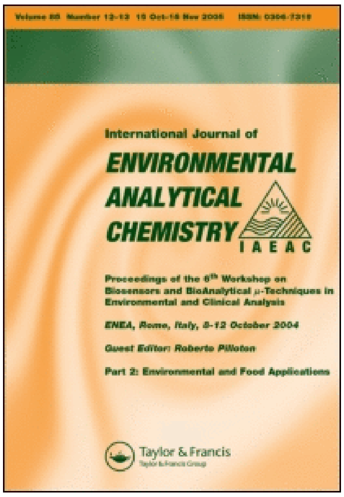

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Methods of Background Environmental Pollution Monitoring Applied in CMEA Member Countries

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Presented are some methods of environmental objects sampling and procedures for determination of sulfur dioxide, sulfate, ozone, nitrogen oxides, mercury, lead, cadmium, arsenic, DDT and other organochlorine pesticides such as 3,4-benzo(a)-pyrene and other PAHs at background levels in environmental media used at CMEA member countries' background stations.

The program and methodology of the quality assurance of the information on pollutants' content in environmental media received when different procedures and devices are applied, are envisaged in the paper.

KEY WORDS: Background monitoring, pollutant analyses procedures.

INTRODUCTION

To obtain information on the background environmental pollution in the framework of Global Environmental Monitoring System (GEMS), a network of stations for the integrated background monitoring is being established. In CMEA-countries (Bulgaria, Hungary, GDR, Poland, Roumania, USSR and Czechoslovakia) a similar regional network has been operated for several years, observational results being annually published in the special bulletin.[1–4]

The program for the observations of pollutant concentrations at GEMS background stations was compiled on the basis of the suggestions to the background environmental monitoring program.[5–7] According to them, precipitations, natural waters, soils, and biotic objects are selected as observational objects, while the dust, aerosol atmospheric turbidity, ozone, nitrogen oxides, sulfur oxides, hydrocarbons, 3,4-benzo(a)pyrene, DDT and other organochlorine pesticides, mercury, lead, cadmium, arsenic content in the atmospheric precipitations are suggested as the monitored matter and indices.

In the above suggestions the list of observational objects complies with the general principle of background monitoring—that of integrity, which allows to assess the flux of pollutants from the atmosphere onto the underlying surface and to trace their migration with the surface and underground waters, as well as along the trophic chains in the ecosystems. The list of substances to be monitored corresponds to the pollutant priorities established by the First Intergovernment Meeting on Monitoring held at Nairobi (1974) according to the criteria which consider pollutant properties and possibilities to measure them.[8,9]

The variety of pollutants and monitored objects, each of which demands individual methodological approach, as well as relatively low level of pollutant concentrations typical for background regions have required developing a complex of methods specially meant for the operations at background stations and relevant analytical laboratories.

The development of methods included the consideration for the technical provision of equipment and conventional methods of analysis in collaborating countries: mutual agreement permitted to use different methods of measuring an ingredient in one and the same environmental object. The necessary condition consisted in obtaining compatible results with the help of the methods applied.

Since current concentrations of pollutants in environmental objects of background regions are low,[1–3] the complex of methods includes the stages of sampling, extracting, and concentrating the pollutants, and their quantitative evaluation.

SAMPLING THE NATURAL OBJECTS

While monitoring the background pollution the technique of sampling the natural waters, soils and biota is far from being specific, therefore well-known methods are applied here.[11]

Methods and sampling devices for selecting representative samples of atmospheric air, precipitation and dry deposition are developed in accordance with physical and chemical properties of monitored matter. Methods of sampling the aerosols are based on the air filtration. Experiments have shown that, in spite of great diversity in the design of aspiration devices and applied filtering materials, filters Sartorius, Synpor 3(4), FN-11, tissues FPP and FPA provide high enough (90%) efficiency of trapping aerosols exceeding 0.3 μm at high-volume (of the order of 100 m^3/hr air sampling).

To provide simultaneous trapping of aerosols and vapour phase (as is required, for instance, while measuring OCP content) the sampling is carried out by means of pumping the air through consequently located FPP filter and adsorbent (silochrome C-80).

