## I. CHEMOSPHERE AND ECOLOGY

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# Protection of the environment and chemical ecology

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A large amount of wide-ranging information on questions of ecology has appeared in the literature in recent years. Ecological problems are being debated not only by scientists pursuing various fields of research but also by journalists, writers, and workers associated with the arts.

Despite the accessibility and array of knowledge on ecology, it would nevertheless be advisable to examine these problems from the chemical standpoint if for no other reason because chemistry and the chemical industry are one of the main sources of disturbance of the equilibrium in the biosphere and because they may provide effective measures and routes for the protection of the environment from so-called anthropogenic activity.

In his studies in the first quarter of this century the eminent Russian scientist, V I Vernadskii, advanced the concept of the biosphere. He perceived the biosphere as the outer membrane of the planet. The Earth, situated within the limits of the atmosphere, hydrosphere, and lithosphere, is covered with living matter. As regards many of their properties the atmosphere, the entire hydrosphere, and a deep layer of the lithosphere are subjected to the same forces as living organisms throughout their life-span and evolution.

The air, soil and water form the totally integrated system of the biosphere, which supports all living matter, generates all energy, and despite its great vitality consists of fragile and vulnerable mechanisms. Vernadskii considered that the combined activity of all organisms on the Earth is the most powerful geochemical factor transforming the Earth's surface and an energy generating factor of planetary proportions. Having developed clear concepts on the role of the biosphere Vernadskii focussed his attention on the fact that the industrial and technological activities of man at the present time is having such a great effect on the change of the face of the Earth that they may be regarded as a "new" geological factor and that human forces have become commensurate with the forces of nature.

The interaction between the biosphere and humankind has proved to be the most important of the modern-day problems of science and technology which are present in abundance and the overall resolution of this problem is a priority for science and technology.

A feature of the modern era is the development of a society which is at variance with the limited life-supporting potential of the biosphere. While the activities of man did not interfere in the affairs of nature, nature herself created the essential conditions for her own development and equilibrium. Processes of self-regulation which balanced human activity have existed in nature. Traditionally this activity, which includes industrial production, has developed on the basis of the concept that nature's resources are unlimited and that the natural environment has limitless ability to undergo self-purification.

On account of compensation mechanisms and huge structural flexibility the biosphere's ecosystem until now has been somehow able to balance the consequences of man's activity. However, increasing human activity, the growth of energy use and technical power of society, and human interference detached from scientific forecasts have led to the contamination and transformation of the biosphere which is becoming an irreversible and frightening process. The resources of dry land and the oceans are becoming depleted, all elements of the environment are becoming contaminated, ecosystems are being degraded, and the biochemical cycles of matter are being impaired.

There are countless ways in which man can pollute the atmosphere, the seas, lakes and rivers. Wash waters from chemical plants, acids, alkalies, dyes and resins, mercury-containing compounds, cadmium, tin, and other metals, wastes from the petroleum, paper, cast-iron, and steel industries, wastes from tanneries, and automobile factories and mines, many tonnes of fertilisers and pesticides washed from the fields, icebergs of detergent foam, and waste products from municipal sewerage. The air, the earth, and the water have been unremittingly diluted and all of these poisonous discharges have been hidden. However the burden has now become inadmissible.

Humankind has finally understood that a strong barrier against the destruction of nature should be erected. A movement in support of the protection of nature is underway, the science of ecology has been created, the government have started to introduce legislation, and state and public organisations have been set up in order to protect the environment in which we live and in which our descendents will live.

The key problems related to ecology are problems of pollution and purification of the atmosphere and the oceans of the world, soil

erosion, depletion of the ozone layer, the global change in the Earth's climate, and the build-up of toxic substances in the biosphere. Most of these problems are associated with a combination of naturally occurring and extraneous chemical substances introduced into the biosphere, and this combination forms the so-called chemosphere. The undesirable changes in the chemosphere mainly on account of anthropogenic activity cause a fall in productivity of natural ecosystems, the death of hydrobionts and forests, and the disappearance of individual species and populations in the plant and animal kingdoms. These factors ultimately have a negative effect on society by retarding its development and they constitute a threat to the survival of humankind.

