Vasil SIMEONOV¹

DIDACTICAL PRINCIPLES OF ENVIRONMENTAL MONITORING

DYDAKTYCZNE ZASADY MONITORINGU ŚRODOWISKOWEGO

Abstract: Environmental monitoring is a very important part of all environmental risk assessment tasks aiming correct estimation of the ecological status of water, air, soil, and biota systems. However, special attention is rarely paid to the problem in the teaching programs for students of bachelor or master degree dedicated to environmental chemistry. The same holds true for secondary school programs for chemical education. It is the aim of the present communication to present in a simple and understandable way the major elements of the environmental monitoring as substantial consistent of the overall scheme of environmental risk assessment as presented to chemistry students and secondary school pupils.

Keywords: didactics, environmental monitoring, pollution analytics

Introduction

Very often didactical schemes for teaching environmental chemistry obligatory include basic analytical methods for monitoring data collection, sampling procedures and sample preparation and, not so often, intelligent data analysis of the collected data. The process of monitoring itself is rarely involved in the teaching programs. That is why we believe that introduction of the principles of environmental monitoring principles should be a major goal in all aspects of teaching environmental chemistry both at secondary schools or universities.

In order to understand the environmental processes and changes as well as the reasons for creation and transportation of pollutants one has to know the qualitative and quantitative parameters of the polluting species in all possible environmental compartments hydrosphere, atmosphere, lithosphere and biosphere. The careful control of each environmental sample allows systematic collection of useful data for their further classification, modelling and interpretation making possible all procedures of the risk assessment and risk management.

The monitoring of environmental objects is a process requiring repeated and systematic observation of one or more features of the sample in time and space coordinates

sciendo

¹ Faculty of Chemistry and Pharmacy, University of Sofia "St. Kliment Okhridski", 1, J. Bourchier Blvd., 1164 Sofia, Bulgaria, phone +359 2 8161426, email: ahvs@chem.uni-sofia.bg

and using suitable methods for chemical analysis (data collection) and for data treatment (chemometrics and environmetrics). Thus, the monitoring ensures important information about the momentary state of the system in consideration. Using data from previous monitoring procedures one is already able to evaluate different trends of the system. The well-organized monitoring is the main source of database necessary for dynamic or statistical modelling of the environmental systems [1].

There are no general monitoring programs for all environmental compartments. The most serious development is observed for monitoring procedures in the hydrosphere. Since the hydrosphere is the most dynamic complex of environmental objects (surface water, underground water, lake water, marine water, rainwater, waste water etc.) the monitoring procedures are of extreme importance in determination of trends and in risk assessment. Therefore, the monitoring is considered as a very substantial element in the process of system management when decisions have to be met and problems to be solved. In solving a certain environmental problem, the following cycle of actions has to be taken into account. The cycle includes several stages:

- clarification of the problem,
- definition of the necessary actions to be undertaken,
- performance of the designed actions,
- estimation of the results obtained.

For each stage observation and control are necessary. In the first stage some preliminary checks are carried out and a careful design of future actions is performed. Further, criteria, goals and limitations of the monitoring process are set up since it is the most important source of results for next actions. The evaluation of the results obtained should lead to the problem solving.

The monitoring process could be considered as a sequence of mutually related actions. If water quality management and assessment is considered this sequence has the following structure:

Water quality management \rightarrow necessity of information \rightarrow strategy for water quality assessment \rightarrow monitoring design \rightarrow data collection \rightarrow data treatment \rightarrow data analysis and modelling \rightarrow model assessment \rightarrow application of the information obtained \rightarrow Water quality management.

The underlined stages are directly related to the very core of the monitoring - data collection by the use of carefully selected control techniques [2].

