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Briefing of activities relating to the studies on the environmental behavior and eco-toxicology of toxic organics

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Abstract. General status of the studies on the environmental behavior and eco-toxicology of toxic organics was briefly reviewed, with the point of view that these kinds of studies are the requirements of sustainable development. Some current activities in this field were introduced, such as the revisions of OECD guidelines and the accomplishments of programme on the advanced evaluations of chemicals finished recently by the Department of Environment Protection of Sweden. The general trend of emphasis of modelling, prediction from Structure-Activity Relationship was mentioned. In cope with the present serious pollutions by chemicals here in China, further united action of different disciplinary studies was recommended.

Keywords: eco-toxicology; toxic organics; structure-activity relationship; chemicals.

THE STUDIES OF ENVIRONMENTAL BEHAVIOR AND ECO-TOXICOLOGY OF ORGANICS ARE THE REQUIREMENTS OF SUSTAINABLE DEVELOPMENT FOR NATIONAL ECONOMY

Since 1950s, following the developments of industry and agriculture, various chemicals have been entering the market. A lot of serious environmental accidents, for examples, the minamata disease (mercurial poisoning) and Yusho rice bran oil incident (PCBs poisoning, accidental poisoning by cooking rice in bran oil contaminated by PCBs) etc. occurred sequentially all over the world. They give rise to pay close attention to the global potential environmental toxic substances in the world. In December 1984, a leak from a pesticides factory in Bhopal, India (the pestilent pesticide vapour of isocyano methyl ester) killed more than 2000 people and blinded and injured over 200000 more, it is the most serious industrial disaster in the world. In the winter 1986, significant amount of toxic agricultural chemicals was discharged into the Rhine River during a ware-house fire in Swizerlands, killing millions of fish and affecting the drinking water supply quality in countries downstream all the way to the Netherlands.

It must pay more attention to the fact that those heavily polluted industries, such as: iron

and steel; non-ferrous metals; chemicals; electric power etc. occupy a significant situation and bring into play a positive effect in whole national economy, and then in a long-term, people neglected their impacts to human health and eco-environment. For instance, the chemical industry is also one of the most dynamic sectors in most countries including many developing ones. Chemicals represent about 10 percent of total world trade in terms of value, its species and quantity of products are annually increasing over exponentially. In recent, Chemical Abstracts Service Computer registry of chemicals contained more than 8 millions distinct entitles, while some 70000—80000 chemicals are now on the market — and hence in the environment (about 30000 in China). Those species and amounts of chemicals entering the environment are rather significant. Furthermore, some 1000—2000 new chemicals enter the commercial market each year, many without adequate prior testing or safety evaluation. By 1985, the total world product was up to 350 millions tonnes. For instance, the global chemical pesticides are in use which increase with a rate of 12.4 percent annually (the amount in use of pesticides in China are estimated in 10 percent to the international market). As previously mentioned, there are still most another chemicals entering the environment for which no risk assessment has been made. However, our knowledge relevant to those chemical substances, particularly, their environmental behavior (such as the photolysis, hydrolysis, microbiodegradation, methylating, sorption, leaching, volatilization and bioaccumulation etc.) and potential hazardous impacts of toxic organics is very incomplete or still unknown. Besides, only a little study about the burning of fossil fuels and vocanic eruption that release a huge amount of toxic substances into environment, some occurring as impurities and intermediates (or metabolites), is available. As a result, an erroneous traditional concept is spreaded by a long period— "There is only one choice between economy and environment". The serious accidents which cause the consequences of disaster, however, are increasing successively. Contamination of soils, ground water, and people by agrochemicals is widening and chemical pollution has spread to every corner of the planet. Pollution problems that were once local are now regional or even global in scale. On the other hands, thousands of the storepile of hazardous wastes which lead to grave consequences is also a serious problem by now." It is becoming increasingly clear that the sources and causes of pollution are far more diffuse, complex, and interrelated" and "The effects of pollution are more widespread, cumulative and chronic than hitherto believed", therefore, the pollution problem becomes a restricting factor for the sustainable development of economy.