The increase in variety and quantity of industrial output also leads to an increase in the amount of wastes consequently generated including the so-called xenobiotics, which previously did not exist in nature and which in many ways are foreign to living organisms. Illnesses (allergic, genetic, teratogenic, endocrinal, etc.), which have become more frequent in recent years, are a consequence of such technogenic changes.

According to World Health Organisation (WHO) statistics 40 – 50% of human diseases are presently associated with an increase in ecological stress. Current forecasts indicate that anthropogenic changes in the environment are creating a real threat to the survival of humankind.

Man's interference in natural processes which causes large-scale changes is primarily manifested as the contamination of the atmosphere, the hydrosphere, and the lithosphere, and these are essentially questions of chemistry.

The vast expanse of the ocean of air leads certain people to the conclusion that there is no need to avoid contamination as in the case of water. However statistics on the growing discharge of chemicals into the atmosphere demonstrate that the conservation of pure air is becoming a major problem and that atmospheric pollution has now reached global proportions.

Industrial gases released into the atmosphere present the greatest danger. Huge metallurgical, chemical and oil refinery plants are concentrated in cities and industrial areas. Power plants, thermal power stations, gas-generating plants, and innumerable automobiles and large numbers of people are concentrated in such locations. With population growth and the expansion of industry the loading of the biosphere with gaseous and aerosol discharges has reached global proportions.

All industrial installations utilise a mineral fuel such as oil, coal, oil shale, solar oil, petrol, and kerosene. When the fuel is burned, in addition to carbon dioxide oxidation products of sulphur-containing compounds, oxides of nitrogen, carbon monoxide, and other harmful gases are formed. It has been calculated that industrial installations and chemical and metallurgical plants and other factories and heat and electric power plants release annually into the atmosphere more than 150 million tonnes of sulphur dioxide, 200 million tonnes of ash, and tens of millions of tonnes of aerosols.

By the year 2000 the discharge of sulphur dioxide could reach 450 million tonnes per annum. Sulphur dioxide is known to be harmful to human health even at a concentration of one part per million. The concentration of this gas reaches 5 parts per million or more in industrial areas. Sulphur dioxide is one of the most terrifying enemies of plants. This gas pollutes the air, sours fresh waters and the soil, and is a cause of acid rain, which annihilates entire forest areas. Depending on the moisture content of the air sulphur dioxide is usually converted into a sulphuric acid aerosol. Discharges of hyrogen sulphide, which is also a toxic gas affecting man and animals, are highly dangerous. Top of the league in this regard is the Astrakhan gas condensate factory, which in 1987 released more than one million tonnes of hydrogen sulphide into the atmosphere.

One of the most potent atmospheric pollutants is carbon monoxide, which enters the atmosphere in amounts reaching tens of millions of tonnes during the combustion of all kinds of fuels and especially automobile and engine fuel. It was previously believed that only high concentrations of carbon monoxide were harmful to man. However, studies have shown that the constant presence of even low concentrations of this gas causes cardiovascular diseases, stenocardia, lesions of coronary vessels, and atherosclerosis, and a decrease in the survival rate following infarction.

Factors associated with atmospheric pollution should also include the release of carbon dioxide which is increasing year by year. During the combustion of all kinds of fuels at least $1 \times 10^{10}$ tonnes of carbon dioxide are released annually into the atmosphere and this gas absorbs a significant proportion of energy emitted by the Earth's surface.

Furthermore carbon dioxide does not impede the penetration of sunlight to the Earth and thereby creates the "greenhouse" effect. It has been suggested that as the concentration of carbon dioxide in the atmosphere increases there will be an increase in the quantity of thermal energy in the surface layers of the atmosphere and on the Earth's surface. By the year 2000 the content of carbon dioxide in the atmosphere may increase from 0.032 to 0.0375 and even to 0.040%. This global increase may cause climatic changes and other deleterious consequences. 1988 was the hottest year this century. The mean temperature in the eighties was found to be 0.34 °C higher than successive decades from 1949 to 1979.

On account of these alarming observations WHO has organised a working group for the study of climatic changes. However it is necessary to investigate and obtain evidence for the "greenhouse" theory, which was initially advanced by Soviet scientists. For example in the last century a similar warming up of the climate was recorded but this was followed by a cooling of the climate. Nevertheless, the danger of ecological changes caused by a cooling of the climate is very serious, since it may lead to a regression of the permafrost, thawing of ice, flooding of the land, and other disasters.

