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**Environmental Sampling**

Chapter 2 ENVIRONMENTAL SAMPLING

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**Chapter 2** **ENVIRONMENTAL SAMPLING**

We might imagine a satellite which could scan the earth’s surface and provide a complete analysis of every part of the environment. This is, of course, in the realm of science fiction. Instead, we must collect representative samples of a small part of the environment in which we are interested, and analyze these to provide information about the composition of the area. For example, it is obviously impossible to analyze all the water in a lake, so portions of the water must be collected and analyzed to determine the true concentrations of materials in the lake. Similarly, to study contamination around a leaking underground gasoline tank, numerous soil samples are needed to map the extent of the pollution.

We must keep in mind that only a small amount of sample (a few grams or milliliters) is collected from a vast heterogeneous area. It is imperative that the samples collected represent the environment as accurately as possible. Major decisions are based on the results of the analyses. The steps involved in environmental sampling are:

1.  Development of a sampling plan, including where and when samples will be collected and the number of samples required.
2.  Collection of the samples.
3.  Preservation of samples during transportation and storage.

**2.1 The Sampling Plan**

The importance of good sampling cannot be over stressed. The sample is the source of information about the environment. If it is not collected properly, if it does not represent the system we are trying to analyze, then all our careful laboratory work is useless. Care must be taken to avoid the introduction of bias or error.

Sampling is done for monitoring purposes, as well as for research. Data may be collected to monitor air and water effluents or to characterize pollutant levels in environmental media (air, water, soil, biota). The objectives may be to comply with regulatory requirements, to identify long and short term trends, to detect accidental releases, or to develop a data base or inventory of pollutant levels. Research may involve studying the fate and transport of pollutants or identifying pollutant exposures for humans and animals. It is important to design these studies scientifically so that they are cost effective and generate statistically significant information.

Intuitively, we see that the number of increments which go to make up a sample, the size of a sample, depends on the inhomogeneity of the system itself. If the system to be analyzed is a bag of marbles, with some red and some blue, an adequate sample size would depend on how homogeneous the sample is. If there are nearly equal numbers of marbles of each color, and they are well mixed, a handful would probably give a good idea of the overall composition. However, if there are only two or three red ones per hundred blue ones, it takes a much larger sample to be sure that the sample is representative. While there are mathematical formulas to determine how much sample is needed, depending on the variation in composition of the particles and the size of these particles, the parameters needed to use these equations are not often available when environmental samples are considered. The number of aspirin tablets coming off an assembly line which must be taken for testing, may be calculated, when the standard deviation of the usual aspirin tablet and the tolerable variation are known. It is not as easy to determine the number of portions of soil required to characterize a landfill. The actual inhomogeneity of the landfill is unknown, and it would probably take more analyses to determine it than anyone would be willing to do.

***Spatial and Temporal Variability***

If an environmental domain was completely homogeneous, a single sample would adequately represent it. However, we seldom come across such a situation, as the environment is highly heterogeneous. One must also distinguish between a *static* and a *dynamic* system. A static system is one which does not change much with time. It must be sampled so that the sample reflects all the inhomogeneity of the system. If a field is to be tested for a long-lived pesticide in the soil, that could be considered to be a relatively static system. Sample increments could be taken over a grid pattern on the field or a randomly selected spots. Remember that the random spots should be chosen in a truly random fashion, and that strolling around with a shovel is not likely to generate a random sample. A calculator with a random number generator can be used in imaginative ways to generate such a sample. For instance, a field might be sampled by making equally spaced traverses across it, generating a new random number every 10 paces, and taking a spadeful of soil each time the random number generator gave a preselected digit.

A dynamic system is one whose content changes with time. Most regions which we wish to characterize by taking samples are dynamic to some extent, and show both spatial and temporal variation. When a river or a waste effluent stream is to be characterized, its concentration will probably change over a period of minutes, days, or hours. This system must be sampled at many different times to collect a representative sample. This may be done by collecting a small constant volume of sample and compositing it for a day or a week, or it may be done by collecting a given volume at random times or on a regular schedule. The rule of random sampling, that any portion has the same chance of being selected, applies here. For instance, if samples are taken at random, these random times should include all periods of time including weekends and nights, as well as business hours.

In air sampling, the concentration of VOCs will vary from neighborhood to neighborhood within a town. It will also change with the time of day. Concentrations of compounds from automobile exhaust are generally higher during peak traffic hours in urban areas. Consequently, to gain a good understanding of the air quality in an area, samples have to be taken or measurements made at different locations and at different times of the day. Even further variation must be considered, since there are changes due to seasonal and weather factors.