Through the lessons of erroneous and reverse we all became wiser. The World Commission on Environment and Development first met in October 1984 and then after 900 days of global surveying by many scientists representing a wide range of different disciplines and specialities from different universities and research institutes published its report "Our Common Future" in April 1987. It was adopted by a resolution of the 8th World Commission on Environment and Development Conference (1987) and then passed through debatting by 42nd UN General Assembly. In this milestone 1987 report, "Our Common Future" emphasized the importance of

environmental protection in the pursuit of sustainable development. A common voice has been expressed, claiming: " Link up the environmental protection with sustainable development" — a new fundamental conception and strategic recognition; "The link of both is to ensure that it meets the needs of the present without compromissing the ability of future generations to meet their own needs"; "Pollution and Progress are not the same thing"; "Pollution is not the synonym of progress"; "Environmental concern arose from damage caused by the rapid economic growth following the Second World War, because man was ignorant in environmental problems". Now, we must assimilate the experience and draw a lesson in fault from developed countries, "Pollution must be controlled, if not, you are transferring this pollution to the community of the whole"; "If pay no emphasis to pollution control, the damage of pollution to human health would be beyond the degree of enduring in cities, and the threat of property and ecosystem will be increasing sustainablly". In addition, be of benefit from the resources obtained and the experiences of environmental management of industrialize nations, thus may be to reduce the expensive cost for pollution control and, to prolong the employment period of resources, to maintain the sustainable development of nations.

Meanwhile, on the premise of recent guideline, new regulation has been made for the restriction of toxic chemicals. The situation is now beginning to change as governments move gradually from a system of post-market testing to one of premarket testing of all new chemicals. By 1986, more than 500 chemicals and chemical products had been banned altogether or had their uses severely restricted in the country of origin. Therefore, the studies of environmental behavior and eco-toxicology of toxic organics are the requirements of sustainable development to the national economy.

TRENDS ON THE STUDY OF CHEMICALS AND THE OECD TESTING GUIDELINES

Since 1970s, multiphasic researches have been developed successively by the member countries of the Organization for Economic Cooperation and Development (OECD) — such as Japan, Former Soviet Union, Germany, Sweden, America and Netherlands ect., and according to the achievements, relevant Standards and Acts of Chemicals had been established. For instance, the U.S. "Clean Water Act" basing on monitoring the 129 priority pollutants (including 114 organics) is still under researching for the renewal of analytical procedures and complementing the monitoring objects sequentially. The U.S. National Toxicology Programme (NTP) has organized decades of units for developing systematic toxicological research of more than hundred chemicals by spending hundreds of millions of dollars each year. Since 1969, the Gesellschaft für Strahlen-und Umweltforschung (GSF), Germany, has carried out various tests for more than two hundred chemicals, the relevant funds on 1986 was estimated about 60 millions of DM. This kinds of work has been noticed by many international organizations. For instances: the United Nations Environment Programme (UNEP) associated with the International

Labour Combination (ILC) and World Health Organization (WHO) for establishing the International Programme of Chemicals Safety (IPCS); the International Registry of Potential Toxic Chemicals (IRPTC) under UNEP; the Scientific Committee on Problems of Environment (SCOPE) under the WHO and International Council of Scientific Unions (ICSU) established a Scientific Group on Methodology for Safety Evaluation of Chemicals (SGOMSEC), and drafted a series assessment approaches of potential hazardous chemicals, more than ten volumes of special monograph in this field were published. In its "Four Cluster Project" on early 1990s, not only integrate the Cluster of "eco-toxicology" with "biogeochemistry cycle" and "global changing", but also integrate with the cluster of "sustainable economic development" directly. The study on ecological effect of chemicals is also an important part of the "Man and Biosphere" project of United Nations Educational, Scientific and Cultural Organization (UNESCO).

The international organization OECD was organized on 1961 by developed countries, including many European countries, America, Canada, Australia, New Zealand, and Japan and so on. The relevant activities of chemicals safety were started in early 1970s. Since 1977, besides formulating the "Minimum Premarketing Set of Data", the 51 trail testing guidelines of chemicals had been published on 1981, including the physico-chemical property, biological effect, degradation and accumulation, and health impacts and so on. Afterwards, calling meetings periodically, and adopting a prudent policy to revise them, till the autumn 1987, OECD had revised 77 testing guidelines. The revised contents are almost all relevant to the toxicological testing, in which the main contents are passed recently as the special toxicity (reproduction toxicity, toxicokinetics, neurotoxicity and so on), the genetic toxicity (reverse mutation, chromosonal mutation, rodent bone marrow cytogenetics, sister chromatid exchange, plague spot and so on), and also renewed the ecotoxicity (daphnia, fish, bird, owl, terrestrial plant, algae and so on) and the acute toxicity (oral, dermal, inhalation, eye irritation/corrosion). Afterwards, a new monitoring method is developed — the high-pressure liquid chromatography (HPLC) for measuring the octanol/water partition coefficient (P_{ow}), the photochemical oxidation decomposition, the fish embryo-juvenile test and, renewed the test procedure of acute toxicity at fishes. The OECD Testing Guidelines are the essential material in adopting widespread.

