

ENVIRONMENTAL ANALYTICAL CHEMISTRY

Chunlong Zhang

University of Houston-Clear Lake, Houston, Texas, U.S.A.

Keywords: environmental analysis, environmental sampling, environmental monitoring, sampling design, sample preparation, instrumental analysis, bioanalysis

Contents

1. Historic Perspectives and Scopes of Environmental Analytical Chemistry
 - 1.1 Historic Perspectives
 - 1.2. Unique Features of Environmental Analytical Chemistry
 - 1.3 Scopes and Discipline Organizations
 2. Environmental Sampling: Purpose, Design Strategy and Techniques
 - 2.1. Importance of Environmental Sampling
 - 2.2. Sampling Design and Strategy
 - 2.3. Sampling Techniques
 3. Sample Preparation for Environmental Analysis
 - 3.1. Purposes of Environmental Sample Preparations
 - 3.2 Types of Environmental Sample Preparation
 4. Instrumental Analysis of Environmental Chemicals
 - 4.1. Classical Methods vs. Instrumental Methods in Environmental Analysis
 - 4.2. Molecular Spectroscopy in Environmental Analysis
 - 4.3. Atomic Spectroscopy in Environmental Analysis
 - 4.4. Chromatography in Environmental Analysis
 - 4.5. Mass Spectrometry in Environmental Analysis
 - 4.6. Electroanalytical Methods in Environmental Analysis
 - 4.7. Thermal Methods in Environmental Analysis
 - 4.8. Radiochemical Methods in Environmental Analysis
 5. Bioanalysis of Environmental Chemicals
 - 5.1. Immunoassay
 - 5.2 Biosensors
 6. Future Perspectives and Challenges of Environmental Analytical Chemistry
- Glossary
Bibliography
Biographical Sketch

Summary

Environmental analytical chemistry has evolved from the traditional analytical chemistry to a well-established discipline and a profession attractive to a diverse group of environmental scientists / engineers, chemists, and educators. Environmental analysis and monitoring is a very challenging and dynamic field in a sense that it involves the most uncertain and error-prone stage of acquiring representative samples, laborious sample preparation from complex matrices, costly instrumental qualification and quantification of contaminants at the parts per million to parts per quadrillion levels, and the ever changing requirements for regulatory compliance in monitoring drinking water,

wastewater, ambient / emission air, and solid / hazardous wastes. The discussions of this chapter start with the historical perspectives, unique features, and scopes of this discipline. The importance of representative sampling, the approaches to select cost-effective sampling design schemes, as well as classical grab / active sampling vs. passive diffusion-based sampling techniques are delineated, followed by the discussions of environmental sample preparation goals, various digestion procedures for inorganic metals, and various extraction and partition based methods for volatile and semi-volatile compounds. Traditional chemical instrumental methods and their corresponding environmental applications are briefly described with respect to spectroscopic, chromatographic, mass spectrometric, electrochemical, thermal, and radiological methods. Complementary bioanalytical methods currently used in environmental analysis such as immunoassays and those with promise in future development such as biosensors are introduced. This chapter concludes with the remarks on the future perspectives and challenges of environmental analytical chemistry. There is an urgent need for advancing sampling methodology for practical applications, instrumental innovations for faster, more sensitive and affordable bench instruments, and miniature sensing devices for real-time monitoring and remote applications.

1. Historic Perspectives and Scopes of Environmental Analytical Chemistry

Environmental analytical chemistry (EAC) can be envisioned as a branch of analytical chemistry as well as a branch of environmental chemistry. If we define analytical chemistry as the study of the separation, identification, and quantification of the chemical components of natural and synthetic origins, then EAC can be defined as the study of the separation, identification, and quantification of the chemical components of environmental importance. Since environmental chemistry can be defined as the study of contaminant behavior (pollution chemistry), analysis (environmental analytical chemistry), and chemical control technology (pollution control chemistry), EAC falls within the boundary of environmental chemistry as one of its sub-disciplines.

