Environmental Research for the Sea of Japan and Adjacent Areas : FEB RAS Experience and Prospective

メタデータ	言語: English 出版者: 公開日: 2017-10-05 キーワード (Ja): キーワード (En): 作成者: Sergienko, Valentine I., Shcheka, Oleg L. メールアドレス: 所属:
URL	http://hdl.handle.net/2297/6365

Proceedings: International Symposium of the Kanazawa University 21st-Century COE Program Vol. 1 (2003)
Edited by Naoto KAMATA
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Environmental Research for the Sea of Japan and Adjacent Areas: FEB RAS Experience and Prospective

Valentine I. SERGIENKO
Far Eastern Branch of the Russian Academy of Sciences, Vladivostok 690950, RUSSIA
Oleg L. SHCHEKA
Department of Physics, Far Eastern State University, Vladivostok 690600, RUSSIA

Abstract - FEB RAS experience of environmental research for the Sea of Japan and North-East Asia is described. Basic experimental and theoretical methods of investigation are overviewed. Program of international cooperation for study of pollutant transport and its impact on environment is proposed.

I. Introduction

The questions considered at the Symposium are very important not only for separate country and even not only for coastal countries. They have transboundary and transcontinental value. State borders do not stop air transport and sea currents. They demonstrate us that Earth is our common house, and problems, appearing in one place, have already not local, but regional, or even global nature. Fast economic development of countries in the Northeast Asia and Pacific region renders a strong influence on the environment, which possibility to regenerations is not unlimited. Thence results need to pay attention to ecological factor at the planning of long-term economic projects. International financial institutions previously, than begin a financing of new investment programs, require from participants to estimate possible impact on environment from realization of project. Global Environment Facility through implementing agencies (UNDP, UNEP, and The World Bank) contributes a financial support to such programs.

Far Eastern Branch of the Russian Academy of Sciences (FEB RAS) has a valuable experience of participation in regional programs of evaluation of ecological status of territory and generation of detailed recommendations on reducing negative anthropogenic impact on environment. At the end of 2002 it was finished the TumenNET project, in which took part China, Republic of Korea, Mongolia, and Russia. The project was targeted to the evaluation of current status and generation of recommendations on protection of biodiversity and international water resources in the Tumen river area and adjacent territory, including west part of the Sea of Japan. Under the FEB RAS leadership international team of experts has prepared transboundary diagnostic analysis, which was based on data of complex monitoring of territory (terrestrial, water objects, and atmosphere) for last ten years [1]. Results of the work were submitted to authorized governmental commissions of participating countries and were presented to the United Nations.

II. Methods

Having enormous human resources and modern techniques, working in the close co-operation with Russian and foreign partners, FEB RAS is able to solve the most complicated tasks of regional nature, to which, certainly, pertain questions of environmental studies in areas of the Sea of Japan. The FEB RAS with more than 2300 scientists on the staff has six Scientific Centers, 35 institutes, 63 research stations and stationeries, three natural reserves, including unique marine reserve in Russia. To get a necessary set of data and build a truthful model of processes of pollutant transport (in atmosphere as well as in the water resources), we fulfill regular monitoring on the extended area. Permanent and temporary stations and expeditions supply an analytical center by reliable information according to certain problems. Moreover, it should be noted that all of them use standard (for each project) set of methods, equipment has a united calibration, and registered data are processed by the united method. Such approach allows not only exactly defining a level of pollutant contents in the concrete place, as well as determining what transformations they are subjected under transportations. Methods of mathematical modeling help do it. Statistician and thermodynamic methods allow defining main transport ways, distribution of different chemical compound concentration, probability of their entering in reactions with main components of atmosphere, water and terrestrial objects, estimating energy characteristics of these reactions. More fine methods of quantum chemistry deepen our understanding, as on the electronic level are realized concrete reactions, and to what physical and chemical change this brings. We can select three main groups of objects of impact by pollutants: 1) atmosphere, 2) condensed state, and 3) alive nature (Fig.1).