When the sample is collected from a large environmental domain, it can be conceptualized as a point in time and space. Space units, S1, S2... denote sites, cities, even countries. Specific sampling locations are located within each space unit, described as a three dimensional space, using x, y, and z coordinates. So, measurements may be taken at each location at different points in time, and at different locations at the same time. For example, we might be monitoring ozone levels in an urban area, where S1 and S2 denote two cities on opposite sides of a river. Within city S1, several locations (L111, L112, ...) are chosen and measurements are taken at two different vertical distances from the ground (V11 and V12). This is illustrated in Figure 2.1. Time periods T1, T2 might represent different seasons of the year. Within each season, t11, t12... would represent daily or weekly averages.

***Development of the Plan***

To do a successful environmental study it is necessary to have a ‘plan of action’, a sampling plan. If the content of heavy metals in a river is being studied, for example, the purpose might be to examine the effect of these metals on fish, or it might be to monitor the content because the river is a drinking water source. The sampling plan will be different for each of these purposes. The first step is to clearly define the problem being studied and identify the environmental "population" of interest. Some of the major steps involved in the development of a successful study are as follows:

1.  Clearly outline the goal of the study. Decide what hypothesis is to be tested and what data should be generated to obtain statistically significant information.
2.  Identify the environmental population or area of interest.
3.  Obtain information about the physical environment. Weather patterns, for instance, are important if air samples are to be taken.
4.  Research the site history.
5.  Carry out a literature search and examine data from similar studies previously carried out. This can provide information about trends and variability in the data. In

the absence of previous data, a pilot study may be necessary to generate preliminary information on which to base a more detailed study.

1.  Identify the measurement procedures to be used, because these affect the way samples are collected and handled.
2.  Develop an appropriate field sampling design. Decide how many samples are to be collected and delimit the time and area to be covered by the study.
3.  Determine the frequency of samples to be taken, both in time and space, depending upon the project objectives. Decide if, for example, 24 hour integrated samples will be collected or individual samples will be taken every few hours.
4.  Develop a plan to insure and document the quality of each of the processes involved in the study: sampling, laboratory analysis, contamination control, etc.
5.  Once the sampling and analysis are complete, assess the uncertainty of the measurements.
6.  Perform statistical analysis on the data. Determine mean concentrations, variability, and trends with time and location.
7.  Evaluate whether study objectives have been achieved. If not, additional work may be necessary to provide the needed information.

***Sampling Strategies***

When it comes to sampling, the essential questions are: where to collect the samples, when to collect them, and how many samples to collect. Most environmental measurement domains are large and it is not easy to answer these questions. Some of the factors to be considered in determining a sampling strategy are:

1.  The study objectives: Different objectives require different sampling strategies. For example, if the objective is to measure the total release of heavy metals into a river by an industry, a 24 hour integrated sample may be taken. However, if the goal is to monitor for accidental releases, then sampling and analysis may have to be done almost continuously.
2.  The pattern and variability of environmental contamination: The number of samples to be collected in space and time depends upon the variability in the concentrations to be measured. For example, pollutant levels in air can vary significantly depending upon meteorological conditions, or traffic patterns. In general, if the spatial or temporal variability is high, a larger number of samples needs to be analyzed.
3.  Cost of the study: If more samples are analyzed, the information obtained will have higher precision and accuracy. However, more samples also require more money, time, and resources. So, it is necessary to design an effective sampling plan within the available resources.

Other factors such as convenience, site accessibility, limitation of sampling equipment and regulatory requirements often play important roles in developing a sampling plan, as well. A well designed strategy is needed to obtain the maximum amount of information from the number of samples. The strategy may be a statistical or a non-statistical one.

There are several approaches to sampling: systematic, random, judgmental (non-statistical), stratified, and haphazard. More than one of these may be applied at the same time. Very often, not much is known about the environmental area to be studied. A statistical approach is taken to increase the accuracy and decrease bias. An industrial discharge into a lake is shown in Figure 2.2. It would be expected that the concentration of the pollutants present in the wastewater outfall are at maximum near the discharge point. A systematic sampling plan would divide the water surface into a grid, and take samples in a regular pattern. Sampling a few of the grid blocks chosen in a genuinely random way constitutes random sampling. Judgmental sampling would concentrate on the area around the outfall. Taking a few samples at locations chosen by the person doing the sampling would be termed haphazard sampling. Finally, a *continuous monitor* may eliminate the time factor by giving real-time measurements all the time. This is still a sampling process, however, as the location of the sensor must serve as a typical location to give information about a larger area.