1.1 Historic Perspectives

From the historical standpoint, however, the origin of environmental analytical chemistry can be traced from analytical chemistry when environmental issues became important and the analysis of environmental contaminants became necessary. In analytical chemistry, the first aluminum beam analytical balance was developed by Florenz Sartorius in 1870. Major developments in analytical chemistry, however, did not occur until after 1900, when many of the basic spectroscopic and spectrometric techniques were developed during the early 20th century and these instrumentations were further refined in the late 20th century (Wikipedia 2012). These spectroscopic and spectrometric techniques still remained in modern day environmental labs for many of the routine analysis, but the major breakthrough was the instruments for trace inorganic and organic analysis since the 1950s, including the first commercial gas chromatography (GC) produced by the Burrell Corp in 1955, first commercial gas chromatography-mass spectrometry (GC/MS) using time-of-flight (TOF) by Bendix Corp, first commercially successful atomic absorption spectroscopy (AA) by Perkin-Elmer Inc. in 1963, and the first true high performance liquid chromatography (HPLC) by Csaba Horvath at Yale University in 1965 (Zhang, 1997). These instruments have

since become the mainstream analytical tools for environmental analysis of heavy metals and organic pollutants such as pesticides, PAHs, and PCBs. The recognition of all of these contaminants, now referred to as legacy contaminants, took place since the environmental movement started in 1950s.

Environmental analytical chemistry evolved from traditional analytical chemistry probably in the early 1980s to the early 1990s. The first textbook bearing the name of Environmental Analytical Chemistry was published by Mr. F.W. Fifield and Mr. P.J. Haines (both were lecturers in Kingston University, UK) that provided a wide ranging review of analytical chemistry having a focus specific to environmental science. It is, however, apparent that books with partial or similar contents had published much earlier. After the 1990s, many other related books have been published, some with a broad coverage (e.g., Loconto, 2001, *Trace Environmental Quantitative Analysis*; Keith, 1991, *Environmental Sampling and Analysis: A Practical Guide*), and others with a specific coverage within the discipline of environmental analytical chemistry (e.g., Erickson, 1995, *Analytical Chemistry of PCBs*). Current textbooks in Environmental Chemistry contain contents of environmental analytical chemistry as a separate chapter, such as Manahan (2000) and Girard (2010). Many of these environmental analytical chemistry books were mostly written by people with traditional analytical chemistry expertise and placed a focus on the “analytical” aspect, whereas “sampling” as a much bigger contributor to the total error in environmental measurements was excluded or kept minimal. Such has been changed when the quality of environmental data was pointed from the laboratory measurement to the field sampling of air, water, soil, and solid waste materials. Sampling guidelines have been published by various governmental agencies, and a textbook addressing both environmental sampling and analysis have also been published (e.g., Zhang 2007, *Fundamentals of Environmental Sampling and Analysis*). Many colleges and universities around the world are now offering an environmental analytical chemistry course or an equivalent course as a proper training needed for students in the environmental curricula. Increasing research attention has been placed on the development of new sampling methodology and innovative instrumentations for environmental measurements, as is evident in published papers among diverse international journals such as *International Journal of Environmental Analytical Chemistry*, *Journal of Environmental Monitoring*, *Analytical Chemistry*, *Journal of Chromatographic Science*, and *Environmental Science and Technology*. Graduates with training and education in this field often find rewarding employment opportunities in government agencies, industrial sectors, consulting firms, research and commercial laboratories, and academic institutions.

1.2. Unique Features of Environmental Analytical Chemistry

Environmental analytical chemistry has the root of analytical chemistry, but as a well-established and an independent discipline, it differs from the traditional analytical chemistry in several aspects (Fifield and Haines, 2000; Zhang, 2007):

- (a) Low concentration: Except for some conventional testing parameters, most environmental pollutants are present at the trace level or ultra trace level rather than in the units of percent (%), molarity (M), or normality (N) commonly seen in the analytical chemistry field. The concentrations could be from as high as

parts per million (ppm), parts per billion (ppb), parts per trillion (ppt), to as low as parts per quadrillion (ppq), or even lower. In laymen's term, 1 ppt (10^{-12}) is equivalent to one drop of water diluted into 20 Olympic-size swimming pools ($50,000 \text{ m}^3$), or about three seconds out of every hundred thousand years. In a similar analogy, 1 ppq (10^{-15}) is equivalent to 1 drop of water diluted into a cube of water measuring approximately 368 meters on a side (fifty million cubic meters, which is a cube about as tall as the Empire State Building's 102 stories), or two and a half minutes out of the age of the Earth (4.5 billion years) (Wiki). Many of the emerging environmental contaminants are present at the ppt levels, and measurements of contaminants at the ppq level have also become feasible.