If one considers the hydrosphere monitoring, a substantial element of the monitoring design is the existence of a monitoring net. It is important to note that similar monitoring nets are necessary for control and observation of the atmosphere, geosphere, and biosphere. The requirements for the monitoring net design are determined to great extent by the specificity of the environmental compartments (just one example from the hydrosphere - there are specificities in monitoring of springs, rivers, river catchments, lakes, estuaries costal zones, dams and artificial lakes, open sea zones) as well as by the geographical characteristics of the respective region of monitoring. By the determination of the monitoring net structure of hydrosystems (river catchments in particular) it is necessary to know the rules and laws of formation of the water flows. The necessity of assessment of anthropogenic impacts requires the monitoring net to include both clean and polluted water bodies. A monitoring net is created not once and forever but it has to be constantly optimized with respect to the controlled features indicating the water quality, to the

sampling sites along or within the net, to the frequency of the sampling and control, to the price of the monitoring operations etc.

The number of indicators which has to be involved in the monitoring being responsible for quality assessment of different environmental compartments constantly increases. At the same time the analytical procedures and techniques required for reliable and precise quality assessment get more and more complicated and expensive. For instance, the monitoring of atmospheric pollutants or soils and sediments is very sophisticated and laborious since it is more difficult to sample and analyse solid samples as compared to the water samples. That is why the most developed and frequently used is the monitoring of water systems.

If one takes into account the monitoring nets for waters it is important to note the number of control parameters constantly grows and strongly depend on the introduction of new technologies having specific requirements to the water resources and to the waste products in waste waters. The recommended by the European environmental protection agency parameters for water quality assessment could be summarized as follows:

- Basic physical parameters (depth of the water body, temperature of the water body, water flow, pH, electric conductivity, dissolved oxygen);
- Suspended matter, turbidity;
- Organic compounds (biological oxygen demand, chemical oxygen demand, total organic carbon, ammonium);
- Biogenic elements or indicators for eutrophication (different forms of nitrogen and phosphorus, phytoplankton, zoo benthos);
- Acidity indicators (alkalinity, sulfates, aluminum);
- Ions in high concentrations (calcium, sodium, potassium, magnesium, chlorides);
- Heavy metal ions (cadmium, mercury, lead, copper, zinc etc.);
- Organic pollutants in low concentrations (pesticides, pharmacy products, waste compounds from industrial processes, most of them toxic);
- Indicators for radioactivity (alpha and beta activity, cesium-137, strontium-90);
- Microbiological indicator organisms (total amount of coli forms, fecal coli forms, fecal streptococci bacteria);
- Biological indicators for the ecological status of the water system (phytoplankton, zooplankton, zoo benthos, fish, macrophytes);
- Indicators for ecotoxicity (acute and chronic).

In general, the air quality control is performed with similar features of the quality and the monitoring procedures are used for observation of gaseous pollutants and for aerosols. Very important samples for the atmospheric quality are the air-born particles (aerosols) which are controlled for size, content of major components (chlorides, nitrates, sulfates, potassium, sodium, magnesium, calcium, ammonia), heavy metals, organic and inorganic carbon (soot, carbonates), aluminum, silicon, barium, different organic tracers (but only for more specific investigations, not as routine checks) for traffic, burning processes (wood, coal or gas combustion), plant debris, domestic cooking etc. Very often instead of monitoring and analytical determination of total organic carbon different organic compounds are separately identified in the aerosol mass (saturated hydrocarbons, polycyclic aromatic hydrocarbons, cellulose, organic acids, aldehydes, ketones etc.).

The traditional monitoring net is designed and automated for gaseous pollutants (nitric oxides, sulphur oxides, ozone, ammonia, total amount of dust, carbon monoxide, carbon dioxide). The monitoring systems for the air quality are usually located in big cities and around big industrial enterprises and work in a continuous regime. Academic laboratories

very often complete the processes of monitoring adding to the conventional results more data about specific aerosol of air constituents.

It has to be mentioned that the monitoring net for soils is organized in a similar way with established sampling points on a grid but due to the difficult and expensive analysis the monitoring procedure normally is once per year. Besides, the soil is a more stable environmental compartment with many options for recreation.