**Systematic Sampling**

Measurements are taken at locations and/or times according to a predetermined pattern. For example, the area to be analyzed may divided by a grid, and a sample taken at each point of the grid. For air pollution studies, an air sample might be taken at fixed intervals of time, say every three hours. This approach does not require the prior knowledge of pollutant distribution, is easy to implement, and should produce unbiased samples. However, systematic sampling may require more samples to be taken than some of the other methods.

**Random Sampling**

The basis of random sampling is that each population unit has equal probability of being selected. Random methods are good if the population does not have any obvious trends or patterns. When we think of random surveys of public opinion, for instance, we can readily see that a survey might come to very wrong conclusions if it relied on a door-to-door canvass taken on weekday mornings. All people who held 9 to 5 jobs would be essentially eliminated from the sample, probably skewing the results. Likewise, it would be foolish to rely on the opinions expressed by sampling a single street, when most of the people who live there are likely to be of the same class or background. If a system varies with time, as a stream might, we must sample at a variety of times, so that any time has an equal chance of being chosen. If the system varies with location within it, as a landfill would, we have to sample across the surface and down into it, so that any point in the three dimensional space of the landfill has an equal chance of being chosen.

Typically, the area to be sampled is divided into triangular or rectangular areas with a grid. Three dimensional grids are used if the variation in depth (or height) also needs to be studied. The grid blocks are given numbers. A random number generator or a random number table is then used to select the grid points at which samples should be collected. If a waste site contains numerous containers of unknown wastes and it is not possible to analyze every container, a fraction of the containers are selected at random for analysis.

**Judgmental Sampling**

This is a non-statistical sampling procedure. Here, the prior knowledge of spatial and temporal variation of the pollutants is used to determine the location or time for sampling. In the lake example, samples might be collected just around the outfall point. This type of judgmental sampling introduces a certain degree of bias into the measurement. For example, it would be wrong to conclude that the average concentration at these clustered sampling points is a measure of the concentration of the entire lake. However, it is the point which best characterizes the content of the waste stream. In many instances, this may be the method of choice, especially when purpose of the analysis is simply to identify the pollutants present. Judgmental sampling usually requires fewer samples than statistical methods, but the analyst needs to be aware of the limitations of the samples collected by this method.

**Stratified Sampling**

When a system contains several distinctly different areas, these may be sampled separately, in a stratified sampling scheme. The target population is divided into different regions or strata. The strata are selected so that they do not overlap each other. Random sampling is done within each stratum. For example, in a pond or a lagoon where oily waste floats over water and sediment settles to the bottom, the strata can be selected as a function of depth, and random sampling can be done within each stratum.

The strata in a stratified scheme do not necessarily have to be obviously different. The area may be divided into arbitrary subareas. Then a set of these are selected randomly. Each of these units is then sampled randomly. For example, a hazardous waste site can be divided into different regions or units. Then, the soil samples are collected at random within each region or within randomly selected regions. Stratification can reduce the number of samples required to characterize an environmental system, in comparison to fully random sampling.

**Haphazard Sampling**

A sampling location or sampling time is chosen arbitrarily. This type of sampling is reasonable for a homogeneous system. Since most environmental systems have significant spatial or temporal variability, haphazard sampling often leads to biased results. However, this approach may be used as a preliminary screening technique to identify a possible problem before a full scale sampling is done.

**Continuous Monitoring**

An ideal approach for some environmental measurements is the installation of instrumentation to monitor levels of pollutants continuously. These real-time measurements provide the most detailed information about temporal variability. If an industrial waste water discharge is monitored continuously, an accidental discharge will be identified immediately and corrective actions can be implemented while it is still possible to minimize the damage. A grab sample would have provided information about the accidental release only if a sample happened to be taken at the time the release was taking place, and that might well not have been when the problem began. A sample composited frequently enough could have identified the accidental release, but the time for preventive action would likely have passed.

Continuous monitoring is often applied to industrial stack emissions. Combustion sources, such as incinerators, often have CO monitors installed. A high CO concentration implies a problem in the combustion process, with incomplete combustion and high emissions. Corrective action can be triggered immediately. Continuous monitoring devices are often used in workplaces to give early warnings of toxic vapor releases. Such monitors can be lifesaving, if they prevent or minimize chemical accidents such as the one which occurred in Bhopal, India.

At present, a limited number of continuous monitoring devices are available. Monitors are available for gases such as CO, NO2, and SO2 in stack gases, and for monitoring some metals and total organic carbon in water. These automated methods are often less expensive than laboratory-analyzed samples, because they require minimal operator attention. However, most of them do not have the sensitivity required for trace level determinations.