At the CMEA-country background network atmospheric precipitation is sampled using the devices whose receiving is made of materials free from measured ingredients. These are: polyethylene for heavy metals, and enamelled metal for organic pollutants. The receiving surface is protected from dry deposition by an automatic lid, in case of its absence precipitation sampler should be washed each day. The selected samples are preserved, which protects them from damage due to the sorption of measured pollutants during the transportation and storage.

METHODS OF POLLUTANT MEASUREMENTS

In accordance with the observational program, the complex of methods under development included: methods for measuring gaseous pollutants (ozone, sulfur dioxide, nitrogen oxides) and sulfate in the atmosphere; methods for measuring inorganic (lead, cadmium, arsenic, and mercury) and organic matter (3,4-benzo(a)pyrene, DDT and other organochlorine pesticides) in the air, precipitation, surface waters, soil and biota.

Modern achievements of analytical technology characterized by selectivity and high sensitivity were used while developing the methods of measuring pollutants.

Below are the primary principles and short descriptions of the developed methods of measuring pollutants in all studied objects envisaged by the program.

Gaseous pollutants

Gaseous atmospheric pollutants are measured either by means of continuous measurement of individual ingredient concentrations by various gas analyzers or using chemical methods of analysis after preliminary accumulation of pollutants on sorbents and in absorbing solution.

Sulfur dioxide: Chemical methods: West-Gaeke (pararosaniline: formaldehyde), thorine and potentiometric ones, are used to obtain background concentrations of sulfur dioxide. Two modifications of West–Gaeke method are used: (1) with the accumulation of sulfur dioxide on the non-drying sorbent (sodium tetrachloromercurate—TCM) applied to the glass granules placed in glass tubes, or (2) with the accumulation of sulfur in the absorbing 0.01 M solution of TCM. The usage of fine-film non-drying sorbent, like it is done in the USSR, due to substantially developed absorber surface facilitates the efficiency of sampling and allows to increase the air flow rate without sulfur dioxide overswing. In the the first case the measurement limit of sulfur dioxide is $0.05\,\mu g/m^3$, in the second case—$2\,\mu g/m^3$.

While using thorine (Poland) or potentiometric (Bulgaria) methods sulfur dioxide is sampled on impregnated filters or by means of absorption in a 2%-solution of hydrogen peroxide, respectively. Sulfur dioxide is oxidized to sulfate whose concentration is measured. The limits of measuring sulfur dioxide by these methods are $0.1\,\mu g/m^3$ and $0.04\,\mu g/m^3$, respectively.

Ozone: At regional background stations of CMEA-countries background ozone concentrations are measured by chemiluminescent

(USSR) and coulometric (GDR) methods. Gas analyzers operate in automatic regime, ozone being measured continuously.

Chemiluminescent method is based on the reaction of ozone with ethylene. The method is selective, ozone measurement limit is equal to 2 $\mu g/m^3$, relative error amounts to 2% in the range of 10–200 $\mu g/m^3$.

Coulometric method is based on the reaction of ozone with potassium iodide in the electrochemical cell. The interfering effect of sulfur dioxide is removed by the air pumping through a special filter.

Nitrogen oxides: Background concentrations of nitrogen oxides are measured using colorimetric methods based on the reaction between sulfur dioxide and (1) sulfanilic acid and N-(1-naphthyl)ethilene diamine (USSR and Poland); (2) Griss–Ilosvay reagent (Poland); Zaltzman reagent (GDR). Nitrate ion concentration in the solution is determined from the color intensity of the formed nitrogen compounds. In the first case (USSR) sulfur dioxide is absorbed from the air by the finefilm sorbent applied to glass granules (potassium iodide, sodium arsenite, glycerol or ethilene glycol) or by the air-bubbled solution of guaiacol, triethanol amine and sodium pyrosulfite in bidistilled water. Measurement limits are 0.3 and 0.7 $\mu g/m^3$, respectively. Measurement technique using Griss–Ilosvay reagent involves sulfur dioxide absorption during air bubble through the solution of sodium hydroxide with triethanol amine, measurement limit being equal to 1 $\mu g/m^3$. The technique using Zaltzman reagent uses impregnated filter (sodium hydroxide solution with guaiacol). In the last case to evaluate the sum of nitrogen oxides a tube with the oxidant applied to silica gel is placed before the filter. Measurement limit is 0.5–0.6 $\mu g/m^3$.