- (b) **Complex matrices:** Environmental matrices are diverse, including air, surface water (river, lake), drinking water, groundwater, soil, aerosol, sediment, sludge, hazardous waste, biological specimen (blood, fat, hair, plant tissues) and many other types, and are sometimes of unknown origins. Detecting trace levels of environmental pollutants from complex matrices requires complex and tedious procedures to remove interference and background bulk chemicals, separate chemicals of interest, and concentrate the aliquot to the detectable levels. Thus, not only instrumental analysis is essential, but also the sample preparation is critical for the expected accuracy and precision of the entire procedure. Many times, this sample preparation adds the critical component of the uncertainty and variability toward the overall environmental measurement.
- (c) **High cost for both sampling and analysis:** Often times, environmental projects involve lots of samples to delineate spatial or temporal patterns of environmental pollutants. The costs for sampling and analysis for a large number of samples will be high. In some cases, sampling cost is low relative to analytical cost (e.g., the cost for a group of trace organic compounds in soils can be in the range of \$50 to \$400 per sample). In other cases, analytical costs might be low compared to sampling, for example, when samples are taken in a remote place for some routine chemical measurements.
- (d) **Demand of in-situ monitoring and automation:** In situ monitoring may become the only option in certain circumstances such as atmospheric monitoring (e.g., SO_2 , O_3 , and NO_x) and effluent from wastewater treatment plants. In most cases, automation (e.g., auto sample collection or injections) is essential when dealing with a large number of samples to avoid labor-intensive and less reproductive manual efforts. A reliable and robust automation and the capacity of in-situ measurements are the key to the success for environmental monitoring.
- (e) **Subject to laws and regulations:** An awareness of “environmental laws and regulations” in the daily work of environmental sampling and analysis is crucial. First, one should recognize that all environmental sampling and analytical work (some academic research excluded) is regulations-driven, such as the work done by the law enforcement agencies (federal, state, and local environmental agencies) and manufacturers/industries whose responsibilities are to assure the regulatory compliance with the effluent and emission standards. Second, many

of the environmental sampling and analytical protocols are in the categories of “regulatory methods” as opposed to “consensus methods”. For the former, they are approved by a regulatory agency and are mandatory under a certain program or law such as the Safe Drinking Water Act and the National Pollutant Discharge Elimination System by the U.S. EPA. The consensus methods are not regulatory enforced methods but are published by a professional organization such as ASTM or NIOSHA.

1.3 Scopes and Discipline Organizations

Environmental analytical chemistry is the applied analytical chemistry concerning environmental pollutants, and in the meantime it is the measurement tool in the field of environmental chemistry to qualify and quantify environmental pollutants. It is important to note that “pollutants” or “contaminants” in this writing has the broad meaning of not only the “chemical” pollutants, but also the biological, thermal, radiological or other physical parameters of environmental interest (Figure 1).

Environmental analytical chemistry can be further grouped into different subjects. As illustrated in Figure 1, its subject contents can be classified according to (a) the types of environmental parameters (inorganic, organic, biological/toxicological, radiological); (b) its operational procedures from sampling, sampling preparation, sample analysis to data analysis; and (c) the types of environmental matrices such as air (ambient atmosphere, emission air), liquid (drinking water, wastewater), solids (soil, sediment, sludge, solid waste and hazardous waste), and biological specimen (foods, plants, animals, and human fluids and tissues).

In the traditional analytical chemistry context that often focuses solely on “analysis”, the analytical methods are divided into wet-chemical methods and instrumental methods. The wet-chemical methods are gravimetric or volumetric types such as those methods used for the measurement of suspended solids (SS), chemical oxygen demand (COD), and biological oxygen demand (BOD).

The instrumental analytical methods nowadays represent the majority of the environmental analytical methods, including molecular spectroscopic methods (UV-VIS, IR), atomic spectroscopic methods (AA, ICP), chromatographic methods (GC, HPLC, and IC), mass spectrometric methods, electrochemical methods, thermal methods, and radiological methods (Figure 1).

In the sections that follow (Section 2 through 5), the fundamentals of environmental analytical chemistry are discussed in the logical order of their operations: environmental sampling, sample preparation, analytical chemical methods based on instruments, and biological based methods.

Certain important topics such as data analysis unique to environmental reporting and quality assurance / quality control (QA/QC) are excluded in the following discussions due to limited space. Interested readers are referred to the books by Helsel (2005), Korte (1999), and Keith (1991) for details.