Recently, the monitoring of river and marine sediments turns to be a very important source of information about pollution events. Seldom a specific monitoring net for sediments is available and the data collection is rather sporadic than regular and strictly organized.

The sensitive reaction of organisms to the quality of their environment, which may be used for indication (monitoring) can be, for example, biochemical, physiological, morphological, chronological, or sociological. All these reactions depend not only on the factor to be indicated (monitored) but also on nutrient and watering status, age, sex, heritage, and concurrence between individuals or species. The same is true of the accumulation of a certain substance. That is why in recent time special attention is paid to biomonitoring and bioindication. Many authors use these two terms more or less as synonyms. The only detectable difference between the official interpretation of the two words in well known encyclopaedia or dictionaries is that indication seems to be more spontaneous and active since monitoring is continuous and passive (the indicator does something. The monitor is use to do something). Nevertheless more and more authors suggest differentiating between indicators and monitors, e.g. "a bioindicator is an organism (a part of an organism or a society of organisms), which gives information on the quality (of a part) of its environment", while "a biomonitor is an organism (a part of an organism or a society of organisms), which quantifies the quality (of a part) of its environment". According to these definitions the distinguishing of three groups of air quality (good, fair, poor) by the use of living organisms is already biomonitoring (although such a differentiation is at best semiquantitative). Other authors call the use of organisms naturally existing in the area of investigation passive biomonitoring (bioindication), while active biomonitoring (bioindication) is done by exposure of organisms in the test area for a defined time span under standardized conditions. It becomes obvious that a great difference between the active and passive method exists. Hence there is no doubt that these terms are necessary, in particular as the clear difference between active and passive is not weakened by translation.

Not only plants (vegetation) but also animals along with the traditional instrumentation can be used to monitor heavy metals in an ecosystem. Each category of monitors has its particular advantages and drawbacks. In principle, the biological monitoring advantages are interception estimation, retrospective effects, low costs, great availability, independence on power sources, biomonitors do not attract vandalism, they have biological relevance, and they take into account synergistic (antagonistic) effects or time-dependent effects. Of course, biomonitors do not possess the opportunity to be standardized, they are not reproducible and enough exact, they do not differentiate, let say, between airborne and soilborne contributions to the total pollutant concentrations.

Higher plants, particularly spermatophytes, are frequently used as accumulative bioindicators of heavy metals. Lichens are well known as indicators of air quality, mosses are used in many countries of the northern hemisphere to estimate atmospheric deposition of metals on a regional scale. Higher fungi monitor successfully heavy metals in soil.

In contrast to lichens, mosses and higher fungi, higher plants (pteridophytes and spermato phytes) generally show a clear division into roots, shoots and leaves. As higher plants are much larger than the members of the other groups mentioned, there is no difficulty in separating the different plant organs for analysis or even in differentiating between tissues. Some important principles are taken into account when selecting higher plant species for biomonitoring. For instance, hairy, rough leaves are better accumulators than leaves with a smooth surface; leaf metal contents show marked seasonal variations; transpiration is an important driving force of heavy metal transport from roots to leaves, e.g. individuals growing on shady sites accumulate fewer than those on sunny sites, leaves from the top of a tree may show a higher accumulation rate than those from the bottom etc.

Finally, there are studies showing that dead plant material like bark could be effective biomonitor because the bark samples are obtained from a living organism and "contain" changes due to anthropogenic or natural impacts similar to sediments in a river, lake, marine or oceanic environment.

The biomonitoring is rather an academic approach in controlling heavy metal pollution of the atmosphere than a standard procedure based on a nation-wide monitoring net [3].

