Chapter 1

Introduction to Environmental Data Acquisition

This introductory chapter will give readers a brief overview of the purposes and scopes of environmental sampling and analysis. Sampling and analysis, apparently the independent steps during data acquisition, are in fact the integrated parts to obtain quality data—the type of data that are expected to sustain scientific and legal challenges. The importance of environmental sampling and the uniqueness of environmental analysis as opposed to traditional analytical chemistry are discussed. A brief history of classical to modern instrumental analysis is also introduced in this chapter.

1.1 INTRODUCTION

The *objectives of environmental sampling and analysis* may vary depending on the specific project (task), including regulatory enforcement, regulatory compliance, routine monitoring, emergency response, and scientific research. The examples are as follows:

1. To determine how much pollutant enters into environment through stack emission, wastewater discharge, and so forth in order to comply with a regulatory requirement.

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2. To measure ambient background concentration and assess the degree of pollution and to identify the short- and long-term trends.
3. To detect accidental releases and evaluate the risk and toxicity to human and biota.
4. To study the fate and transport of contaminants and evaluate the efficiency of remediation systems.

This introductory chapter briefly discusses the basic process of environmental data acquisition and errors associated with field sampling and laboratory analysis. A unique feature of this text is to treat sampling and analysis as an entity. This is to say that sampling and analysis are closely related and dependent on each other. The data quality depends on the good work of both sampler and analyst.

The *importance of sampling* is obvious. If a sample is not collected properly, if it does not represent the system we are trying to analyze, then all our careful lab work is useless! A bad sampler will by no means generate good reliable data. In some cases, even if sampling protocols are properly followed, the design of sampling is critical, particularly when the analytical work is so costly.

Then what will be the data quality after a right sample is submitted for a lab analysis? The results now depend on the chemist who further performs the lab analysis. The *importance of sample analysis* is also evident. If the analyst is unable to define an inherent level of analytical error (precision, accuracy, recovery, and so forth), such data are also useless. The analyst must also know the complex nature of a sample matrix for better results. The analyst needs to communicate well with the field sampler for proper sample preservation and storage protocols.

1.1.1 Importance of Scientifically Reliable and Legally Defensible Data

All environmental data should be scientifically reliable. *Scientific reliability* means that proper procedures for sampling and analysis are followed so that the results accurately reflect the content of the sample. If the result does not reflect the sample, there is no claim of validity. Scientifically defective data may be a result of unintentional or deliberate efforts. The examples include the following:

- An incorrect sampling protocol (bad sampler)
- An incorrect analytical protocol (bad analyst)
- The lack of a good laboratory practice (GLP)
- The falsification of test results.

Good laboratory practice (GLP) is a quality system concerned with the organizational process and the conditions under which studies are planned, performed, monitored, recorded, archived, and reported. The term “defensible” means “the ability to withstand any reasonable challenge related to the veracity, integrity, or quality of the logical, technical, or scientific approach taken in a decision-making process." As scientific reliability must be established for all environmental data, legal defensibility may not be needed in all cases such as the one in most academic research projects. Legal defensibility is critical in many other circumstances such as in most of the industrial and governmental settings. Components of legally defensible data include, but are not limited to:

- Custody or Control
- Documentation
- Traceability.

Custody or Control: To be defensible in court, sample integrity must be maintained to remove any doubts of sample tampering/alteration. A *chain-of-custody* form can be used to prove evidence purity. The chain-of-custody form is designed to identify all persons who had possession of the sample for all periods of time, as it is moved from the point of collection to the point of final analytical results. "Control" over the sample is established by the following situations: (1) It is placed in a designated secure area. (2) It is in the field investigator's or the transferee's actual possession. (3) It is in the field investigator's or the transferee's physical possession and then he/she secures it to prevent tampering. (4) It is in the field investigator's or the transferee's view, after being in his/her physical possession (Berger et al., 1996).