A. Quantum Chemical Simulation

As to atmosphere, this is the simplest quantum-chemical task. We well know a composition of atmosphere, and so not difficult calculate reactions of pollutants with most important its components: molecular nitrogen, oxygen and

carbon dioxide. We have a set of modern non-empirical (*ab initio*) methods, approved on much more complicated systems. Validity of calculations here is very high, so sometimes it is not necessary to prove the results by the experimental data. We calculate a velocity of chemical reactions, expressed through the Gibb's activation energy, balance constant, that is

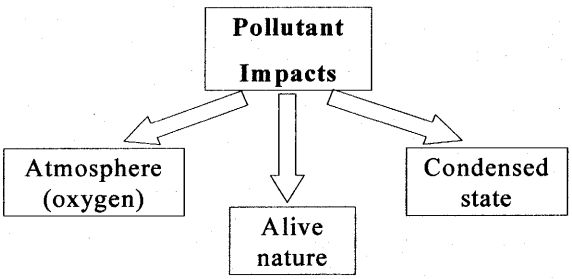

Fig.1. Main groups of objects of pollutant impact.

a function an enthalpy, entropy, and absolute temperature, as well as enthalpy change under the reactions [2,3]. Last function may be calculated easily, if distribute it on three components, corresponding to valent orbitals of π- and σ-type and core orbitals:

$$\Delta H^{\neq}=\Delta H_{\pi}^{\neq}+\Delta H_{\sigma}^{\neq}+\Delta H_{core}^{\neq} \quad (1)$$

In simple case under interaction of **A** and **B** molecules **ΔE** may be determined in the first order perturbation theory as sum of all overlap integrals on occupied and vacant molecular orbitals. In terms of MO LCAO (molecular orbital as linear combination of atomic orbitals) method we obtain:

$$\Delta E = 2\sum_{j}^{occ}\sum_{i}^{vac}\frac{c_{Aj}^{2}c_{Bi}^{2}}{\varepsilon_{j}-\varepsilon_{i}}\beta_{AB}^{2} \quad (2)$$

where ε_i and ε_j are one electron energies of molecular orbitals (MO) for ground state, β_{AB} – integral of resonance interaction, c_{Bi} and c_{Aj} – MO decomposition coefficients on atomic orbitals (AO), sums are calculated on all molecular orbitals.

To the group "condensed state" we refer soils, water objects, and construction buildings. Amongst last ones, according to studies, particularly subjects to influence are metal constructions. For them we accumulated a most experience of the cluster calculations, well confirmed by experimental studies. In this case we study a chemical composition, geometry and electronic structure of surface and adsorbed layers, as well as mechanism of intermediate state formation. Traditional set of experimental methods, as a rule, used together, is: gas chromatography (pollutant detecting), ultraviolet and x-ray photoelectron spectroscopy, absorption spectroscopy (in ultraviolet and visible ranges) and x-ray emission spectroscopy. For interpreting experimental data we, as a rule, use non-empirical discrete-variational method of local-density approximation, for the first time tested else 15 years ago [4]. Herewith, we pay most attention such parameters, as a total system energy, Mulliken's overlap populations, energy gate between occupied and vacant levels, energy distance between upper bonding and lower anti-bonding orbitals, characterizing system stability, as well as structure of valent occupied molecular orbitals. Calculations allow predicting a degree of destroying a surface of metal constructions under the concrete pollutant impact.

Tasks on modeling of pollutant transformations in soils and water objects are more complicated owing to the large number of compounds being present there. But if we need to calculate an interaction with the concrete material, the task is solved more simply. For this aim we have a big set of non-empirical and semi-empirical methods, allowing calculate multi-atomic systems. Here is important to make task the most concrete.