If we consider a traditional monitoring net functioning with a set of rules, an important element for the process is the determination of the sampling frequency. This frequency changes within broad ranges and depends on the specific monitoring program. High sampling frequency is applied if the ultimate goal of the procedure is to determine time trends. Then the monitoring program is either constant in time or lasts for a very long time period. Low frequency of sampling is preferred when the momentary (acute) situation is assessed. Sometimes high frequency monitoring is performed but the controlled parameters are a limited number. For instance, conductivity, pH, dissolved oxygen, turbidity (for surface water monitoring) are subject to every day control, organic pollutants are controlled once per month, and biological indicators - twice per year. If a seasonal change of the ecosystem status is observed, the monitoring procedure should take into account the seasonal factor.

The monitoring sample frequency in controlling the quality of the hydrosphere depends on:

- state of the water body (clean or anthropogenically influenced),
- hydrological and hydrodynamic parameters,
- parameters of the water flow,
- seasonal effects on the water quality,
- economic and technical options of the monitoring institution,
- indicators for determination of the self-cleaning ability and the assimilation ability of the river catchments,
- type of introduction of pollutants into the flow stationary, non-stationary, constantly.

The monitoring system has to be continuously optimized and related to the changes in the anthroposphere - new technologies, new pollutants, constantly changing requirements for water supply etc.

If the monitoring results are normally distributed, the number of the necessary samples for analysis is determined by the following empiric formula:

$$n = S^2 \cdot A^2 / b \tag{1}$$

where *n* is the number of samples, S^2 is the monitoring results variance for a certain parameter, *A* is the confidence interval of the mean value and *b* is the half of the confidence interval.

The most objective and correct way of determining the sampling frequency is the so called spectral approach. The necessary monitoring frequency is determined by a theoretical theorem according to which the discriminating ability of a certain type of investigation should be twice as much as the minimal period of alternation of the process observed. For instance, if a parameter is monitored having a daily alternation, the samples should be taken twice a day. Analogically, any other frequency of sampling could be determined using the dependence

$$f \ge 0.5 \ \gamma \tag{2}$$

where f is the frequency of observation and γ is the periodicity of alternation of the phenomenon (or quality parameter).

The monitoring results include data from physical, chemical, and biological measurements of specific environmental samples (water, air, soil, biota). If one considers the assessment of water quality, all three types of control are similar with respect to their weight in formation of the overall result of the water quality. There are, however, differences, related to the specificity of the controlling methods. Another important moment in the whole monitoring procedure (except specific samples, specific sample preparation and specific methods of measurement) is the unavoidable bias reflecting the uncertainty and precision of the results obtained. Thus, each monitoring method should be treated not only with respect to its physical theoretical background but also with respect to its information ability. That is why if a monitoring data set has to be interpreted, the preliminary question to be answered is if the data set is of respective quality.

In the entirely physical (instrumental) monitoring methods the dominant role plays the instrument (apparatus) for measuring. The instrumental measurements are the backbone of many accepted as chemical methods for monitoring. The typical chemical analytical methods rely on a preliminary operation known as sample pre-treatment, e.g. dissolution, extraction, dilution, concentration, co-precipitation etc.

The standard procedures for physical monitoring are relatively simple and are directly applied in one-stage operations like calibration of a measuring unit. If chemical analysis is needed for monitoring, standard (reference) materials are required in order to tune the entire chemical operation. The reference material should resemble the real environmental sample subject to monitoring. Then multistage operations are needed to achieve the goal of the monitoring procedure. These operations aim not only instrument calibration but also estimation of the chemical nature of the sample, e.g. analyte to be determined, sample matrix, interfering species possibly presenting in the real sample etc.

Recently, biological monitoring becomes more and more important. Biomonitoring and bioindication were already discussed as information sources about the ecological status of a certain environment. It could be summarized that the effectiveness of a given bioindicator depends on two major groups of factors. The first one characterizes the bioindicator organism (bacteria, lichens, mosses, plankton, zoobenthos, plants, fish, etc.) and is of biological nature. The second group responds to the environmental reactions and situations of the system in consideration (e.g. surface water) and is abiotic in its nature.