Documentation: Documentation is something used to certify, prove, substantiate, or support something else. In a civil proceeding, documentation is anything that helps to establish the foundation, authenticity, or relevance leading to the truth of a matter. It may become evidence itself. Photos, notes, reports, computer printouts, and analyst records are all examples of documentation. The chain-of-custody form is one such piece of very important type of document. Documentary evidence is the written material that "speaks for itself."

Traceability: Traceability, otherwise known as a "paper trail," is used to describe the ability to exactly determine from the documentation that which reagents and standards were used in the analysis and where they came from. Traceability is particularly important with regard to the standards that are used to calibrate the analytical instruments. The accuracy of the standards is a determining factor on the accuracy of the sample results. Thus, each set of standards used in the lab should be traceable to the specific certificate of analysis (Berger et al., 1996).

Similar to the components of scientifically defective data, legally weak data may be a result of unintentional or deliberate efforts. In the case of misconduct, the person involved will be subjected to the same punishment as those who commit criminal acts, such as those frequently reported (Margasak, 2003). *Misconducts* in environmental sampling and analysis can be a result of the following:

- Outside labs oftentimes work for the people who hired them
- Poor training of employees in nongovernmental or private labs
- Ineffective ethics programs
- Shrinking markets and efforts to cut costs.

This text will not discuss the nontechnical or legal aspects of sampling and analysis, but the reader should be cautious about its importance in environmental data acquisition. The legal objective can influence the sampling and analytical effort by specifying where to sample, defining the method of sampling and analysis, adding additional requirements to a valid technical sampling design for evidentiary reasons, and determining whether the data are confidential (Keith, 1996). Sampling and analytical protocols must meet legal requirements for the introduction of evidence in a court, and the results of a technically valid sampling and analytical scheme might not be admissible evidence in a courtroom if the legal goal is not recognized early on in the presampling phase. A brief introduction to important environmental regulations will be presented in Chapter 2.

Practical tips

- In governmental and industrial settings, lab notebooks are the legal documents. In most of the research institutions, the rules about notebooks are loosely defined. In any case, date and signature are part of the GLP.
- Do not remove any pages and erase previous writings. Write contact information on the cover page in case of loss. A typical life of a laboratory notebook ranges from 10 to 25 years (Dunnivant, 2004).

1.1.2 Sampling Error vs. Analytical Error During Data Acquisition

During data acquisition, errors can occur anytime throughout the sampling and analytical processes—from sampling, sample preservation, sample transportation, sample preparation, sample analysis, or data analysis (Fig. 1.1). Errors of environmental data can be approximately divided into sampling error and analytical error. In general, these errors are of two types: (1) *Determinate errors* (systematic errors) are the errors that can be traced to their sources, such as improper sampling and analytical protocols, faulty instrumentation, or mistakes by operators. Measurements resulting from determinate error can be theoretically discarded. (2) *Indeterminate errors* (random errors) are random fluctuations and cannot be identified or corrected for. Random errors are dealt with by applying statistics to the data.

The quality of data depends on the integrity of each step shown in Figure 1.1. Although errors are sometimes unpredictable, a general consensus is that most errors come from the sampling process rather than sample analysis. As estimated, 90% or more is due to sampling variability as a direct consequence of the heterogeneity of environmental matrices. It is therefore of utmost importance that right samples are collected to be representative of the feature(s) of the parent material being investigated. A misrepresentative sample produces misleading information. Critical elements of a sample's representativeness may include the sample's physical dimensions, its location, and the timing of collection. If representativeness cannot be established, the quality of the chemical analysis is irrelevant (Crumbling et al., 2001).