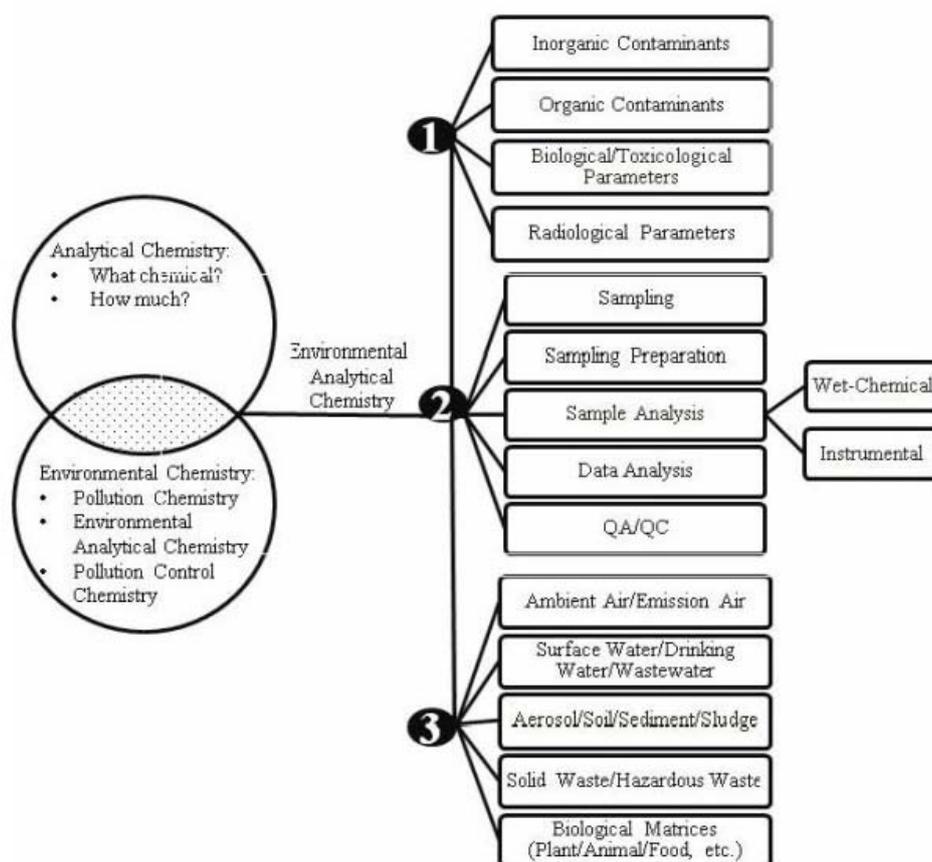


Figure 1. Environmental analytical chemistry in relation to analytical chemistry and environmental chemistry, and its three different types of organization framework.

2. Environmental Sampling: Purpose, Design Strategy and Techniques

2.1. Importance of Environmental Sampling

The purpose of sampling is to obtain representative samples in a cost-effective manner. Sampling theory and practice is not something developed just for the collection of “environmental” samples. This old scientific discipline was based on sound probability, statistics, and applied sciences in a wide range (social, political and natural sciences) such as social surveys as well as sampling in metallurgy, pharmaceutical science, material sciences and petroleum industries.

Even though some sampling theories were developed almost a century ago, sampling work of most environmental projects is still performed in an empirical or semi-empirical manner. As early as in 1954, Murphy indicated in an editorial note in *Analytical Chemistry* that sampling is a subject analogous to weather in that many people talk about it but do nothing to improve the situation. This statement is still true today for environmental sampling. In most published environmental work, laboratory and instrumental analyses are fully justified with regard to accuracy and precision, but sampling design and representativeness are hardly mentioned. Ort et al. (2010) found that only 11% of the 87 papers in the studies of pharmaceutical and personal care

products in wastewater systems provided justifications for sampling in clear contrast of 99% on analysis.

Two factors probably contribute to the above-mentioned lack of awareness of sampling relative to analysis in the environmental community. The first is the technical difficulty in quantifying the sampling error contribution to the total error. This is in clear contrast with the readiness of the quantification of analytical errors in the lab by the determination of recovery and precision. The second factor is the subjective misconception among many environmental professionals that sampling error is small in comparison with the analytical error.