**2.2 Types of Samples**

*Grab sample:* A grab sample is a discrete sample which is collected at a specific location at a certain point in time. If the environmental medium varies spatially or temporally, then a single grab sample is not representative and more samples need to be collected.

*Composite sample:* A composite sample is made by thoroughly mixing several grab samples. The whole composite may be measured or random samples from the composites may be withdrawn and measured.

A composite sample may be made up of samples taken at different locations, or at different points in time. Composite samples represent an average of several measurements and no information about the variability among the original samples is obtained. A composite of samples which all contain about the same concentration of analyte can give a result which is not different from that obtained with a composite made up of samples containing both much higher and much lower concentrations. During compositing, information about the variability, patterns, and trends is lost. When these factors are not critical, compositing can be quite effective. When the sampling medium is very heterogeneous, a composite sample is more representative than a single grab sample. For example, in a study of the exposure to tobacco smoke in an indoor environment, a several hour composite sample will provide more reliable information than several grab samples.

Composite samples may be used to reduce the analytical cost by reducing the number of samples. A composite of several separate samples may be analyzed and if the pollutant of interest is detected, then the individual samples may be analyzed individually. This approach can be useful for screening many samples. A common practice, for example, in clinical laboratories screening samples for drug abuse among athletes is to analyze a composite of about ten samples. If the composite produces a positive result, then the individual samples are tested.

A typical compositing scheme is shown in Figure 2.3. Here a field sample is taken at a random time point once within each hour. These twenty four field samples per day are mixed to form two composites. From each composite two sub-samples are taken and each subsample could also include two repeat samples.

**2.3 Sampling and Analysis**

Even a perfect analytical procedure cannot be rectify the problems created by faulty sample collection. A good sampling plan will ensure that the samples obtained will, on average, closely represent the bulk composition of the environment being measured. In addition, the sample must be collected and handled in a such way that its chemical composition does not change by the time it is analyzed. Finally, the sampling must be done with the requirements of the analytical method in mind.

Proper steps should be taken so that the pollutants are not lost or chemically altered during sample collection, preservation, and transport. Organic materials in water or soil samples, for instance, can be readily attacked and digested by bacteria present in the sample. A preservative to prevent bacterial action may be added as samples are collected, or the samples may be frozen or chilled to reduce these losses. Of course, the preservative must be carefully selected so that it does not interfere with the analyses to be done.

The sample size must be adequate. If a one milliliter water sample containing one ng/l of a pesticide is collected, the sample would contain such a small quantity of pesticide that it could not be detected by conventional analysis. Therefore, a larger volume of water must be collected, from which the pesticide can be concentrated.

The most common environmental samples are air, water, soil, biological materials, and wastes (liquids, solids or sludges). Each matrix is sampled using different techniques, but the underlying concepts are same in each case. It is always good to know as much about the sampling site as possible, especially about the sources of the pollutants being investigated, and the mechanisms for their removal. Before choosing a site for air sampling, pollution sources in the vicinity, such as industries and traffic should be surveyed. Knowledge of previous activities at a hazardous waste site may be helpful in finding the location of maximum contamination. Another important consideration is the physical environment. To predict the migration and distribution of pollutants in a contaminated site, for example, one should know about factors such as soil type, ground and surface water flows. Similarly, for air sampling it is important to take into account factors such as wind direction, temperature, and relative humidity.

***Samples in the Laboratory***

When the sample, composited or not, reaches the laboratory, it may have to be reduced in size. A *reduced sample* is prepared by taking a representative portion of the original sample, usually by a mixing and dividing process. These processes depend strongly on the form of the sample and the analytes being sought. A loose solid, such as a soil sample, may be screened, ground, dumped into a pile and quartered, with opposite quarters being selected, and the other two quarters discarded. This process can be repeated several times to reduce a large sample to a reasonably sized reduced sample.

*Subsamples* are portions of this sample, and after a reduced sample or a subsample is subjected to the laboratory processes needed to prepare it for analysis (grinding, dividing, mixing) it is referred to as a *test sample*. From the test sample, *test portions* are removed for the analysis. This must be of the proper size and concentration to be readily run on the instrument or to be analyzed by the chosen method. Often this test portion is dissolved, digested or extracted to obtain a *test solution*, and this is sometimes further treated with chemicals to derivatize or react some of its components. In that case, it becomes a *treated solution*. Sometimes the test solution is subdivided into equal portions, often to allow replication of the analytical method. These portions are termed *aliquots*, and this term almost always refers to a portion of a liquid. When a solution is made up in a 100 ml volumetric flask, and a 25 ml portion is taken out by pipet, that portion is a one quarter aliquot of the original solution.