The biological factors influencing the bioindicator functions are level of pollutant accumulation, mode of pollutant elimination, ecophysiological status of the bioindicating

organism, environmental status, and pollutant toxicity. The abiotic factors are temperature, pH, level of mineralization, precipitation and sedimentation.

The application of each monitoring procedure is related to estimation of the experimental bias at any stage of the monitoring process. Since each act of measuring is subject to errors being either systematic (shifting the true result in one direction with usually with known source of bias) or random (with unknown origin and causing not simple shift of the true result into one direction but into different directions). Usually, the systematic errors influence the precision and accuracy of the true result since random errors affect the uncertainty of the monitoring method used and could be assessed by statistical calculations and criteria. The identification and control of the different errors throughout the monitoring process is the goal of a specific activity of the operating units usually called data quality control.

Many of the parameters controlled by monitoring present in the environmental samples at very low concentration levels. This is real challenge to the analytical methods identifying and quantifying pollutants. That is why each analytical method offered as an environmental monitoring procedure possesses a respective limit of detection the determination of which is often reason for discussions and uncertainties. The detection limit reflects the lowest concentration which could be determined by the respective analytical method with sufficient adequacy, within the borders of a confidence interval. The analytical signal at the detection limit should be distinguishable as a definite value above the level of noise (level of blank sample). As in any analytical procedure in the monitoring process when low pollutant concentrations are registered, two type of bias are very often: errors of first kind when the measuring method detect presence of analyte without its real presence in the sample or errors of second kind when the methods does not register the analyte although it presents in the sample [4].

The correct application of the methods of monitoring aiming high quality data sets requires performing of an uncertainty budget, i.e. when all stages of the monitoring process from the sampling to signal measurement are carefully assessed with respect to the possible errors.

Many of the parameters controlled by monitoring present in the environmental samples at very low concentration levels. This is real challenge to the analytical methods identifying and quantifying pollutants. That is why each analytical method offered as an environmental monitoring procedure possesses a respective limit of detection the determination of which is often reason for discussions and uncertainties. The detection limit reflects the lowest concentration which could be determined by the respective analytical method with sufficient adequacy, within the borders of a confidence interval. The analytical signal at the detection limit should be distinguishable as a definite value above the level of noise (level of blank sample). As in any analytical procedure in the monitoring process when low pollutant concentrations are registered, two type of bias are very often: errors of first kind when the measuring method detect presence of analyte without its real presence in the sample or errors of second kind when the methods does not register the analyte although it presents in the sample.

The correct application of the methods of monitoring aiming high quality data sets requires performing of an uncertainty budget, i.e. when all stages of the monitoring process from the sampling to signal measurement are carefully assessed with respect to the possible errors.

Conclusion

The monitoring process is a substantial element of the complete system of assessment of the ecological status of the environmental phases and should not be neglected from didactical point of view. It makes it possible to select the reliable sampling points for the different environmental systems and to ensure trustworthy information about the physical and chemical parameters of each system in consideration (water, air, soil, sediment, wetland, plant, rock, etc.). The monitoring is the necessary link between the data evaluation strategies (chemometrics, environmetrics, data mining, and intelligent data analysis) and the decision making procedures of environmental risk assessment. Thus, it should be a substantial part of any teaching program in the field of environmental chemistry.

References

- Simeonova P, Lovchinov V. Introduction to Environmental Physics. Sofia: Avangard Prima, S; 2008. ISBN: 9789543233502.
- [2] Manahan SE. Environmental Chemistry. Boca Raton: Lewis Publishers/CRS Press; 2000. ISBN: 1566704928.
- [3] Cunningham WP, Saigo BW. Environmental Science, a Global Concern. New York: C. Brown/McGraw-Hill; 1998. ISBN: 9780071180726.
- [4] Alexander DE, Fairbridge RW, editors. Encyclopedia of Environmental Sciences. Hingam: Kluwer Academic Publishers; 1999. ISBN: 9781402044946.