It is very important owing to its urgency the task of modeling of pollutant impact on the alive nature. Objects of impact are much diversified: from relatively simple organic compounds, being included in alive organisms, up to immune system. Technically a calculation of reaction with concrete pollutant is relatively easy. Despite of greater sizes of organic molecules, constructing them atoms are easy parameterized, so it is not difficult to build a full wave function. Problem here is in other: too large amount of compounds may be objects of impact in each alive organism so a simulation of all types of reactions is not possible. So we need to narrow greatly a statement of the problem, selecting the most impacted objects that help to do a close co-operation with biologists and physicians. We accumulated a large experience of similar work in interdisciplinary fields with the participation of specialists from FEB RAS different institutes, universities, foreign scientific institutions. For realization of each such project we establish coordinating units, managing process of work implementation that allows minimizing expenses of time and financial resources.

B. Experimental

One more important point of work in the field of studying an environment is a choice of optimum methods of monitoring, development of new strategies with using the last achievements of science and technology. Below we briefly overview what methods are available for FEB RAS at present.

Gamma-resonance studies - for the analysis of metallic alloys (amorphous and nano-crystal state) and natural iron samples.

Gamma-spectroscopy - for the analysis of atmosphere compounds, soils, water, plants, products of bestial and vegetable origin (determinations of contents in them radioactive isotopes of artificial and natural origin).

Alpha-spectroscopy - for the analysis of atmosphere, loose and amorphous samples of various nature for the

$$aA + bB = cC + dD$$

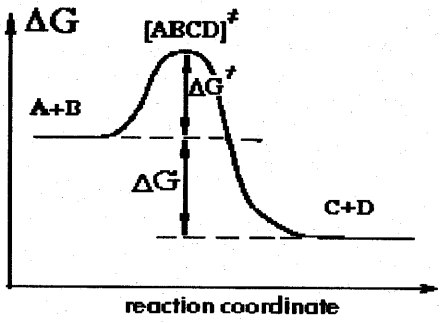

Fig. 2. Molecule transformation way under chemical reaction.

reason finding in them heavy radioactive isotopes, determinations of their isotope composition and value of activity of samples.

Low-phone measurement of radioactivity of samples from environment (samples of seawater and soils).

For the determination of radioactive isotopes of natural and artificial origin, basing in the environment, in particular in soil samples and seawater, selected in different regions of Vladivostok area and Amursky bay, we measured gamma-quantum energy distribution. The results of study have allowed installing an activity and contents of all radioactive isotopes in samples of soils and seawater. In particular, it was found presence of radioactive components of heavy metals (Pb^{212}, Pb^{214} Bi^{214}, Ra^{226}). We made correlation of increased contents of heavy radioactive metals with the intensity of car motion (on soil samples) or with the intensity of ground water currents (on seawater samples).

Laser induced breakdown spectroscopy (LIBS) is a variety of method of atomic emission spectroscopic analysis. Emission spectra of analyzing sample are generated by the laser spark of the short laser pulse, sharply focused on surfaces of analyzing sample. It is necessary to note that principles of calibration and calculation of unknown concentrations are traditional for methods of emission atomic spectroscopic analysis. But LIBS has some advantages: speed, absence of preliminary preparing the samples for the analysis, possibility of an analysis outside of dependencies on the phase state of the sample, absence of the direct contact with the analyzed sample that allows using LIBS for the remote analysis.

LIBS wholly can be applying to problems of determination of element composition of seawater, oils [5, 6], other natural and techogenic liquids, bio-plankton, bottom sediments, for what on the base of FEB RAS and FESU laboratories the analytical laser spectroscopic center was established, designed by methods of analysis of different substances and methods of processing spectroscopic data.

Implemented studies have shown that above-mentioned techniques and methods of experiment allow to fulfill, for example, qualitative analysis of industrial and sewages, check a contents of soluble organic compounds (on intensities of spectroscopic carbon bands) and soluble oxygen, carry out an evaluation of quality of fresh water resources, determine a content of different elements in coast sea areas of water and etc.

For the study of inorganic and organic compounds in crystalline, amorphous, liquid and vapor states we use traditional optic spectroscopic methods: infrared, visible, ultraviolet, luminescent spectroscopy, which allow to determine particularities of geometric and electronic structure of compounds studied, regularities of their forming, quantitative and qualitative composition; allow to study different processes, including fast processes, occurring under the impact of different external factors.

