POPs - Persistent Organic Pollutants

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Introduction

Slide 1 Bo Jansson

Ladies and gentlemen, good afternoon. My name is Bo Jansson, and I'm a professor at the Institute of Applied Environmental Research at Stockholm University in Sweden, and I would like to thank the organizers of this meeting for inviting me to give this lecture. I was trained as an analytical chemist and became interested in environmental pollutants when I worked together with Sören Jensen when he discovered the polychlorinated biphenyls (PCBs) in environmental samples in the mid 1960's. I continued this work with halogenated compounds for many years to come, but left the practical laboratory work some 10 years ago to work more in the interface between science and management, a link that often still is rather weak. Today my main tasks are to support international bodies, such as the European Commission and UNEP, and national authorities with advice on their work with chemicals, and I will today give an overview of persistent organic substances, some of which also are, or are suspected to be, endocrine disrupters.

Risk, hazard and exposure

Slide 2 Risk = hazard x exposure

The exposure to chemicals may pose a risk to both humans and the environment, and these risks are estimated in a process called risk assessment. The risk connected to a certain chemical is a function of the properties of this chemical (hazard) and the exposure to it, but unfortunately both of these factors are difficult to measure.

The effects are normally studied in experimental animals and an uncertainty, or safety, factor is used to protect for differences between individuals. A few species are studied and the results are then extrapolated to all other species, and an additional uncertainty/safety factor is used to cover possible differences between the species. These factors are rather arbitrary and not always covering worst-case situations and may in other cases be overprotective. There may also be effects that we are not aware of and therefore have not studied, and it is obviously not possible to protect for those. Endocrine disruption is a good example of an effect that was not paid much attention a few years ago, and we still not know the exact consequences of this effect.

The exposure can be measured by analytical chemical methods, and the major part of these measurements gives a measure of external exposure, such as concentration of the chemical in air or food, and those determinations will just describe the situation at the place and the time of the sampling. To get a picture of the total exposure a large number of these measurements have to be performed to cover all exposure routes over time. An alternative is to measure the concentration in the exposed organism, or still better in the organ that is affected by the investigated substance, often called the internal or target organ dose, but this is not always possible.

An alternative, or perhaps better a complement, to measurements is to use models to predict the exposure. These models are based on the knowledge gained from earlier measurements and calculations of

the distribution of the chemical in the environment. They are often able to predict the exposure rather well, but in other situations the estimates may be orders of magnitude off the true value. Models thus have to be used with caution and in most cases a combination of models and measurements is the best way to estimate the exposure.

The major factors determining the exposure to a specific chemical are the used volume, the use pattern and the properties of the substance. It is not difficult to realize that large volumes of a chemical widely used by consumers will cause a higher exposure to humans than a small volume chemical used only as an intermediate in a chemical plant. Several properties of chemicals, such as vapour pressure and water solubility, are determining their distribution in the environment. To be able to interact with a living organism, the compound also has to enter the cells, and the molecular size and shape is in some cases setting limits for this.

PBTs, vPvBs and POPs

Slide 3 PBTs, vPvBs and POPs

Chemicals with low degradation rates are often called persistent (P). This term is relevant for the elements, such as the metals, but most organic substances tend to be degraded sooner or later. The term persistent is anyhow used also for organic substances that are slowly degraded in the environment, and these may build up to high concentrations even if the emissions are modest. These long-lived substances may also be distributed over large areas due to different transport mechanisms (e.g. winds, currents and biota migration) and can cause adverse effects far away from their sources, and it is therefore often difficult to connect observed effects with these sources. The affected organisms are also exposed to a large number of chemicals, and it is also difficult to bind the effect to a specific substance. There may also be combinations of chemicals that are responsible for the effects, either additive or more or less than additive.

Chemicals with a high solubility in lipids, known as lipophilic substances, will at equilibrium be present in the lipid of an organism at a higher concentration than in the surrounding medium. This enrichment process is known as bioconcentration, and may be amplified by an indirect exposure via the organism's food, also contaminated from the surrounding medium. These combined enrichments are known as bioaccumulation (B), and the difference between concentrations at two levels in the food web is often called biomagnification.

A toxic (T) compound gives one or several adverse effects in the organism, and there are a large number of such effects described. Some of these are believed to have threshold under which no effect will occur, while others are thought to give effects also at very low levels. In general, however, the effect (risk) is dependent on the potency of the substance and the exposure.

Chemicals combining high values for the properties persistency, bioaccumulation potential and toxicity (so called PBT chemicals) thus need special attention. This was realized already around 1960 for some pesticides and disseminated to a wider public by e.g. Rachel Carson in her book "Silent Spring". Several chemicals, including a number of halogenated pesticides, have since that time been banned in large parts of the world, but there are still compounds being produced (both intentionally and unintentionally), which combine these properties.