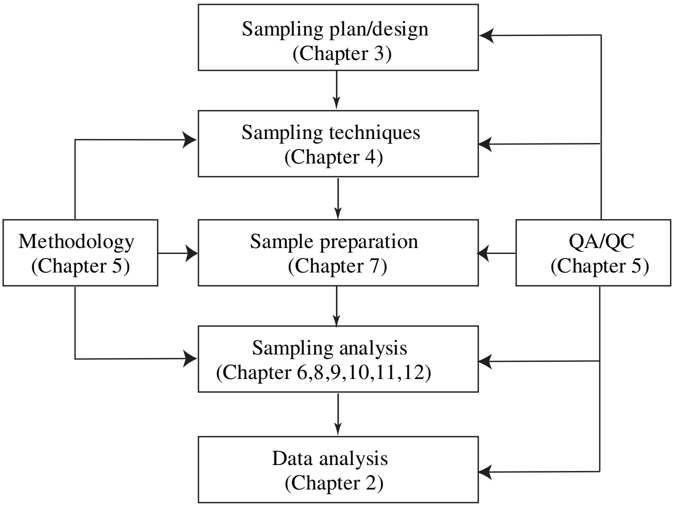

Figure 1.1. Environmental data acquisition process

Unfortunately, there is a general misconception among many environmental professionals that the quality of data pertaining to a contaminated site is primarily determined by the nature of analytical methods used to acquire data. This assumption, which underestimates the importance of sampling uncertainties, can lead to a pronounced, negative impact on the cost-effective remediation of a contaminated site. In fact, it is of little use by placing an emphasis only on analytical uncertainty when sampling uncertainty is large and not addressed (Crumbling et al., 2001).

Errors in environmental data acquisition can be minimized through the proper design and implementation of a quality program. Two main parts of a quality program are quality control (QC) and quality assurance (QA). QC is generally a system of *technical* activities aimed at controlling the quality of data so that it meets the need of data users. QC procedures should be specified to measure the precisions and bias of the data. A QA program is a *management* system that ensures the QC is working as intended. QA/QC programs are implemented not only to minimize errors from both sampling and analysis, but many are designed to quantify the errors in the measurement. Details on QA/QC will be presented in Chapter 5.

1.2 ENVIRONMENTAL SAMPLING

1.2.1 Scope of Environmental Sampling

The scope of environmental sampling can be illustrated by a sample's life with the following seven consecutive steps (Popek, 2003). Since these steps are irreversible, a mistake can be detrimental. These seven steps of a sample's life are as follows: (1) a sample is planned ("conceived"); (2) a sampling point is identified; (3) the sample is collected (“born”); (4) the sample is transferred to the laboratory; (5) the sample is analyzed; (6) the sample expires and is discarded; and (7) the sample reincarnates as a chemical data point. Simply, the *scope of environmental sampling* addressed in this book will include the following aspects related to sampling:

- Where to take samples
- When to take samples
- How to take samples
- How many samples to take
- How often samples will be taken
- How much sample is needed
- How to preserve samples
- How long the sample will be stable
- What to take (air, soil, water)
- What to analyze (physical, chemical, biological)
- Who will take samples (sample custody)?

1.2.2 Where, When, What, How, and How Many

Many think of field sampling as simply going out to the field and getting some material, then bringing it back to a lab for analysis. Although such “random” sampling is often suggested as the basis of a sampling design, it is rarely the most appropriate approach, particularly when there is already some knowledge of the nature of the sample source and the characteristics of the variable being monitored. The choice of where (spatially) and when (temporally) to take samples generally should be based on sound statistics (simple random sampling, stratified random sampling, systematic sampling, composite sampling, as given in Chapter 3).

Although guidelines exists (detailed in Chapters 3 and 4), there is no set rule regarding the number, the amount, and the frequency of samples/sampling. For instance, the optimum number of samples to collect is nearly always limited by the amount of resources available. However, it is possible to calculate the number of samples required to estimate population size with a particular degree of accuracy. The best sample number is the largest sample number possible. But one should keep in mind that no sample number will compensate for a poor sampling design. In other words, quantity should not be increased at the expense of quality. Data in a poor quality will have more inherent error and, therefore, make the statistics less powerful.