Chemiluminescent method with automatic gas analyzer is the most promising one (though not widespread yet) which allows to measure separate concentrations of nitrogen monoxide and total nitrogen oxides. Measurement limit of nitrogen monoxide for modern chemiluminescent gas analyzers is 0.6 $\mu g/m^3$.

Sulfate: To measure sulfate in the atmospheric air and precipitation at the background stations five methods have been developed: turbidimetry (USSR), spectrophotometry (Poland), isotopic dilution (Hungary) ring furnace (GDR), and potentiometric titration

(Bulgaria). Numerous interlaboratory and field calibrations have shown that all methods provide the required practical compatibility of results. Turbidimetric method is based on measuring the intensity of the solution turbidity after the reaction between sulfate ions and barium salts. Measurement limit is $0.1\,\mu g/m^3$ for the air and 0.25 mg/l for atmospheric precipitation. Spectrophotometric method involves measuring the resultant complex of thorine and the excess of barium ions unconnected by sulfate. Measurement limits of sulfate ions are $0.3\,\mu g/m^3$ in atmospheric air and 0.1 mg/l in atmospheric precipitation. The method of ring oven is based on the transformation of soluble sulfate into sulfide which react with lead to form a coloured compound. The range of measured sulfate concentrations is 0.2–$20\,\mu g/m^3$. Potentiometric titration using ion selective electrode is applied to analyze atmospheric precipitation. The limit of sulfate measurement is 0.1 mg/l.

Heavy metals

The background monitoring program envisages systematic measurements of heavy metals (lead, cadmium, arsenic, mercury) in the atmosphere, precipitation, natural waters, bottom sediments, soil and vegetation, of modern analytical methods having low measurement limits (such as neutron activation, X-ray fluorescence, atomic emissions with plasma excitation source, atomic absorption, chronovoltametry, etc.), atomic absorption (AAS) and chronovoltametry are applied to measure the above mentioned pollutants. Chronovoltametry is used in Poland.

The application of AAS as a basic method in CMEA-countries is attributed to the sufficiently good quality of equipment and relatively low costs, as well as the possibility to measure the metals which are included in the priority list.

To transform measured metals from solid samples into solution at CMEA-country laboratories various methods of treatment are used with or without preliminary mineralization. AAS method with flame atomization involves concentration of lead and cadmium from atmospheric precipitation and natural water samples by extraction of metal chelates or by sample vaporization. AAS with electrothermal atomization allows to measure cadmium and lead in water samples without preliminary concentration. Arsenic in water samples is measured by AAS after concentrating by vaporization on atomic absorption spectrophotometer using Zeeman effect.

The application of atomic absorption spectrophotometers which use Zeeman effect for automatic correction of spectral interferences enable to analyze both liquid and solid samples without preliminary chemical treatment.

Depending on the applied equipment AAS method has the following analytical limits of measurement: with flame atomization for lead 120–200 ng/ml, for cadmium 20–60 ng/ml; with electrothermal atomization in graphite dish for lead 0.25 ng/ml, for cadmium 0.02 ng/ml, relative error being equal to 10–15% in both cases. The analysis of liquid and solid samples by atomic absorption spectrophotometer using Zeeman effect provides analytical limits of measuring lead—0.05 ng, cadmium—0.02 ng and arsenic—0.4 ng.

Inverse chronovoltametry is characterized by the following analytical measurement limits: lead—20 ng/ml, cadmium—0.4 ng/ml, relative error being 20%. The advantage of the method is the possibility to analyze low-volume samples.

Spectrophotometric method is based on the reduction of arsenic to hydrogen arsenic and the absorption of the latter by the solution of silver diethyldithiocarbamate in pyridine. Analytical limit of arsenic measurement is 0.12 μg/ml.

Atomic absorption method of “cold vapour” is the most selective and highly sensitive one for measuring mercury in various natural objects. Two-beam spectrophotometers with mercury hollow-cathode tube and a special dish instead of the burner, or a specialized device MAS-50 for measuring mercury are used for the analysis. The ability of vaporous mercury to form amalgams with noble metals is used while accumulating and concentrating mercury. The developed AAS (“cold vapour”) method allows to measure mercury in the atmospheric air with its accumulation on silver (USSR) or golden (GDR) sorbent (amalgamator), measurement limit being 0.5–2 ng/m^3 depending on the applied analytical equipment, relative error being 10%; measurement limit in natural waters and atmospheric precipitation is equal to 0.05 μg/l, with concentration on golden amalgamator—0.5 ng/l; measurement limit of mercury in soils, bottom sediments and vegetation amounts to 4–10 ng/g depending on the method of sample mineralization and the applied measuring equipment.