**2.4 Statistical Aspects of Sampling**

Uncertainty in environmental measurements can come from both the sampling and the analytical measurement. The total variance is the sum of the two factors:

σ2T = σ2s + σ2a ( Chapter 2 .1)

where the subscript T stands for total variance; subscripts *s* and *a* stand for the sampling and analysis processes respectively. The variance in the sampling process is more difficult to account for. The total variance can be estimated by collecting and analyzing several samples which are expected to produce identical results. The variance of the analytical process can then be subtracted from the total variance to obtain the sampling variance. The variance in the sample not only comes from variation in the sample population, but also from variability during sampling:

σ2s = σ2p + σ2sa ( Chapter 2 .2)

where *p* and *sa* represent population and sampling procedure respectively. The variation in the population may be due to stratification or to temporal variability.

The most important question is the minimum number of samples needed for meeting the measurement objective. In environmental sampling, the situations vary case by case, and it is not easy to form a sampling strategy based on classical statistical prediction. The discussion here offers a simplified approach to predicting the minimum number of samples required to estimate the average pollutant concentration in a certain population. The total uncertainty, E, at a specific level of confidence, is selected. The value of E, and the confidence limit can be used to estimate the quality of the measurement:

E = z σ/ n ( Chapter 2 .3)

where σ is the standard deviation of the measurement, z is the percentile of standard normal distribution depending upon the level of confidence and n is the number of measurements. In environmental measurements, the E, σ and n can be assigned to the sources from which the variations arise.

If the variance due to sampling, σs2 , is negligible and the major source of uncertainty is in the analysis, the minimum number of analysis per sample is given by:

na = [z σa/Ea]2 ( Chapter 2 .4)

The number of analyses can be reduced by choosing an analytical method which has higher precision, i.e., a lower σa or by using a lower value of z, which means accepting a higher uncertainty.

If the measurement uncertainty is negligible (σa → 0), the minimum number of samples, ns is given by:

ns = [z σs/Es]2 ( Chapter 2 .5)

Again the number of samples can be reduced by accepting a higher uncertainty or by reducing σs. The sample variance can be reduced by using a larger number of samples or by taking composite samples.

When σa and σs are both significant, the total error ET is given by:

 ( Chapter 2 .6)

This equation does not have an unique solution. The same value of error, ET, can be obtained by using different combinations of ns and na. Combinations of ns and na should be chosen based on scientific judgment and the cost involved in sampling and analysis. In the usual environmental case, the parameters of the equation are probably not known accurately or even well estimated. Therefore, while statistical equations for determining the number of samples and the number of replicates can be derived, these are seldom of practical use, except as general guidelines.

A simple approach to calculating the number of samples is to collect and analyze a few samples to estimate an overall standard deviation, s. Using Students-t distribution, the number of samples required to achieve a given confidence level is calculated as:

 n = (ts/e)2 ( Chapter 2 .7)

where t is the t-statistic value selected for a given confidence level, and e is the acceptable level of error or uncertainty. The degrees of freedom which determine t can be first chosen arbitrarily and then modified by successive iterations. If an experimental value of σs is not available, an estimate may be done from previous similar studies.

*Example:*

*Preliminary analysis of a few samples from a contaminated site showed Cr(VI) concentrations between 5 to 20 μg/g, and a standard deviation of 3.25. Calculate the number of samples required so that the sample mean would be within ±1.5 μg/g of the population mean at the 95% confidence level. Let us assume 10 degrees of freedom. Using equation 2.7 and the t-table:*

t = 2.23, s = 3.25, and e = 1.5

n = (2.23\*3.25/1.5)2 = 23 Since 23 is significantly larger than 10, an iteration must be done with a new value of t corresponding to 23 degrees of freedom:

n = (2.069\*3.25/1.5)2 = 20

Therefore, 20 samples should be tested. To reduce the number of samples a higher level of error or a lower confidence level may be accepted.

**2.5 Water Sampling**

Water samples can come from many sources: ground water, precipitation (rain or snow), surface water (lakes, river, runoff, etc.), ice or glacial melt, saline water, estuarian water and brines, waste water (domestic, landfill leachates, mine runoff, etc.), industrial process water and drinking water. Pollutants are distributed in the aqueous phase and in the particles suspended in the water. Solids and liquids with densities less than water (such as oils and grease) tend to float on the surface, while those with higher density sink to the bottom. The composition of stagnant water varies with the seasons and also with ambient temperatures. In rivers, lakes and oceans the concentration of pollutants varies with depth and may also depend on the distance from the shore.

