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The Significance of the Analytical Sciences in Environmental Assessment

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Abstract : The quality of human life is directly related to the quality of the environment. To assess environmental quality we must first determine the MCLG(Maximum Contaminant Level Goal), MCL(Maximum Contaminant Level), environmental impact and so on. The MCLG is the concentration at which no known adverse health effects occur. The MCLG is determined by risk assessment identifying which process is hazardous assessing, dose-response, human exposure, and characteristics of risk. With consideration of analytical methods, treatment technology, cost and regulatory impact, the MCL is set as close to the MCLG as possible. In this way, determination of the concentration and national distribution of contaminants is important for assessment of environmental quality The analytical sciences pose potential problems in assessing environmental quality. Continuing improvement in the performance of analytical instruments and operating technique has been lowering the limits of detectability. Contaminant concentration below the detection limit has usually been reported as ND(Not-Detected) and this has often been misunderstood as equivalent to zero. Because of this, more the contaminant concentration in the past was below the detection limit, whereas contaminants can be quantified now even though the contaminant concentration might remain the same or may even have decreased. In addition, environmental sampling has various components due to heterogeneous matrices. These samples are used to overestimate the concentration of the contaminant due to large variability, resulting in excess readings for MCL. In this paper, the significance of the analytical sciences is emphasized in both a conceptual and a technical approach to environmental assessment.

Keywords : MCLG (Maximum Contaminant Level Goal), MCL(Maximum Contaminant Level), risk assessment, analytical science, aluminum, quality control.

1. Introduction

Environmental pollution, which ranges from local to global coverage has been a pressing issue since the 20th century. The environmental pollution problems are various ranging from subtle health effects to lethal catastrophe. Also, the present environmental issues may be different from the past since the type and amount of environmental pollutants have changed. For example, global warming due to the depletion of stratosphere ozones is one of the present environmental issues which was not a concern before. The leading causes of death in 1900 were pneumonia, influenza and tuberculosis, whereas in 1995 the most common cause of death is cancer. These changes may result from the change of life style and increased life expectancy due to better nutrition, the clinical use of antibiotics and so on. However, there is growing evidence that environmental pollution may contribute to these changes in varying degrees. Therefore, many countries consider environmental protection as a priority because the quality of human life is directly related to the quality of the environment(Quevauviller et al., 1993).

Then how can we assess the quality of the environment? Ideally, everyone wants to live in a safe and pleasant environment without any potential risk to human health and ecosystem. MCLG (Maximum Contaminant Level Goal) is the concentration of environmental contaminants in food, water, air and soil at which no known adverse health effects occur. However, in reality, it is not always possible to reduce the amount of contaminants down to MCLG. By judging the ideal and the reality, we arrived at a compromised agreement by accepting a certain degree of contamination, known as MCL(Maximum Contaminant Level) or Maximum Permissible Level. Maximum Contaminant Level Goal are nonenforceable health goals, whereas Maximum Contaminant Level, set by a regulatory agent, is an enforceable guideline(USEPA, 1990). In other words, contamination above MCL is not accepted by law, which means environmental deterioration above MCL, is considered as a crime. The process for the determination of MCLG and MCL, the most important guidelines to assess environmental quality, is discussed in more detail.

The first thing for the assessment of environmental quality is to know the concentration and national distributions of contaminants by measuring the present contaminant level in the environment. It requires the qualitative and quantitative analyses of pollutants which are regarded as straightforward and simple. However, there are many potential problems to which we have not paid much attention.

In this paper, these potential problems of analytical sciences, which affects environmental assessment, are reviewed in both conceptual and technical approaches. It may contribute to the improvement of environmental assessment.

2. Risk assessment for the determination of MCLG and MCL

The MCLG, which are nonenforceable health goals, is the concentration at which no known adverse health effects occur. The MCLG is determined by risk assessment which is the process of characterizing the nature and magnitude of the risks. Standardized method for risk assessment has been being developed by the USEPA (United States Environmental Protection Agency) since the 1970s and includes four steps: hazard identification, dose-

Table 2-1. Guidelines on the use of uncertainty factors

Uncertainty factor	*Guideline*
1-10	When a NOAEL from a human study is used
100	When a LOAEL from a human study is used, incorporating a factor of 10 to account for lack of a NOAEL and a factor of 10 for intraspecies diversity; or, when a NOAEL from an animal study is used, incorporating a factor 10 to account for interspecies diversity and a factor 10 for intraspecies diversity.
1,000	When a LOAEL from an animal study is used, incorporating factors of 10 each for lack of NOAEL, interspecies diversity, and intraspecies diversity.
1-10	Additional uncertainty factors, ranging from 1 to 10, may be incorporated on a case-by-case basis to account for deficiencies in the database.