The true fact of the matter is that sampling errors usually dominate the total errors of the environmental data acquisition. Mar et al. (1986) indicated that analytical measurement errors are typically 25% for physical/chemical parameters and 50% for biological parameters. However, sampling errors due to natural variations can be in the range of 100% to 400%. With this assumption, Zhang and Zhang (2011) employed Monte Carlo simulation and obtained the following regression between the total error (y) vs. sampling error (x_1):

$$y = 1.01x_1 + 23.9 \quad (R^2 = 0.97) \quad (1)$$

The R^2 value of 0.97 reveals that over 90% of the errors can be explained by the error during the sampling process. Whereas for the relationship between total error (y) and the analytical error (x_2), the following linear regression was obtained:

$$y = 1.25x_2 + 141 \quad (R^2 = 0.04) \quad (2)$$

The low R^2 value of 0.04 and the insignificant relationship between the total error and analytical error implied that improvement in analytical measurement will not significantly improve the overall data quality if sampling error is large. These Monte Carlo simulation results should make sense in practice because sampling is the first step in the overall data acquisition process. If an unrepresentative sample is collected, or if a bad sample is collected due to a poor technique or cross-contamination, then the subsequent analysis by an analyst in the lab is wasted. A poor sample will by no means result in good data representative of the population to be sampled. In fact, such data may give misleading information.

-
-
-

TO ACCESS ALL THE 41 PAGES OF THIS CHAPTER,
Visit: <http://www.eolss.net/Eolss-sampleAllChapter.aspx>

Bibliography

Erickson, M. D. (1995), *Analytical Chemistry of PCBs*, second edition, Lewis Publishers, 667 pages. [This is the most authoritative single source book for the analysis of PCBs, having both general and detailed PCBs-related literature of about 2,000 bibliographic citations].

Fifield, F. W.; Haines, P. J. (2000), *Environmental Analytical Chemistry*, second edition, Blackwell Science, London, UK, 512 pages. [A balanced textbook with principles of analytical chemistry and contexts of environmental analysis].

Girard, J. E. (2010), *Principles of Environmental Chemistry*, second edition, Jones and Bartlett Publishers, Sudbury, Massachusetts, 687 pages. [An easy to read environmental chemistry textbook that also includes chapters for the analysis of pollutants in air, automobile emission, water and wastewater].

Greenwood, R.; Mills, G.; Vrana, B. (2007), *Passive Sampling Techniques in Environmental Monitoring*, Elsevier, 486 pages. [Written by international specialist experts, this book offers a comprehensive review of passive sampling for pollutants in air and water, their theories and applications].

Helsel, D. R. (2005), *Nondetects and Data Analysis: Statistics for Censored Environmental Data*, Wiley, Hoboken, NJ, 250 pages. [This book presents statistical methods for interpreting and analyzing censored environmental data involving concentrations below detection limits].

Keith, L. H. (1991), *Environmental Sampling and Analysis: A Practical Guide*, Lewis Publishers, Boca Raton, FL, 143 pages. [A concise book offering practical advice and tips on planning, sampling, analysis, QA/QC, and reporting].

Korte, N. (1999), *A Guide for the Technical Evaluation of Environmental Data*, Technomic Publishing Co., Inc., Lancaster, PA, 195 pages. [A book with an emphasis on the explanations of analytical data to indicate the presence of environmental contaminants not expected from the site or point source under investigation].

Loconto, P. R. (2001), *Trace Environmental Quantitative Analysis: Principles, Techniques, and Applications*, Marcel Dekker, Inc., New York, 646 pages. [A book with an insight into the principles of trace environmental quantitative analysis, focusing on data reduction and interpretation, sample preparation and instrumental analysis from a wide range of environmental matrices].

Manahan, S. E. (2000), *Environmental Chemistry*, seventh edition, Lewis Publishers, Boca Raton, 898 pages. [A popular environmental chemistry textbook that also has chapters for the analysis of water, wastewater, solid wastes, air and gas].

Mar, B. W.; Horner, R. R.; Richey, J. S.; Palmer, R. N.; Lettenmaier, D. P. (1986), Data acquisition: cost-effective methods for obtaining data on water quality, *Environmental Science and Technology*, 20:545-551. [This paper presents methods to optimize environmental sampling design for cost-effective data acquisition in water quality monitoring].

Marco, M.-P.; Barceló, D. (1996), Environmental applications of analytical biosensors, *Measurement Science and Technology*, 7:1547-1562. [This article is a review of the fundamental aspects and environmental applications of affinity based biosensors and catalytic biosensors].

Marco, M.-P.; Gee, S.; Hammock, B. D. (1995), Immunochemical techniques for environmental analysis I. Immunosensors, *Trends in Analytical Chemistry*, 14(7):341-350. [This paper introduces the principles and potential environmental applications of various immunosensors currently in the research and developmental stage].

Murphy, W. J. (1954), editorial note, *Analytical Chemistry*, 26, 441. [This is a short editorial note regarding the importance of sampling].