Precipitation water changes with meteorological conditions and atmospheric concentrations of the species of interest. The concentration of rainwater components may be higher when precipitation begins, and drop as the pollutants are washed out of the atmosphere. Concentration of water soluble gases such as H2S, SO2, NOx are also higher in the early part of a precipitation event. Ground water shows seasonal variation and is especially affected by rain or snow. Many of these sources exhibit spatial and temporal variation and sampling devices should be chosen with these variations in mind.

Many different types of manual and automatic samplers are commercially available. They are designed to collect grab samples or composite samples. Particular attention is given to material of construction of the sampler. Stainless steel or Teflon are preferred because of their inert nature.

***Surface Water Sampling***

Sampling surface water sources such as lakes, ponds, lagoons, flowing rivers and streams, sewers and leachate streams can be quite challenging. Shallow depths can be sampled as easily as dipping a container and collecting water. However, sampling at depth in stratified sources can offer unique challenges. Prior to sampling, surface water drainage around the sampling site should be characterized. In a flowing water stream, sampling should be carried out down stream before sampling upstream, because the disturbance caused by sampling may affect sample quality. Similarly, if water and sediment samples are to be collected at the same point, the water sample should be collected before the sediment is stirred up.

The simplest sampling device is a dipper (or a container) made of stainless steel or Teflon. The device is filled by slowly submerging the sampler into the water with minimum disturbance and the water is transferred to the sample bottle. This type of device is not good for volatile pollutants which can be lost during sample transfer or by sticking to the surface of the dipper. An example of a surface sampler is shown in Figure 2.4. For sampling from a pond or lagoon, a telescopic pole is attached to the dipper so that the sample can be collected at a distance.

Several different devices are commercially available for collecting samples at different depths. Most of them work on the general principle that a weighted bottle is lowered to the specified depth. At this point, a stopper or a cap is opened and the bottle is allowed to fill. Then the stopper is closed to prevent any water from flowing in or out and the bottle is pulled out. An example of such a device is shown in Figure 2.5.

***Ground Water Well Sampling***

To obtain ground water samples, monitoring wells, from which water samples can be collected, are drilled into the ground. Care should be taken so that the water does not get contaminated during the drilling process or contaminants do enter the water from the surface through the well. To ensure that the sample represents the water in the well and contaminants from drilling are not present in the sample, some water is removed from the well before a sample is collected. The amount of water purged depends upon the diameter, depth and the refill rate of the well. The purge amount is usually 3 to 10 times the well volume. In some cases, the pH, conductance or temperature are monitored until a constant value is reached. Then a sample is collected.

Various bailers and pumps are used in ground water sampling. Bailers are made of stainless steel or Teflon with a check valve at the bottom. The check valve opens to fill the sample, but closes when the sample is brought up. A sketch of the bailer is shown in Figure 2.6. They can be used to obtain samples with minimum disturbance and are useful for samples containing volatile pollutants or those which may degrade with contact with oxygen.

Peristaltic pumps, among others, are used in ground water sampling. Peristaltic pumps are common because the water does not come in contact with any pump parts. Teflon tubing is inserted into the well and is attached to a flexible tubing which is wrapped around the pump rotor and connected to the discharge tube. As the rotor turns, the tubing is squeezed and released and water is forced through the tubing with a peristaltic action.

**2.6 Biological Tissue Sampling**

Contaminants in water or soil often find their way into the food chain and bioaccumulate in plant or animal tissues. The sampling and analysis of various specimens from the biota may be a good way to establish the extent of contamination. Often more pertinent information on the extent of damage done by a particular contaminant can be found in this way, rather than by analyses of water and sediment. A contaminant which is present in a very stable, insoluble form in sediment may remain inert for long periods of time, with no effect on the ecosystem. Yet, the substance would be found in a routine analysis of the sediment. As an example, the extent of water contamination is often determined by a study of fish or other aquatic organisms. This is not only useful for checking on water quality, but also provides a guide to the acceptability of the fish for consumption. Fish tissues are often analyzed for metals and for organic pollutants such as PCBs, and pesticides.

The fish may be caught by hook and line, in nets or traps, or by stunning them with an electrical shock. Because of the uncertainty involved with individual fish, replicates are important. Fish should be chilled immediately by placing them on wet ice in an insulated container. Data on the weight of the fish as well as the time and location of the catch should be recorded. Fish can be stored on ice for a maximum of 24 hours, but should be frozen if longer storage is necessary. In preparing samples for analysis, the fillets should not be skinned. Many fat soluble pollutants such as chlorinated pesticides tend to be concentrated in the layer of fat underneath the skin. Many pollutants tend to accumulate in the liver, so this should be dissected and analyzed. All sampling equipment, as well as dissecting tools should be carefully cleaned and decontaminated by washing with detergent, isopropyl alcohol and finally with analyte-free water, to avoid cross contamination of samples.