Table 2-2. EPA carcinogenic assessment categories

A. Human carcinogen, based on sufficient evidence from epidemiological studies

B. Probable human carcinogen, based on at least limited evidence of carcinogenicity to humans(B1), or usually a combination of sufficient evidence in animals and inadequate data in humans(B2).

C. Possible human carcinogen, based on limited or equivocal evidence of carcinogenicity in animals in the absence of human data

D. Not classifiable, based on inadequate evidence of carcinogenicity from animal data

E. No evidence of carcinogenicity for humans (no evidence of carcinogenicity in at least two adequate animal tests in different species or in both epidemiological and animal studies)

Table 2-3. EPA's three-category approach

Category	*Evidence of carcinogenicity*	*EPA group*	*MCLG setting approach*
I	Sufficient evidence in humans or animals	A or B	0
II	Limited or equivocal evidence in animals	C	1) RfD approach with additional safety factor 2) 10-5 to 10-6 cancer risk range
III	Inadequate or negative evidence from animal data	D or E	RfD approach

response assessment, exposure assessment and risk characterization(NAS, 1983). Hazard identification is the first step for risk assessment or risk analysis. It is defined as the process of determining whether human exposure to an agent could increase the incidence of a health condition. Dose-response assessment is examined in two classes of contaminants. For noncarcinogens and noncarcinogenic effects, dose-response relationships are established, by which NOAELs (No Observed Adverse Effect Levels) and LOAELs (Lowest Observed Adverse Effect Levels) are derived. The Reference Dose (RfD) is an estimate of the amount of pollutant exposed to the human population for one day without an appreciable risk of deleterious health effects during a lifetime. The RfD is the NOAEL or LOAEL (in mg/Kg/day) divided by an uncertainty factor. Uncertainty factor is illustrated in *Table 2-1*(USEPA, 1990). For carcinogens and carcinogenic effects, statistical models, such as the linearized multistage model, are applied to estimate risk levels to humans, based on animal data. Human exposure to pollutants occur through many routes including breathing, drinking water, eating foods, dermal absorption and so on. Assessment of human exposure attempts to identify and quantify the levels of the contaminants. Risk characterization is the final step in risk assessment which combines all of the information to determine the possibility of humans experiencing any potential toxicity associated with a pollutant.

The Environmental Protection Agency classified pollutants according to the weight of evidence for carcinogenicity as shown in *Table 2-2*(USEPA, 1990). The MCLG for a pollutant is then established in one of three ways based on its carcinogenicity classification, which is explained in *Table 2-3*(USEPA, 1990).

The MCLs are set as close to the MCLGs as possible with consideration to analytical methods, treatment technology, cost and regulatory impact. The procedures for the determination of MCLG and MCL are summarized in *Table 2-4*(USEPA, 1990).

Table 2-4. MCL/MCLG development

Risk Assessment	***Risk Management***
Hazard Identification	Risk Assessment
+	+
Dose-Response Assessment	Analytical Methods
+	+
Human Exposure Assessment	Technology and Costs
+	+
Risk Characterization	Economic and Regulatory Impact
↓	↓
MCLG (Health-Based Goal)	MCL (The Legal Limit)

The consideration of analytical methods includes technical and economic availability that would be acceptable for accurate measures of compliance, limits of analytical detection, laboratory capabilities, and costs of analytical techniques. The MCLG is often equal to the MCL, especially for noncarcinogens. However, the MCLG for carcinogens is frequently lower than the MCL because the MCLG for those contaminants are zero. In short, analytical sciences play an important role in determining MCLG (especially human exposure assessment) and MCL.