All forms of transport create great ecological losses. Exhaust gases, wash waters, and solid wastes from transport account for more than 30% of total pollution.

During the combustion of chemical fuel in the recovery of metals from ores and electrolysis of salts heavy metals (mercury, lead, vanadium, tin, etc.) are introduced into the environment and constitute dangerous sources of poisoning for humans, animals, and plants. For example with each tonne of caustic 600 grammes of mercury are lost. This metal in itself is a hazard and becomes especially dangerous, when this element is transformed into organomercurial compounds.

Contamination of the atmosphere with oxides of nitrogen and the Freon 11 and 12 type of propellants leads to the depletion of the ozone layer in the atmosphere which being in the upper layers of the atmosphere serves as a defence against the ultraviolet rays of the sun.

In normal operating periods nuclear power stations discharge gaseous aerosol products (krypton-85, xenon-133, radioactive iodine-131, and tritium) into the atmosphere. In addition to gases, solid radioactive fission products (promethium-147, ruthenium-106, cesium-137, strontium-90, zirconium-95, etc.) are also formed, and

the half-life period of these components varies from several months to thirty years. Almost all fission radioactive isotopes apart from the gaseous products undergo transformation into acidic waste solutions during the treatment of fuel elements. These solutions accumulate in nuclear chemical plants and present a difficult problem in regard to reprocessing and safe storage. The quantity of radioactive fission isotopes is increasing together with the increase in nuclear power engineering and burial of these products presents an exceptionally difficult problem. In fact when the Soviet Union constructs nuclear power stations abroad, it regulates the nuclear fuel and fuel elements, and they are returned with the radioactive fission products for reprocessing and burial. Thus there is a requirement to store not only Soviet radioactive wastes but also radioactive wastes from abroad. The safety of operation of the nuclear power stations themselves creates a special ecological problem as is exemplified by the Chernobyl disaster.

The amount of oil being extracted worldwide is in excess of three billion tonnes. Not taking into account accidents and catastrophes the losses of oil during transportation are equivalent to 1% of this figure. This implies that more than 30 million tonnes of oil are transferred largely into the oceans of the world. In the USSR 400 million tonnes of petroleum products are transported per annum by railroad alone. These products pollute the soil and water and other elements of the environment. In the USA petroleum products are conveyed to the consumers by a system of supply lines. A 2200 thousand kilometer network of pipelines enable losses of fuel to be sharply reduced. Of course oil is less harmful to nature than other pollutants but the huge volume produced and the corresponding volume of losses make a significant contribution to the contamination of the natural environment.

Large-scale pollution of water resources is taking place. The total quantity of water in the hydrosphere is 1400 million cubic kilometres, and 97% of this water is present in the oceans and seas, 2.14% exists in the form of ice, while only 0.29% is present in the form of fresh water on the land. In the USSR the amount of freshwater available is extremely small. Furthermore river basins including the Volga basin are being continually polluted. The ecological situation of water basins is deteriorating as a result of the multitude of chemical plants, paper and pulp mills, oil refineries, and textile factories located in areas of water. For example a single chemical plant on the banks of the Volga annually discharges forty five thousand tonnes of wastes from aniline dye manufature into the Volga.

Thousands of establishments situated along river banks in the USSR discharge annually into these rivers more than three million cubic metres of dilute acids, approximately two million cubic metres of liquid wastes including petroleum products, and millions of cubic metres of water contaminated with salts, alkalies, mineral oils, and dyes. Where do these wastes come from? Contaminated water is the result of modern-day industrial technology. The production of one tonne of synthetic fibre generates 500 cubic metres of sewage water, and this volume is increased several-fold when one takes into account the dilution of the sewage.

Present-day industrial manufacturing processes create enormous irreversible losses of fresh water leading to an increase in shortages of fresh water.

Water is also polluted at farms in which plant protection measures are adopted. We live in an age in which chemicals are extensively used in agriculture and forestry. In addition to artificial fertilisers large quantities of chemical agents are used for pest and weed control. They are of great benefit by helping to preserve the harvests of agricultural crops. For the Soviet Union alone they preserve 18–20% of the harvest.