**2.7 Soil Sampling**

Soil is quite heterogeneous containing rocks, trapped gases, and liquids. It varies across the surface, and with depth. This variation is caused by contact with the atmosphere and the biosphere, as well as by the flow of ground water. Soil sampling devices must be made of tough material which can be forced into the soil. These are usually brass, steel or plastic, sometimes Teflon coated to prevent contamination of the samples by the metals used in construction of the sampler. Stainless steel sampling devices are most popular. Chrome and nickel plated devices should be avoided since scratches and flaking can contaminate samples with trace elements. When the sampling device is forced into the soil, there is much friction between the tool and the soil sample. Since most of the possible contamination will occur on the surface of the sample which comes in contact with the tool, contamination can be reduced by collecting samples with high volume to surface ratio.

Soil samples collected from the uppermost foot of soil can be obtained using a sample scoop. The soil can be loosened with a shovel or a spade and a scoop can be used to collect the sample. A device for collecting an undisturbed sample is a thin walled tube 3 to 8 cm i.d. and 30 to 60 cm long. This tube sampler is pressed or hammered into the soil and then is pulled out, bringing up a core sample which preserves differences in the soil composition with depth.

For obtaining samples from a greater depth, a device that can drill into the ground has to be used. Samplers of many different designs are available for doing this. A thin walled tube sampler is usually used with an auger bit to drill a hole to the desired depth in the soil. The auger bit is then replaced with a tube corer which is lowered down to the bottom of the hole and is pushed into the soil to the desired depth. The tube is then withdrawn and the sample is collected. This device is quite versatile. Samples can be collected at the surface by using only the tube corer. Devices like this may be used to collect samples down as far as 6 meters under ideal conditions. However, because rocks may be encountered, or the bore hole may collapse in softer soils, the normal sampling depth is usually less than 2 meters. Different types of cutting tips are available for coring dry, moist, sandy, or hard rocky soil. This sampler is depicted in Figure 2.7

The Veihmeyer sampler consists of a sampling tip, sampling tube, a drive head, and a drop hammer. The sampling tube is constructed of chromium molybdenum steel, and its length can be anywhere from 3 to 16 ft. The tube is calibrated every 12 inches. The drive head is attached to the top of the tube to prevent the hammer from deforming the tube when it is driven into the ground. The sampling tip is removable, and different tips are available for different types of soils. The drop hammer is made of cast iron, weighs about 15 lb., and is used to drive the sampling tube into the ground. A puller jack may be used to pull the tube sampler out when sampling is done at a greater depth, or when the soil is hard.

**2.8 Sampling Stratified Levels in Containers**

Sampling the contents of containers of non-homogeneous materials, for example, barrels of hazardous waste, can offer additional challenges especially when the liquid is stratified within the container. An oily liquid will float over an aqueous waste, while solids may settle to the bottom. Several different types of samplers have been developed for taking samples from containers of this type. An example is the stratified sample thief, shown in Figure 2.8. This consists of an outer sheath and an inner rod. Along the rod round, flexible wipers are positioned to hold the sample in place, and prevent the different layers of liquid from mixing with one another. First the outer sheath is raised, exposing the center rod. The rod is gently lowered into the container from which the sample is to be collected. Then the outer sheath is moved down, trapping the liquid in place. When the sampler is withdrawn, samples of the liquid at each level can be recovered.

**2.9 Preservation of Samples**

The sample must be representative of the environment. Both physical and chemical processes may be involved in changing the composition of a sample after it is collected. Common physical processes which may degrade a sample are volatilization, diffusion, and adsorption. Possible chemical changes include photochemical reaction, oxidation and microbial degradation.

The collected sample is invariably exposed to conditions very different from the original source. For example, if a ground water sample is exposed to sunlight after it is collected, photochemical reactions may degrade some of the analytes of interest. Samples often must be preserved in some way, to keep them stable until the analysis is completed. Table 2.1 shows some sample types and the appropriate preservation methods. These methods must not only keep the sample stable, but must not interfere with the analyses to be done.

The steps commonly taken to minimize sample degradation are the use of proper containers, temperature control, addition of chemical preservatives, and observance of the recommended maximum sample holding time. The holding time depends upon the analyte of interest and the matrix under considerations. For example, some metals in water can be held for months, while Cr(VI) analysis should be performed within 24 hours. If the holding time is unknown, one can make up a spiked sample, or store an analyzed actual sample, and analyze it at fixed intervals to determine the optimum holding time.