Murray, R. (2010), Challenges in Environmental Analytical Chemistry, *Analytical Chemistry*, 82(5):1569. [This is a short editorial note pointing to the challenges in environmental analytical chemistry].

Organizing Committee for the Workshop on the Environment, Committee on Challenges for the Chemical Sciences in the 21st Century, National Research Council (2003), *The Environment: Challenges for the Chemical Sciences in the 21st Century*, 190 pages (<http://www.nap.edu/catalog/10803>).

html). [A report developed by a group of well-known scholars summarizing the important past discoveries and future challenges in environmental chemical science].

Ort, C.; Lawrence, M. G.; Rieckermann, J.; Joss, A. (2010), Sampling for Pharmaceuticals and Personal Care Products (PPCPs) and Illicit Drugs in Wastewater Systems: Are Your Conclusions Valid? A Critical Review, *Environmental Science and Technology*, 44 (16):6024–6035. [Based on results from previous and current work, the present paper demonstrates that sampling errors can lead to over-interpretation of measured data and ultimately, wrong conclusions].

Richardson, S.D. (2002), Environmental mass spectrometry: Emerging contaminants and current issues, *Analytical Chemistry*, 74:2719-2742. [This biennial review covers developments in environmental mass spectrometry over the period of 2004-2005 with an emphasis on emerging contaminant analysis].

Rogers, K. R.; Mascini, M. (2009), Biosensors for Analytical Monitoring, <http://www.epa.gov/heads/edrb/biochem/intro.html> [This U.S. EPA website gives a perspectives of biosensors in environmental analysis and monitoring with a description of biological elements and various transducers].

Sadik, Q.A., Wanekaya, A.K., Andreescu, S. (2004), Advances in analytical technologies for environmental protection and public safety, *Journal of Environmental Monitoring*, 6, 513-522. [This paper provides an overview of how advances in environmental analytical methodologies could be adapted to design reliable sensors for public safety and environmental surveillance of chemical and biochemical toxins].

Skoog, D. A.; Holler, F. J.; Nieman, T. A. (1998), *Principles of Instrumental Analysis*, 5th Edition, Saunders College Publishing, 960 pages. [This classical textbook for instrumental analysis has a detailed account of the principles of various instruments currently used in analytical chemistry].

U.S. Environmental Protection Agency (1986), Testing Methods for the Evaluating Solid Wastes: Physical/Chemical Methods, EPA SW 846 online: <http://www.epa.gov/epaoswer/hazwaste>. [This online resource has a detailed update of Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, also known as SW-846].

U.S. Environmental Protection Agency (2002), Guidance on Choosing a Sampling Design for Environmental Data Collection for Use in Developing a Quality assurance Project Plan, EPA/240/R-02/005. [This U.S. EPA guideline provides assistance in developing an effective QA Project Plan involving statistically based sampling schemes beneficial for program managers, analysts, and planning teams].

Wikipedia, Analytical Chemistry, http://en.wikipedia.org/wiki/Analytical_chemistry. [This website has some information about the historical perspectives of analytical chemical, and the framework of this discipline involving classical as well as instrument methods].

Zhang, C. (1997), *Fundamentals of Environmental Sampling and Analysis*, John Wiley & Sons, 456 pages. [This unique textbook for environmental analytical chemistry or a related subject focuses on the overall framework and various methodologies in environmental sampling and analysis].

Zhang, J.; Zhang, C. (2011), Sampling and sampling strategies for environmental analysis, *International Journal of Environmental Analytical Chemistry*, In Press. [This critical review addressed several key issues in the development of an optimal sampling strategy in an effort to obtain representative samples while minimizing sampling and analytical costs].

Biographical Sketch

Chunlong (Carl) Zhang is a Professor of Environmental Science and Chemistry at the University of Houston-Clear Lake, and a registered Professional Engineer in the State of Louisiana. He received his Bachelor of Science degree in Environmental Science and Master of Science degree in Environmental Chemistry from Zhejiang University, and earned his Ph.D. in Environmental Engineering from Louisiana State University. He teaches several undergraduate and graduate level courses including environmental chemistry, lab for environmental analysis, environmental sampling and monitoring, contaminant fate and transport, and environmental remediation. His research interests are in the areas of emerging contaminant analysis, contaminant fate and transport at the air-water-sediment interfaces, biodegradation of explosives in contaminated soils, and development of novel remediation technologies. He is the author of a well-

received university textbook entitled *Fundamentals of Environmental Sampling and Analysis* published by John Wiley & Sons in 2007.

UNESCO – EOLSS
SAMPLE CHAPTERS