1.3 ENVIRONMENTAL ANALYSIS

Whereas some of the environmental analyses are conducted in the field, the majority of the work is conducted in the laboratory. Depending on the data objectives, standard analytical methods should be consulted. This in turn depends on the analyte concentration, available instruments, and many other factors. Method selections are discussed in Chapter 5. This is followed by the common wet chemical analysis (Chapter 6) and instrumental methods (Chapters 8–12). Chapter 7 is devoted to sample preparation that is very critical to most of the complicated environmental samples.

1.3.1 Uniqueness of Modern Environmental Analysis

Environmental analyses are very different from the traditional chemical analysis entailed in analytical chemistry. Regardless, the majority of environmental analytical work has been traditionally and currently, are still, performed by the majority of analytical chemists. In the early days, this presented challenges to analytical chemists largely due to the complex nature of environmental samples and the analyses of trace concentrations of a wide variety of compounds in a very complex matrix. As Dunnivant (2004) stated, “my most vivid memory of my first professional job is the sheer horror and ineptitude that I felt when I was asked to analyze a hazardous waste sample for an analyte that had no standard protocol. Such was a life in the early days of environmental monitoring, when chemists trained in the isolated walls of a laboratory were thrown into the real world of sediment, soil, and industrial waste samples.”

Today’s analytical chemists, however, are better prepared for environmental analyses because a wealth of information is available to help them to conduct sampling and analysis. Nevertheless, professionals who are not specifically trained in this area need to be aware of the uniqueness of modern environmental analysis listed below (Fifield and Haines, 2000):

- There are numerous environmental chemicals, and the costs for analysis are high.
- There are numerous samples that require instrument automation.
- Sample matrices (water, air, soil, waste, living organisms) are complex, and matrix interferences are variable and not always predictable.
- Chemical concentrations are usually very low, requiring reliable instruments able to detect contaminants at ppm, ppb, ppt, or even lower levels.
- Some analyses have to be done on-site (field) on a continuous basis.
- Analysts need not only the technical competency but also the knowledge of regulations for regulatory compliance and enforcement purposes.

1.3.2 Classical and Modern Analytical and Monitoring Techniques

Environmental analyses are achieved by various “classical” and “modern” techniques. The difference between “classical” and “modern” analytical and monitoring techniques is a little arbitrary and ever changing as technology advances and many instruments continue to be modernized. For example, the analytical balance was, for a long time, considered to be the sophisticated instrument. With today's standards, however, those early balances were rather crude. Many of such yesterday's sophisticated instruments have become today's routine analytical tools. They are essential and continued to be improved and modernized (Rouessac and Rouessac, 1992).

Table 1.1 is a chronological listing of selected analytical instrumentations. In general, volumetric and gravimetric methods (wet chemicals) are the *classical methods*. Spectrometric, electrometric, and chromatographic methods are good examples of *modern analytical instrumentation*. Today's environmental analyses rely heavily on modern instrumentations. This, however, does not imply that classical methods will be vanished anytime soon. As can be seen, analytical instrumentations have become increasingly sophisticated to meet the analytical challenge. The advancement has made it possible to detect what would not had been detected in the past.

In the 1950s *gravimetric methods* were primarily used to estimate analyte's mass and concentration by precipitation, infiltration, drying, and/or combustion. Although gravimetric methods were sufficient, colorimetric and spectroscopic methods offered a greater precision. *Wet-chemistry-based methods* were developed that altered the spectroscopic properties of chemicals such as DDT and made these