However on account of the large-scale and at times incorrect methods of application these substances have become a serious factor in regard to the increase in ecological stress. The use of chemical products in agriculture and forestry has become the target of acute and well-founded criticism. Many negative aspects of the use of pesticides are associated with the fact that scientifically based use recommendations are abused in practice. Rates of application, use periods, and instructions for use are disregarded. However, there is another side to this problem.

In the USSR large miscalculations have been made in the elaboration of chemical systems for plant protection and the justification of their use. This situation has led to the extensive development of the production of several kinds of chemicals harmful to man and to the concentration of large quantities of dangerous chemicals and chemical plants in certain areas of the country. Underestimation of the danger of excessive production of organochlorine compounds has left its mark.

The danger of chlorine production is determined not only by the acute and chronic toxicity associated with the production of large tonnages of compounds such as hexachloran, DDT, polychlorocyclodienes and other compounds but also by polychloropolycyclic compounds (PCPC)†, which are formed as impurities in many processes involving the use of elemental chlorine and chlorine-containing substances together with aromatic organic compounds (dioxin, dibenzofuran, chlorazobenzene, and similar substances) and which are responsible for significantly more harmful and distant effects. These substances are particularly dangerous on account of their high biological activity, high chemical stability in the environment and in living organisms and their ability to be transferred from one living organism to another in nature. Even when present in negligible concentrations PCPC compounds suppress the immune system of organisms and reduce their ability to become adapted to the changing conditions of the outside world.

This type of action is accompanied by an increase in the sensitivity of the organisms to infection, particularly viral diseases, and by a decline in mental and physical working capacities. At higher concentrations (several tens of parts per trillion) PCPC compounds are found to exert a mutagenic, carcinogenic, teratogenic, and embryotoxic effect, and these compounds adversely affect the central and peripheral nervous sytem, the alimentary canal, and other organs.

Polychloropolycyclic compounds primarily 2,3,7,8-tetrachlorodibenzo-*p*-dioxin or simply dioxin inhibit all aerobic microorganisms in ecosystems, the organisms known to be responsible for the accumulation of organic substances and for the conservation and growth of the organic potential. In the human body these compounds inhibit genetically encoded mechanisms of adaptation to the natural environment, i.e. the immune system.

Intensive accumulation of PCPC compounds in nature commenced in the period in which DDT and hexachloran production unfolded. Especially large quantities of these agents began to be produced after plants were created for the production of polychlorophenols and polychlorinated biphenyls. However the manufacture and use of chlorine-containing pesticides is not the only source of PCPC compounds.

† For more detailed information see the paper by A F Kolomiitsa "Polychloropolycyclic xenobiotics" in the present issue.

These compounds are also formed in paper and pulp mills, when the paper pulp is bleached with chlorine or chlorinating agents. One cannot rule out the possibility that these xenobiotics will appear in water during chlorine disinfection procedures.

Dioxin and dienzofuran may appear in exhaust gases in non-optimised regimes for burning rubbish and wastes containing organochlorine materials. Burning articles made from polyvinyl chloride has proved to be particularly dangerous.

Exacerbation of the medical and ecological situation in cotton-growing regions of central Asia and Moldavia and the rice-growing areas in the Sea of Azov region, and the stressed state of ecosystems in the Sea of Azov and the Caspian Sea in may ways is the result of the underestimation of the effects of chlorine production and plants from which PCPC compounds are introduced into the natural environment. For example on the territory of Uzbekistan alone over the last decade approximately six thousand tonnes of chlorine-containing pesticides (in terms of active ingredient) have been used each year, despite the fact that the use of these compounds has been banned abroad.

The herbicide, propanil, which contains harmful polychlorazobenzenes and the use of which is prohibited abroad, has been introduced and is extensively used in this country. In the USSR production of hexachloran and DDT continues. Hexachlorophene and dichloraniline, which contain harmful xenobiotics or their precursors, are also produced.