INVESTIGATION ON THE ADVANCED ASSESSMENT APPROACHES OF CHEMICALS

The transformation and effects of chemicals in the environment (in general, including two facets of exposure analysis and effect analysis) are often very complex, it is not easy to obtain reliable and complete data. Therefore, besides the sequential improvement of the approaches proposed by organizations such as OECD and so on, great efforts have been also made by using model compounds selected to develop the in-depth studies, so as to improve the existent rather "traditional" assessment approaches and parameters into more effective and reliable ones. Recently, the National Swedish Environmental Protection Board has fulfilled a five-year research

project, the "ESTHER programme (Systems for Testing and Hazard Evaluation of Chemicals in the Aquatic Environment), it is a good example for advanced assessment and is scientifically well attempted. It means not only to complete the preliminary (initial) assessment, but also to develop an advanced approach.

The essential factors considered in this advanced assessment (aquatic environment) are as follows:

(1) Biotransformation of organics-chemicals that have been given priority as being of concern relating to their environmentally hazardous properties are not only due to their own preferential persistency, but also due to their various biotransformations taking place in the aquatic environment, particularly, the possible formation of metabolites with properties even more hazardous than those of the parent compound. However, this kind of knowledge is rather short, so there is a need to consider the in-depth assessment of those hazardous metabolites.

(2) Sorption (uptake) by sediment— The significance of strong sediment-binding of xenobiotics or bioavailability to various organisms has to be considered. Uptake of this kind may occur not only directly from the aqueous phase but via particulate matter. Besides, the sorption (uptake) may not only take place for the initial chemical compounds, but also relate to the metabolites and other transformation products. Sometimes the sediment sorption behavior of a chemical can not be properly predicted from its octanol/water partition coefficient (P_{ow}), used in preliminary assessment. Moreover, the significance of strong sediment-binding of xenobiotics cause many problems in testing.

(3) Bioavailability— In the preliminary assessment, the bioconcentration behavior of organic xenobiotics can usually be estimated from the P_{ow} value. However, lately several exceptions are found. Through the fish gills membrane adsorption test, the bioavailability of organic xenobiotics is considered to be one possible important reason for the deviations. Using a series advanced studies of the uptake rate of various xenobiotics across the gill membrane, no positive correlation of bioconcentration was found for compounds with higher P_{ow} value. Moreover, the sorption rate of ionizable compounds was found pH-dependent, and thus influenced the uptake rate.

(4) Use of fish bile for monitoring— The traditional way of monitoring loading of persistent xenobiotics is to extract fat from organisms and analyze for the actual compounds. However, bioaccumulation is diminished in the presence of polar groups (hydrophilic). Probably, the latter form water-soluble conjugates and thus diminish the bioaccumulating tendency of fat (or liver), so the traditional method presented above is limited in use. Analysing the concentration in fish bile (the main species is conjugate form), an approximately linear correlation between the concentration of xenobiotic in water and in bile was obtained. Therefore, the "bile method" in field monitoring programme may be a successful way.