We are able fulfilling lidar zonding of atmosphere as well as zonding based on methods of using sun light or reflected moon light.

One of the important research directions is development of complex biogeochemical approaches to estimate water ecosystems state, estimation of anthropogenic effect on the sea medium. Modern methods of hydrophysics, hydrochemistry and hydrobiology are widely used, new devices are developed, and numerical experiments are carried out. It allows studying spatial-temporal variability of heavy metals and oil hydrocarbons content in sea water, hydrochemical fields influenced by "rapid" processes, nature and anthropogenic factors affecting the ecosystems state. Objects of studies are biochemical mechanisms of the hydrobionts reactions in the environment polluted by heavy metals. Studies are carried out concerning forms of inorganic microelements occurrence in the seawater, processes of energy and matter transfer in water ecosystems.

One more direction is studying different physical fields and processes in the ocean and atmosphere, and their interaction. Methods and devices are developed and used for numerical modeling. Physical basis and devices are developed for the remote sensing of the ocean and atmosphere. Electromagnetic fields are studied and used to solve various hydrophysical and geophysical problems. Laser-optical methods and means for probing are developed. Methods of contour dynamics for studying fronts and vortices are used. Devices are developed and spectrophotometric studies are performed to investigate the ocean surface. New methods for gas-chromatographic analyzing content of gases dissolved in seawater, silt water and bottom sediments are elaborated in FEB RAS institutes.

III. Prospective

Complex approach to studying the processes of pollutant transport, based on the analysis of varied experimental data and calculations, allows to build reliable mathematical models, which not only explain an appearance of separate chemical compounds in one or another place and nature of

their impact on objects of environment, as well as predict possible consequences of anthropogenic activity in the region. Such models take all factors into account: seasonal temperature fluctuations, moisture, level of fallen out precipitation, directions of winds, presence of large-scale water objects and currents in them, dynamics of regional industrial development, changing a demographic situation, and many the others.

For such regions as a Sea of Japan area a decision of the task is impossible without international cooperation. For obtaining a full set of data it is necessary to combine efforts of scientists and specialists from Russia, Japan, Republic of Korea, DPRK, China. Also we are likely to take into account an impact of sandy storms, arising in Mongolia. There are positive examples to organizations of such international cooperation. Aside from already mentioned the TumenNET project we may note the 210th meridian project, in which participated representatives from Russia, Japan, Australia and New Zealand. For an implementation of such complicated work it is very important to organize timed systematic measurements in different places of sea area, on the coast (west coast of Japan, east coast of Korean peninsula, south of Primorsky district of Russia), in adjacent continental territories (at presence of there mountains it looks useful fulfilling measurements on different heights). Processing experimental data must be held at agreed united method. Attractive looks participation of foreign specialists from collaborating countries in the research work of the national teams. This, on the one hand, promotes to the exchange by the experience of the studies, but, on the other hand, excludes a possibility of methodical divergences.

What plan of work can we suggest?

1. Identified participating countries, interested in implementing a project.
2. Countries nominate the institutions that are responsible for implementing a work, and contact persons.
3. Geographical places of monitoring are defined and agreed.
4. Agreed upon the timeline and outline of experimental studies.
5. Conducted calibration and inter-calibration of equipment.
6. Experimental data are collected.
7. Parallel is established Environmental Information and Management System.
8. Obtained data are regularly processed on the united method.
9. Built mathematical model of pollutant transport and impact on objects of environment in the Sea of Japan area and adjacent territories.
10. Worked out recommendations for governments of participating countries on the realization of priority actions on reducing a press on the environment.

IV. Conclusion

During a project implementation the regular workshops are held, to which a current status of research is discussed and necessary corrections may be done. It is necessary to provide broad participation of young people in the scientific studies. Participation in such project will become for graduate students, postgraduate students, and young specialists by the good training. It looks attractive to hold scholastic seminars in universities of participating countries, where methodical questions on organization of scientific studies and main results of work on the project will be presented. Such approach will allow implementing a big volume of work and forming a strong foundation for future studies.

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