Certain pesticides which have been banned abroad have until recently been imported (for example keltan, tophos, diuron). In this country the large-scale production of polyvinyl chloride, and articles manufactured from this compound is carried out and the use and destruction of the latter are not controlled. A large number of outmoded pulp and paper mills are still in operation and in these establishments there are no facilities for the effective purification of sewage waters, and treatment of drinking water with chlorine has still not been replaced by ozonisation. It is possible to list more examples of this type.

These inconsistencies primarily arise as a result of a lack of any understanding of ecological problems and a low level of ecological awareness. Thus, so far no scientific strategies for the assessment of the ecological hazards of chemical reagents have been elaborated in the USSR. There is a lack of methodology for the prediction of ecologically acceptable routes for the advancement of chemical sciences and industry. Fully developed chemical ecology does not yet exist in this country.

Resolutions of questions concerning the control of chemical pollution reflect outdated approaches to the evaluation of the ecological hazard of chemical agents, since these approaches are based on the study of the properties of individual chemicals. Such a strategy does not take into account many associated factors. Under real life conditions a living organism in nature is exposed to the action not of a single substance but a combination of all naturally occurring and man-made chemical compounds present in the biosphere. In this case it is essential to take into acocunt the possible additive, antagonistic, and synergistic effects of the compounds in the chemosphere. For example in the presence of dioxins there is an abrupt increase in the hazard associated with the action of mycotoxins (aflatoxins and nivalenols) and carcinogen precursors (arylamines) and neurotoxic poisons on the body.

It should be emphasised that it is not the susbtances themselves but the impurities, decomposition products, and products of metabolism which may affect man and nature. One should also take into consideration the fact that, with the appearance of foreign substances in natural environments and their associated harmful effect on ecosystems, a change in the composition of the chemosphere occurs and the direction and consequences of this type of change can not yet be predicted.

The examples and facts presented indicate the importance and significance of the action of chemicals on the stressed state of the biosphere and the need to thoroughly investigate questions of chemical ecology.

It is evident from the experience gained in ecological studies carried out in the industrially developed countries that comprehensive characterisations of the ecotoxicity of chemical agents may be obtained on the basis of a fundamental knowledge of the chemosphere and its effect on ecosystems. Moreover it is surprising that the "Project of Concepts in the Programme of Biosphere and Ecology Studies by the Academy of Sciences of the USSR in the Period up to the Year 2015", which was assessed in the general assembly of the Academy of Sciences of the USSR devoted to ecology, does not include a unit concerned with the chemistry of the biosphere and chemical anthropogenic effects on nature as one of the main directions of research. Questions concerning the chemistry of the environment included in separate units of the project do not span the complete range of problems of chemical ecology but reflect an outmoded utilitarian approach to the evaluation of the ecological hazards of chemical agents.

It would be expedient to include "The Study of the Chemosphere" as a separate priority direction in this project. Fundamental studies within the framework of this unit should provide for the following sections:

—The establishment of the fundamentals of ecotoxicology as a science concerned with the effect of chemical agents on the biosphere and the development of methods of ecological normalisation. In this case it would be necessary to start from the position that, when chemical agents are used for intensive farming practices, efforts to achieve maximum bioproductivity are incompatible with the conservation of the natural environment. Thus from the ecological standpoint it is necessary to approach so-called intensive agricultural technology with great caution.

—The elaboration of scientific bases for the prediction of ecologically safe routes for advancement in the chemical industry, the creation of ecologically balanced industrial technologies and use of chemical agents. In this case the potential hazards presented by the chemical plants themselves should be assessed. Mathematical modelling of the spread of all kinds of pollution is also a necessity. At this stage it would probably be necessary to include a study of the problem of alternative fuels and studies on the sharp reduction in water consumption by industry, as for example in the "close-up" of water systems.

—The creation and organisation of essentially novel resource-saving technologies in which no wastes or very small quantities of wastes are generated.

—The elaboration of effective techniques for the purification of gaseous, liquid and solid wastes based on sorption, membrane, catalytic, and other technological processes.

—The development of pathways for the prevention of chemical and microbiological contamination of agricultural products and the environment.

—The elaboration of scientific strategies for improving the sanitation of ecosystems adversely affected by chemical agents.

—The creation of non-persistent pesticides and other chemical agents which are readily degraded and rapidly assimilated into the

natural environment and which have no harmful effect on the environment.