***Volatilization***

Analytes with high vapor pressures, such as volatile organic compounds and dissolved gases, such as HCN, SO2, will readily escape from the sample by evaporation. Filling sample containers to the brim, so that they contain with no head space is the most common practice to minimize volatilization. The volatiles cannot not equilibrate between the water and the vapor phase above, if no air space is present at the top of the container. The samples are usually held at 4oC, on ice, to lower the vapor pressure. Agitation during sample handling should also be avoided, to minimize air-sample interaction.

***Choice of Proper Containers***

The surface of the sample container may interact with the analyte. For example, metals can adsorb irreversibly on glass surfaces, so plastic containers are often chosen for water samples to be analyzed for their metal content. These samples are also acidified with HNO3 to help keep the metal ions in solution.

Organic molecules may also diffuse in or out of the sample if the proper container is not used. Plasticizers, such as phthalate esters can diffuse from plastic containers into the sample. For organic analytes, it is best to collect sample in glass containers. Bottle caps should have Teflon liners to preclude contamination from the plastic caps.

Oily materials in water samples will adsorb strongly on plastic surfaces, and samples to be analyzed for such materials are usually collected in glass bottles. Oil which remains on the bottle walls should be removed by rinsing with a solvent and returned to the sample. Sometimes, oily samples are emulsified with a sonic probe to form a uniform suspension of the oil and then removed for analysis.

***Absorption of Gases from the Atmosphere***

Water samples can dissolve gases from the atmosphere as they are being poured into containers. Such components as O2, CO2 as well as volatile organic compounds may dissolve in the samples. Oxygen may oxidize species such as sulfite or sulfide to sulfate. Absorption of CO2 may change conductance or pH measurements. This is one reason why pH measurements are always done in the field. Dissolution of organic compounds may lead to the detection of compounds that were actually absent. Field blanks should show if the samples have been contaminated with organic compounds which have been absorbed during sampling or transport.

***Chemical Changes***

A wide range of chemical changes in the sample are possible. For inorganic samples, controlling the pH can be useful in prevention of chemical reactions. For example, metal ions may react with oxygen to form insoluble oxides or hydroxides. The sample is usually acidified with HNO3 to a pH less than 2, as most nitrates are soluble and excess nitrate ions will prevent precipitation. Other ions such as sulfide, or cyanide, are also preserved by pH control. Samples collected for NH3 are acidified with sulfuric acid to stabilize the NH3 as NH4SO4.

Organic species can also undergo changes due to chemical reactions. Photooxidation of polynuclear aromatic hydrocarbons, for example, is prevented by storing the sample in amber glass bottles. Organics can also react with free chlorine to form chlorinated organics. This type of problem is common for samples collected in treatment plants after the water has been chlorinated. Sodium thiosulfate, added to the sample, will remove chlorine.

Samples may also contain microorganisms which may biologically degrade the sample. High or low pH conditions, and chilling can minimize microbial degradation. The microbes can also be killed by addition of mercuric chloride or pentachlorophenol, if these preservatives will not interfere with the planned analyses.

***Sample Preservation for Soil, Sludges, and Hazardous Wastes***

Handling of water samples is better understood than solid and sludge samples, as these can be more varied in composition, but similar methods are used. Commonly encountered problems are biodegradation, oxidation-reduction and volatilization. Storing the sample at low temperature is always recommended to reduce volatilization, chemical reaction, and biodegradation.

A preservation temperature of 4oC is most commonly used, because ice storage is convenient, and because a lower temperature may freeze the water, and separate the organic phase from the aqueous. Minimizing head space is also important for reducing volatilization losses. This also eliminates oxygen so that aerobic biodegradation or chemical oxidation are reduced. Samples to be analyzed for volatile organic compounds are sometimes collected directly into a known quantity of a solvent. In the laboratory, the analytes are either extracted or purged from the solvent. Methanol and polyethylene glycol have been used for this purpose.

**References and Suggested Readings**

1. Statistical Methods for Environmental Pollution Monitoring; R. O. Gilbert, Van Nostrand Reinhold, New York 1987.
2. Environmental Sampling and Analysis for Technicians; M. Csuros, Lewis Publishers, Boca Raton, 1994.
3. Sampling for Environmental Data Generation; P. Grieco and R. Trattner, SciTech Publishers, Matawan, NJ 1990.
4. Principles of Environmental Sampling, L. D. Keith, American Chemical Society, Washington, DC 1988.

**Study Questions**

1. Describe the steps in a well-designed sampling plan.
2. What is the importance of a good sample?
3. What factors must be considered when obtaining a sample?
4. What factors must be considered when storing and transporting a sample?