al* (1990, 1993) have used artificial lipophilic material to predict the bioaccumulation of hydrophobic chemicals in natural waters. All these methods do however have their limitations. Head space analysis, for example, can only be applied to relatively volatile chemicals and with dialysis, significant amounts of the hydrophobic chemicals may bind to the dialysis tube itself leading to unreliable results.

Recently, solid phase micro-extraction (SPME) has been suggested as an alternative biomimetic extraction technique by Vaes *et al* (1996a,b; 1997). At the Research Institute of Toxicology (RITOX) in The Netherlands, the solid phase extraction (SPE) disk (Empore™ disk) and SPME technique have been used to measure dissolved concentrations. In particular the SPME technique is a very promising tool to measure dissolved concentrations. SPME can be performed in such a way that the extraction does not lead to any significant depletion of the sample. Therefore, equilibria between the dissolved and the bound chemical remains undisturbed during the measurement and only the dissolved chemical will partition to the SPME fibre. The SPME and SPE method have been used to measure protein binding, binding to microsomes, binding to humic acids (Freidig *et al,* 1998), membrane-water partition coefficients and freely dissolved concentrations in *in vitro* tests of several organic chemicals. The Empore™ disk, resembles extraction techniques using semi-permeable membranes or similar devices as introduced by Sødergren (1987) and Huckins *et al* (1990, 1993). The advantage of using an extraction disk is the possibility to use very small volumes of the hydrophobic phase which makes it possible to apply biomimetic extractions at laboratory scale.

Determination of bioavailable fraction is also possible by analysis of fractionated water samples. Filtration is often used to separate the particulate fraction from the water soluble fraction. When the particles are removed from the water sample, the water chemistry also often changes. Adsorption of compounds in the water soluble fraction to the filter surface is likely to occur. Use of in-line solid phase extraction also runs the risk of equal problems. The use of an *in situ* water sampler, for collecting large volumes of water by filtration followed by solid phase extraction (XAD-2) of the filtrate, is claimed to minimise these problems (Durell and Uhler, 1997).

Bioavailability can be measured biologically by *in situ* monitoring, or by microcosm/mesocosm studies. In biological monitoring, biomarkers are often used to measure responses that are indicators of exposure or a certain effect. These include (Huggett *et al*, 1992):

■ physiological   and non-specific biomarkers (direct enzyme inhibition, energetic responses, endocrine responses, blood chemistry, growth rate);

■ metabolic products (metabolites of xenobiotic chemicals, endogenous metabolites);

■ DNA alterations;

■ histopathologic biomarkers;

■ immunological biomarkers;

■ enzyme and protein synthesis as indicators of contaminant exposure and effect.

The use of biomarkers in environmental monitoring requires good control of the influence on the response of other factors (temperature, salinity, light, sex, season), a dose- or time-dependent response of the exposure or the effect, and a natural variation in the response within acceptable limits (Huggett *et al*, 1992). For PAHs the biomarkers most commonly used are DNA adducts, MFO induction and immune responses (Peakall, 1992).

Caged fish may be used in environmental monitoring programmes to investigate the bioavailability of compounds from the water and their effects. The propensity of fish to biotransform PAHs rapidly through activation of the mixed function oxidase system severely limits possible correlation of PAH concentrations in fish tissue with exposure concentrations in water. It is therefore difficult to predict bioavailability of certain compounds by this technique.

Relevance of total body residues (TBR) in risk assessment

Two major approaches are used in the risk assessment of polluted sites, namely the "chemical approach" and the "effect approach". A risk assessment of complex mixtures based on chemical data (chemical approach) is often not possible because of a lack of data on concentrations in the field and/or effect concentration data. Additional limitations of the chemical approach are:

■ it does not take into account joint effects of mixtures, or has to make assumptions such as additivity;

■ it does not consider bioavailability, and any elimination via biotransformation would make the material less bioavailable.

The effect approach will supply direct information on potential adverse effects. On the other hand, an assessment solely based on effect studies does not give any information regarding the chemicals that are responsible for the observed effects.

A new method is being developed at RITOX in the risk assessment of chemicals in water, incorporating bioavailability and mixture effects. An instrument has been developed to measure the total body residues (TBR) using biomimetic extraction in combination with a total molar concentration measurement. The procedure estimates TBR in biota after exposure to (complex) mixtures of organic chemicals in water. It is based on a simulation of bioconcentration using a hydrophobic phase and on the measurement of total molar concentrations on this hydrophobic phase via vapour pressure osmometry and gas chromatography-mass spectrometry.

The major advantages of this biomimetic extraction are:

■   it measures only the bioavailable concentration;

■   it is a selective extraction technique for hydrophobic (and therefore highly bioaccumulative) contaminants;

■   it determines total molar concentrations of all organic chemicals, including those that can not be identified or quantified because they are unknown or because they are present below their detection limits.

This new parameter however, also has its limitations:

■   it does not take into account other routes of exposure;

■   it ignores the fact that some chemicals accumulate less because of biotransformation.

The great advantage, nevertheless, is that the parameter supplies information on the total amount of a whole class of important pollutants.

Biomimetic extraction to simulate bioconcentration.

Briefly, a biomimetic extraction simulates, in a chemical manner, bioaccumulation in biota. The major characteristics of bioaccumulation in biota in the field are:

■   hydrophobic chemicals are accumulated to a proportionately greater extent than hydrophilic ones;

■   in the field the uptake into biota will not affect the concentration of chemicals in the water.

A chemical simulation of bioaccumulation in the laboratory should fulfil these two requirements (hydrophobicity dependence and no depletion). This negligible depletion can only be reached by introducing a very small amount of a hydrophobic phase into a large volume of water (similar to a fish in a river). The concentration of an individual chemical on the hydrophobic phase (C_h) is then equal to $C_a.K$, in which C_a is the concentration in the aqueous phase and K is the partition coefficient of the

chemical between the hydrophobic phase and water. This equation is similar to the accumulation in biota, where the concentration in biota (C_b) is equal to C_a.BCF, in which BCF is the bioconcentration factor.

Hydrophobic materials such as octadecane (C_{18}) have properties that resemble the lipids in biota and are therefore a suitable surrogate material for simulating the bioaccumulation process. A simulation of bioconcentration does not take into account biotransformation in biota, nor uptake via sources other than the aqueous environment. For most chemicals, however, and in particular for base-line toxicity compounds, these influences are minor.

By measuring the total concentration in this surrogate material, the total body residues can be estimated and the parameter TBR is related to the total accumulated amount in biota and is also a measure for the total base-line toxicity of complex mixtures.

Additional advantages of the biomimetic extraction are that it only measures the freely dissolved and bioavailable concentration of organic chemicals and that it extracts organic chemicals in a hydrophobicity selective manner. Because of this selective character, the analysis of chemicals with a high bioaccumulation potential is much more sensitive as has been shown in the analysis of biomimetic extracts of sewage treatment works.

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