Information on the state of natural systems especially in regard to chemical and other kinds of contamination is of enormous importance for the protection of the environment. Most of the operative information on the biosphere is currently provided by the Earth's artificial satellites which have a resolving power of better than 10 m. However such information is suitable for "the monitoring of areas" but is inadequate for "the monitoring of the state" of natural systems. The elaboration of convenient techniques, equipment, and instruments for obtaining quantitative measurements of environmental parameters is of great importance for attaining progress in terrestrial monitoring. In this regard the design of instruments and the development of techniques which employ chemical or physicochemical principles will play an important role. The design of novel and readily obtainable instruments and techniques will improve the accuracy, validity, and range of measurable parameters in natural systems.

These are merely a few of the directions for research into the field of chemical ecology and they will undoubtedly be supplemented by new directions in the elaboration of a chemical ecology programme.

On account of the sharp increase in potential hazards to man and nature posed by the accumulation of xenobiotics in the environment, special national programmes have been organised on this aspect of chemical ecology by the industrially developed countries and through international collaboration. For example since 1980 international conferences on dioxin have been held. Of the major producers and users of chlorine products only the Soviet Union is not participating in the international collaboration on this problem and so far has no kind of programme for engaging in research into this problem. Extension of international collaboration on questions of chemical and other aspects of ecology is also an urgent necessity and should constitute a significant part of the programmes being prepared and projects targetted towards the protection of the environment.

The main objective of chemical ecology is the conservation of the vital qualities of the biosphere and the prevention of progressive pollution of the natural environment by reorganisation of anthropogenic activity which would promote the growth of industrial and agricultural output and which would exclude any unfavourable effect on nature. Ultimately the problem concerns the elaboration of conditions and measures which would promote the further development of human civilisation and the survival of humankind.

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# The chemical physics of the ozone layer

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The ozone layer exerts a significant effect on the properties of the middle atmosphere and creates the conditions under which the flora and fauna can exist on the Earth's surface. These features of the ozonosphere are in a sense caused by the unique physicochemical properties of ozone. The ozone molecule absorbs solar radiation intensely in the wavelength region below 290 nm, which is harmful to biological matter, and also (although less intensely) the "terrestrial" infrared radiation at a wavelength of 9–10 μm thereby enhancing by 10% the greenhouse effect caused by carbon dioxide and other radiatively-active components of the atmosphere. On the other hand ozone molecules are highly reactive on account of the low value of the energy bond between the "third" oxygen atom and the oxygen molecule. It is correct to say that the chemistry of the atmosphere and the troposphere and particularly the chemical processes associated with anthropogenic contaminants and their destruction in the atmosphere are controlled by ozone, albeit with the loss of the molecule itself.

As regards the effect of atmospheric ozone on global ecology it can be ascertained that the ozone layer is important as a factor providing a biologically safe level of ultraviolet radiation close to the Earth's surface and is involved in the conservation of the Earth's overall climate and controls the content of certain anthropogenic and natural contaminants in the atmosphere. It is noteworthy that the latter usually is under the shadow of the opposite problem, the effect of anthropogenic impurities on the ozone content. However these problems are evidently closely associated.

The stratification of the middle atmosphere caused by the change in temperature and distribution of ozone with altitude is shown in Fig. 1. The stratosphere contains the main reserves of ozone. The maximum concentration is found at an altitude of 20–25 km. At these altitudes the relative content of ozone in the atmosphere is about 1 ppm, and the total quantity of ozone in the atmosphere is equivalent to 3.3 billion tonnes. This quantity would correspond to a gas layer 3 mm in depth at normal temperature, and pressure. It should also be mentioned that ozone is not uniformly distributed over the Earth. On average there is less ozone in the tropics and more at the poles. In addition at all latitudes the total content of ozone changes with the seasons.

The above-mentioned aspects of the ecological significance of ozone will now be discussed.

## I. The role of the ozone layer as a filter for biologically harmful ultraviolet radiation

This effect is caused by the fact that short-wave radiation at $\lambda < 300$ nm is harmful to many biological molecules, especially for DNA. The ozone layer which exists at present successfully fulfils a radiation protective function which may be judged according to the change in the intensity of sunlight in the 210–290 nm wavelength range with altitude. There is a distinct dip in the intensity of