Table 1.1 Selected milestones for analytical instrumentations

Year	Instrument
1870	First aluminum beam analytical balance by Florenz Sartorius
1935	First commercial pH meter invented by Arnold O. Beckman
1941	First UV-VIS spectrophotometer (Model DU) by Arnold O. Beckman
1944	First commercial IR instrument (Model 12) by Perkin-Elmer
1954	Bausch and Lomb introduced the Spectronic 20 (still used today in teaching)
1955	First commercial GC produced by the Burrell Corp (Kromo-Tog), Perkin-Elmer (Model 154), and Podbielniak (Chromagraphette)
1956	First spectrofluorometer by Robert Bowman
1956	First commercial GC/MS using time-of-flight (Model 12-101) by Bendix Corp.
1963	First commercially successful AA (Model 303 AA) by Perkin-Elmer
1963	First commercial NMR from a German company Bruker
1965	First true HPLC was built by Csaba Horváth at Yale University
1969	First commercially available FI-IR (FTS-14) introduced by Digilab
1970	First commercial graphite furnace AA by Perkin-Elmer
1974	First ICP-OES became commercially available
1977	First commercial LC–MS produced by Finnigan (now Thermo Finnigan)
1983	First commercial ICP–MS (Elan 250) by MDS Scix

AA = atomic absorption spectroscopy; ICP = inductively coupled plasma; OES = optical emission spectroscopy; IR = infrared spectroscopy; FT-IR = fourier transform infrared spectroscopy; NMR = nuclear magnetic resonance spectroscopy. See also Appendix A for a more detailed list of abbreviations and acronyms used in this text.

chemicals suitable for colorimetric determinations. These methods offered some advantages, but were still tedious and imprecise.

Soon, *chromatographic methods* made inroads into resolving separate components from a mixed solution. Chromatography is a physical method of separation that relies on the interaction of substances within a mixture when they are exposed to both a stationary and a mobile phase. Early thin-layer chromatography (TLC) and paper chromatography (PC) techniques used in the 1950s and 1960s separated compounds that were detected by measuring their intensity using ultraviolet and visible (UV-VIS) spectroscopy techniques.

Gas chromatography (GC) and high performance liquid chromatography (HPLC) were developed in the 1960s, becoming the methods of choice for residue analysis and replacing TLC and PC in the 1970s. GC and HPLC techniques efficiently "resolve" individual components from a complex mixture and can accurately quantify how much of an individual substance is present in the mixed component sample. The primary difference between GC and HPLC is that the former relies on resolution of substances being swept through a chromatography column in the gas phase at elevated temperatures, while the latter relies on the substance in a solution being chromatographically separated when in contact with a solid stationary phase.

Mass spectroscopy (MS) developments in the 1980s dramatically enhanced the scope of detection to include most semi- to nonpolar, and thermally-stable compounds. The first generation combined GC–MS relied on electron impact (EI) ionization to fragment the molecule into an array of positive mass ions. Continued refinement in GC–MS and maturation of HPLC-mass spectrometry has resulted in increasingly sensitive detections at even lower levels. Overall, the advances in instrumentation and technology have provided analysts with powerful tools to rapidly and accurately measure extremely low levels. Advanced analytical instrumentations tend to detect small quantities of almost anything.

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*Suggested Readings

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QUESTIONS AND PROBLEMS

1. Give examples of practice that will cause data to be scientifically defective or legally nondefensible.
2. Define and give examples of determinate errors and random errors.
3. Describe scopes of environmental sampling.
4. Why sampling and analysis are an integral part of data quality? Between sampling and analysis, which one often generates more errors? Why?
5. Describe how errors in environmental data acquisition can be minimized and quantified?
6. How does environmental analysis differs from traditional analytical chemistry?
7. Describe the difference between "classical" and "modern" analysis.
8. A chemist is arguing that sampling is *not* as important as analysis. His concern is whether there is a need for a sampling course in an environmental curriculum. His main rationale is that most employers and governmental agencies already have their own training courses and very specific and detailed procedures. Another consultant, on the contrary, argues that sampling should be given more weight than analysis. His main rationale is that a company always sends samples to commercial laboratories for analyses, and you do not become an analytical chemist by taking one course. For each of these two arguments, specify whether you agree or disagree and clearly state your supporting argument why you agree or disagree.