3. Potential problems of analytical sciences : conceptual approach

To set the MCLG at zero may pose problems since an absolute zero level of contaminant can not be attained based on the analytical detection level. In more detail, the analytical detection level includes several kinds of definitions(USEPA, 1990). First, the minimum detection limit, which is used in setting the laboratory performance requirements, is the minimum concentration of a pollutant that can be measured and reported with 99 percent confidence that the true value is greater than zero. Second, practical quantitation level is the lowest measurement level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The practical quantitation level is able to provide a uniform concentration measurement for setting standards. Continuing improvement in the performance of analytical instruments and operating technique is lowering the limits of detectability. Thus, while the contaminant concentration in the past was often below the detection limit, today, contaminants can be quantified even though the contaminant concentration might have remained the same or even have decreased. However, many instrumental methods are able to detect as much as a microgram (10^{-6} g) or a nanogram (10^{-9} g) depending on the compound being studied and the procedure employed, although only selected methods are capable of idetifying picogram (10^{-12} g) and femtogram (10^{-15} g) limits. The detection limits of several instrumental methods are shown in Table 3-1 under optimized conditions and procedures.

Table 3-1. Detection limits of selected instrumental methods

Method	*Sensitivity (g)*
Gas chromatography	10^{-8} to 10^{-12}
Thin layer chromatography	
Color reaction	10^{-6}
Fluorescence	10^{-9}
Mass spectrometry	
Electron impact	10^{-12}
Spark source	10^{-13}
Ion probe	10^{-15}
Chemical ionization	10^{-10}
GC/MS/computer	10^{-11}
Liquid chromatography	10^{-6} to 10^{-11}
Refractive index detector	10^{-6}
Ultraviolet/visible detector	10^{-9}
Fluorescence detector	10^{-10}
Atomic absorption spectroscopy	
Flame	10^{-9}
Flameless	10^{-12}
Infrared spectroscopy	10^{-6} to 10^{-9}
Standard techniques	10^{-6}
Fourier transform infrared	10^{-9}
Ion-selective electrodes	10^{-15}

Nonetheless, contaminant concentration below the detection limit has been usually reported as ND(Not-Detected) which has often been misunderstood as equivalent to zero. It is very important to realize that ND does not mean the absolute absence of contaminant.

Although detection limit is one of the most important factors to determine the MCLG and MCL, detection limit is not a reliable index of representing the complexity of the analysis or the difficulty of detecting specific compounds in a matrix of interferents. Rather, for any one method. instrumental design and operating technique may be the most important factor in determining the detection limits. For example, volatile organic compounds in ground and

surface waters have been analyzed by the Purge and Trap Concentrator and Gas Chromatographic/Mass Spectrometric method (Eichelberger and Budde, 1989). In cases involving the same system and a same operator, the replacement of packed column by capillary column lowers the detection limits considerably. Survey data on error propagation for one method shows that operator-generated error is responsible for approximately 20% errors(Majers, 1993). Thus of all the regulatory agency is recommended to specify the detailed instrumental design and operating technique of each analytical method suitable for the detection of a contaminant.

As mentioned earlier, precision and accuracy of analytical methods also influence the setting of environmental guidelines. Unfortunately, analytical data of environmental samples have large variability due to heterogeneous matrices and low level presence. Therefore, it is used to overestimate or underestimate the concentration of the contaminant, which incurrs unnecessary costs or jeopardizes human health. To overcome these problems, each step of analysis such as sampling, sample stabilization, pretreatment and preparation, separation, qualitative and quantitative analysis, data acquisition or reduction, and data interpretation must be performed carefully(Toro et al. 1994), especially sample collection and analysis have to be strictly performed in accordance with quality assurance which is a set of operating principles that will produce data of known and defensible quality. Quality control and quality assessment are included in quality assurance(Standard method, 1993). A good quality control program consists of the following elements: certification of operator competence, proper calibration of instrumentation, recovery of known additions, analysis of externally supplied standards, analysis of reagent blanks, calibration with standards, analysis of duplicates, participation in interlaboratory studies and maintenance of control charts. An intercomparison (participation in interlaboratory studies) is useful in several aspects: (i) to detect the pitfalls of a commonly applied method and to ascertain its performance in practice, (ii) to measure the quality of a laboratory, (iii) to improve the quality of a laboratory in collaborative work and (iv) to certify the contents of a reference material(Quevauviller et al., 1993). Certified reference materials are recommended as externally supplied standards, if available. The certified reference materials are sold by National Institute of Standards & Technology (NIST), National Research Council (NRC), U.S. Environmental Protection Agency (USEPA) and so on.