Organic Pollutants

The number of organic pollutants subjected to background monitoring includes organochlorine pesticides (OCP) and polynuclear aromatic hydrocarbons (PAH), 3,4-benzo(a)pyrene (BP) in particular. To measure background concentrations of OCP and PAH highly sensitive instrumental methods are used which require preliminary chemical treatment of samples including the extraction by organic solvents, concentration, removal of interfering admixtures, and in a number of cases separation of a complex mixture into small fractions and identification and measurement of individual component content in the compound.

Organochlorine pesticides and polychlorinated biphenyls: Gas chromatographic method used at Soviet background stations is developed to measure OCP and PCB in natural objects. Concentrations of individual components in the analyzed sample, preliminary subjected to chemical treatment, are measured using gas–fluid chromatography with electron-trapping detection. Measurement limits are: for DDT and its metabolites in the air 0.01–0.03 ng/m^3, in precipitation and natural waters—1–2 ng/l and 0.2–0.4 ng/g in solid samples; for HCCH isomers 0.005 ng/m^3, 0.5 nl/l and 0.1 ng/g, respectively; for PCB 0.6 ng/m^3, 40 ng/l and 10 ng/g. Relative error for measuring OCP and PCB in extracts does not exceed 15%.

3,4-Benzo(a)pyrene and other polynuclear aromatic hydrocarbons: To measure BP and other PAH a highly sensitive selective method of fine-structure spectrofluorometry on the basis of Shpolsky effect has been developed and put into operation in the USSR in two versions: the method of universal standard when the concentration of each PAH is measured by comparing fluorescence spectrum of phosphorescence of the studied extract (eluate) with the intensity of analytical line 419.2 in the similar spectrum of the universal standard (1,12-benzoperilene).

Analytical measurement limit for 3,4-benzo(a)pyrene, perilene and 1,12-benzoperilene is 0.1 ng/ml, for other PAH—1–3 ng/ml. Relative error equals to 10%. The method of additions, when hydrocarbon (BP) is measured from the difference between analytical line intensities, has measurement limit equal to 0.05 ng/ml and relative error no more than 15%. The method is appropriate for analyzing samples from all natural environments.

Fluid chromatography with UF and fluorescent detection is another method for measuring background concentrations of BP and PAH, developed in Hungary and recommended for background monitoring. The method is noted for low measurement limits, allows to identify a number of PAH, BP included, and quantitatively evaluate their content in various environments, though requires a rather complicated chemical treatment of samples.

Assessment of the results compatibility

To assess the compatibility of the results a program for calibrating the methods and equipment was developed, which included:

—interlaboratory analysis of model solutions and reference samples;

—interlaboratory analysis of unified samples of atmospheric precipitation, soil and vegetation;

—simultaneous sampling of atmospheric air and precipitation by various sampling devices during joint expeditions and the analysis of the above samples at national laboratories.

First series of interlaboratory analyses of unified and reference samples were carried out, and four joint expeditional experiments were held in background regions of Bulgaria, Hungary, GDR and Czechoslovakia to perform the above program. The obtained results allowed to assess the compatibility of data and to suggest recommendations on using the tested methods within the system of background monitoring stations.[10]

The values of relative mean square deviation (maximum permissible magnitude was equal to 30%) was used as a criterion for assessing the compatibility of data during interlaboratory analysis of reference samples and unified model or natural samples.

Compatibility of the results during simultaneous sampling and analysis was assessed using such statistics as t-criterion and correlation coefficient r.

CONCLUSION

Being developed within the framework of scientific and technological cooperation between CMEA-countries on the problem of Global Environmental Monitoring System, and tested with respect to compatibility, the method of pollutant measurement have been operated at background network and since 1982 have enabled to obtain systematic information on the state of environmental pollution in non-urbanized regions of East European CMEA-countries.

Collected papers "Unified Methods of Background Environmental Pollution Monitoring" published in 1986 comprise techniques developed in the framework of scientific and technological cooperation.

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