(5) Ecologically relevant effect studies— Using the results of the traditional toxicity testing on aquatic organisms in the laboratory, sometime has low relevance for predicting effects on natural environment, and does not represent studies in eco-toxicology, therefore, the recent tendency is

to pay attention to design experimental parameters close to natural conditions or to direct performance of field experiments. The multi-species and multi-factors test systems were used both in short-term tests and long-term studies for more than one year. This kind of test system has also been used in the ESTHER programme to develop and validate a new eco-toxicological concept and approach in effect studies, namely "Pollution— induced Community Tolerance" (PICT). The intact communities of phytoplankton or periphyton were brought to laboratory in these studies. The PICT approach has lately attracted great interest among eco-toxicologists, since it overcame the difficulties of traditional experiment, for instance, one of the difficulties in performing short-term tests with algae is that there are only a small fraction of all algal species can be held in laboratory culture, and those which can be kept are not the sensitive ones to the testing chemicals. This difficulty can, however, be circumvented by using intact algal communities. Thus, the PICT indicated correctly the changes in compositional structure of species and net production of the community, thus the new approach has been found to be a sensitive and efficient eco-toxicological tool with a high degree of ecological realism.

(6) Model (simulant) ecosystems— The multi-species test systems of microcosms and mesocosms ecosystems were set up for use in long-term studies of fate and effect of chemicals, among them, some represent the marine benthic microcosms, some represent the marine littoral-zone benthic mesocosms and some represent the fresh-water pelagic-benthic limnocorrate.

The advantages of these multi-species model ecosystems can be used to observe the effects of the durnal and seasonal variations or seasonality in nutrient flow on the species and community. They allow the identification of the system components that are most sensitive to a certain chemical substance and a close follow-up of secondary (or tertiary) effect after restructurization or breakdown of the original system.

Through advanced assessment of the three types of model chemical compounds, it was found that the results of the single-species algal test of initial assessment only, according to the OECD Testing Guidelines, perhaps, are impossible to define the chemical compounds under study as environmental hazardous substances, but by using the advanced assessment through algal community test (multi-species test systems), even in lower concentration, a more sensitivity effect can be detected. Therefore, a different conclusion to the chemicals of being environmentally hazardous should be made from the further assessment.

REGULARITY, MODELLING AND PREDICTION

In the task of assessment of chemical substances, various regularities summarized and the relationship of various parameters were noticed by scientists in the prior studies to predict certain behaviors of them. For instance, as mentioned above, positive correlation between P_{ow} and bioaccumulation has been established some years ago. Of course, some exceptions were found in further studies as proposed previously, but in those exceptions, there are also another rules do exist that promote to establish the new monitoring methods.

With the increase in requirement of assessment task day by day, because of the rather expensive cost of bioassessment testing (the cost of testing is estimated by U.S. to be 2000 – 3000 of dollars for each acute toxicity test, 6000 – 10000 of dollars for each bioconcentration test), and the costly and time-consuming nature of environmental fate testing, Quantitative Structure-Activity Relationships (QSAR) have been used to screen large classes of chemical compounds and flag those that appear to warrant more thorough testing. The fundamental principle of QSAR is that: "Fundamental connections and relationships do exist between molecular structures and biological activities and toxicities, as well as the environmental fate of chemicals".

The pattern recognition (PR) methods have become available for studying mutagenicity and carcinogenicity of chemical compounds, so as to classify into active and non-active groups or to group into tree clusters or box clusters after processing the data. In QSAR modelling, besides obtaining a bulk of experimental data of chemical compounds, the essential point is to choose the suitable descriptors. The most commonly used descriptors in environmental QSAR studies are molecular connectivity indices, log p, the other descriptor is molar refractivity (MR) that has been used to improve correlations. It is correlated to many physico-chemical properties, for instance: the polarization in molecule, sediment sorption coefficient and bioconcentration and so on. Bioassays were developed to quantify biological activity in terms of LC_{50}, and bioconcentration factor (BCF). There were quite a few successful instances, therefore, the Toxic Substances Control Act (TSCA) under U.S. Environmental Protection Agency (USEPA) now accepts QSAR results, as an alternative to testing data; besides, a lot of models have been suggested.

Recently, the methods of predicting physico-chemical properties have been used in studying the mixture of chemical substances, and QSAR in ecological models can predict the temporal and spatial distribution of environmental contaminants and their behavior in the various compartments of the eco-environment, as well as the fate modelling of homologs. Of course, QSAR has a certain limitations, and it is not expected to replace experimental verifications. The current trends in QSAR development are towards establishing integrated computer programs, large data bases and applying artificial intelligence.

The studies on the environmental behavior and eco-toxicology of toxic organics concern a wide range of different disciplines and specialities, particularly, requiring the cooperation and effort of environmental chemists, environmental toxicologists, environmental biologists and geoscientists and so on.

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