4. Aluminum measurement by electrothermal atomic absorption spectrometry: technical approach

Aluminum is ubiquitous in the environment since it is the most prevalent metal and the third most abundant element in the earth's crust, composing 8% of the earth's crust (Martin, 1988). In addition, aluminum is added intentionally into the drinking water as a coagulant during water purification process. Aluminum is widely used as a food additive, such as leavening agents, emulsifying agents and anticaking agents (Pennington and Jones, 1989) and is used in pharmaceutical preparations, including antiperspirants, adjuvant in parenteral vaccines, buffered analgesics and antacids (Hem and White, 1989). Aluminum is regarded as the responsible agent for anemia, dialysis-dementia and osteodystrophy. Therefore, aluminum measurement in biological

as well as environmental samples is often inevitable. Electrothermal atomic absorption spectrometry is the most common method of aluminum measurement since it has increased sensitivity and requires a very small volume of sample. However, an accurate aluminum measurement is very difficult to access due to the generally low levels in samples compared to the high levels ubiquitous in the environment. Thus, contamination is always a problem. In practice, to decrease the variability and inaccuracy, aluminum analysis is briefly reviewed.

It is strongly recommended to plan the experimental design at the beginning of the experiment. The types of samples (biological samples such as plasma, urine, bone, etc, or environmental samples such as air, water, soil, etc), the types of statistics (student's t-test, F-test, etc), the number of replicates, analytical methods, the fraction of aluminum (dissolved, suspended, total, or acid-extractable) and so on have to be decided to meet the objectives of the experiment.

Polypropylene or TFE utensils are preferred to avoid leachable aluminum from glassware. In the case that glassware has to be used, glassware should be soaked in 50% nitric acid overnight and rinsed either 10 times in triple distilled water or once in 1% nitric acid, once in 10% W/V EDTA (ethylenediaminetetraacetic acid), and twice in triple distilled water to avoid aluminum contamination, (Fulton et al., 1989). Triple distilled water has to be metal-free and commercially available high-purity acid must be purchased to minimize the contamination. To avoid airborne contaminants use clean laboratory facilities such as commercially available laminar-flow clean-air benches or custom-designed work stations and analyze blanks that reflect the complete procedure.

The proper acidification of sample prevents the loss of aluminum by adsorption on and /or precipitation in the sample container. Preserve samples immediately after sampling by acidifying with c-HNO_3 or HCl. After acidifying sample, store it in a refrigerator (4 ℃) or freezer (-80℃).

Colorless, transparent samples such as drinking water may be analyzed directly by atomic absorption spectroscopy without pretreatment. However, samples containing particulates or organic material generally require pretreatment before analysis. The most commonly used pretreatment is nitric acid digestion which is digested in 3 volume of 75% HNO_3 at 60℃ for 1-2 hrs, evaporated on a hot plate, and then diluted with deionized, distilled water (Ahn et al., 1995). Recently, microwave- assisted digestion is available and has many advantages over acid digestion (Hasty and Revese, 1995). Then the all concentration is analyzed using a graphite furnace atomic absorption spectrophotometer and autosampler. An aluminum lamp was operated at 10mA with a wavelength of 309.3nm and a band width of 0.5nm(Ahn and Jeffery, 1994)

The Following procedures are recommended as quality assurance. The standard addition method is performed to demonstrate freedom from interferences for a new or unfamiliar matrix of sample. Verify the absence of interferences by analyzing such samples undiluted and in a 1:10 dilution; results should by comparable. The detection limit is determined and make sure the concentration of sample should be above the detection limit. A calibration curve should be composed of a blank and two or more standards which is comprised of the sample concentration, an external reference standard, a replicate, and the known additions. Standard tissue samples

for the external reference standard can be purchased from National bureau of Standards. To verify the stable instrumental calibration, analyze a midpoint check standard and calibration blank at the beginning throughout normally after each set of unknowns (Standard method, 1993). Calibration standards and known addition solutions are also verified against an outside source. Participation in interlaboratory studies is strongly recommended due to the reasons mentioned earlier.

5. Concluding remarks

Environmental protection, for which we have spent a lot of money and effort, is the major concern of many countries. It is generally accepted that analytical science is only small part of environmental assessment so the importance of analytical science for the assessment of environmental quality has been underestimated. However, the accurate and precise measurement of a contaminant, which is not always simple and straightforward, is the beginning of environmental assessment. A lot of money has been wasted because of careless analysis. The analytical sciences, especially in the field of environment, still have many potential problems and have to be improved. This task is accomplished successfully by the coorporation of universities, companies and government.

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