During the last couple of years special attention has also been paid chemicals that are very persistent and very bioaccumulative (so called vPvB chemicals), and the reason for that is that it is never possible to say that a compound is absolutely non-toxic. There may be effects that have not been studied or which are not known today, and the endocrine disruption is a good example, where we today see effects of compounds that were earlier thought to be safe. If new effects are found due to a vPvB chemical that

has been in use for a while it is impossible to do anything as it is already distributed to the environment and will stay there for a long time, we can't possibly retrieve them from the environment. Therefore, as a precaution, the Swedish government has decided to ban the use of vPvB chemicals in products in the future, and the new chemicals policy being discussed within the European Union also pays special attention to this group of substances.

The special problems connected to PBT chemicals have resulted in several international agreements to reduce the use and emissions of such substances. The mandate of the Oslo-Paris Commission (OSPAR) is to protect the northeast Atlantic and in that framework a large number of chemicals have been screened for PBT properties. A number of these substances have been given high priority and the goal is to stop the emissions totally and to bring the environmental concentrations to background levels. The agreement within this forum is, however, not legally binding, but the member states are doing a good work to reach the goals, mainly by applying best available technique for the production and use of the chemicals.

POPs is an acronym for Persistent Organic Pollutants, which is a subset of the PBTs, and there are two protocols for signed within the UN framework for these chemicals. None of these are yet ratified by the number of countries needed for the conventions to come into force, but this is expected to happen within 1-2 years. The two conventions are the UN-ECE LRTAP protocol on POPs and the UNEP POPs Convention and I will now describe these.

UN-ECE, LRTAP Convention, POPs protocol

Slide 4 UN-ECE Map

United Nations Economic Commission for Europe (UN-ECE) was set up after World War II and has 55 member states in Europe, North America and Central Asia, and as both Canada and the Former Soviet Union are included in the region, it covers a large fraction of the top of our globe as can be seen in this slide.

Slide 5 POPs definition in LRTAP

This organization has a Committee on Environmental Policy, which is responsible for a Convention on Long-Range Transboundary Air Pollution, often abbreviated LRTAP. This convention was signed already in 1979 and entered into force in 1983, and under its umbrella a number of protocols have been signed, some of them also ratified. In 1998 a Protocol on Persistent Organic Pollutants (POPs) was signed and it is expected to come into force next year. The objective is to control, reduce or eliminate discharges, emissions and losses of POPs.

The definition of POPs in the ECE protocol is "organic substances that: (1) possess toxic characteristics; (2) are persistent; (3) bioaccumulate; (4) are prone to long-range transboundary atmospheric transport and deposition; and (5) are likely to cause significant adverse human health or environmental effects near to and distant from their sources". A working group prioritized among 107 candidate substances, mainly taken from marine conventions, such as OSPAR for the northeast Atlantic and HELCOM for the Baltic. First compounds with an atmospheric half-life under 2 days or clear evidence for a high biodegradation were excluded, as well as chemicals with a high volatility. This step excluded 20 compounds. Using a scoring system based on bioaccumulation and toxicity 70 of the remaining chemicals were ranked, the other 17 could not be treated due to lack of data. Of the 70 the 17 with the highest score were reviewed for risk assessments and the group finally prioritized 13 substances

or group of substances for inclusion in the protocol. The final list looks somewhat different, one of the suggested compounds disappeared and three has been added, and I don't know the reasons for these changes. In the protocol these chemicals are divided into three different lists, depending on what kind of action was agreed.

Slide 6 UN-ECE, Annex I

The first group contains substances scheduled for elimination, which means a ban on both production and use, but as you can see in this table there are some exemptions, especially for DDT and PCB. The other exemptions are rather minor and mainly for countries with economies in transition.

Slide 7 UN-ECE, Annex II

This second list contains substances scheduled for restrictions on use, and here we can again see DDT and PCB. DDT will be allowed until suitable alternatives are available for health protection from diseases such as malaria and encephalitis. Production of PCB will be allowed in countries with economies in transition up to 2005, and the use of PCB in liquids should be eliminated at the end of 2010, 2015 for countries with economies in transition. In the European Union legislation the term PCB include also the polychlorinated terphenyls and Ugilecs, but not in some other parties, and this question is now going to be revisited. The technical hexachlorocyclohexane (HCH) is a mixture of several isomers and this is only allowed as an intermediate in chemical manufacturing, while Lindane, which is the biologically active isomer, will be allowed for some specific applications.

Slide 8 UN-ECE, Annex III

A third list specifies three substances, which are difficult to eliminate as they are produced as by-products or reaction products in different processes. The protocol says that each party shall reduce its total annual emissions of these substances from a level in a reference year, normally 1990, and they have to apply best available technique to reach these goals. For waste incineration there are also limit values on the emissions to air that has to be fulfilled.

Discussions are now underway to include also other compounds in the LRTAP POPs protocol, and chemicals being discussed now are pentabromodiphenyl ether, Lindane, Ugilec, polychlorinated terphenyls, dicofol, pentachlorobenzene and polychlorinated naphthalenes. On the agenda is also chlorinated paraffins and pentachlorophenol.

UNEP-POPs, Stockholm Convention

Slide 9 UNEP

The United Nations Environmental Program (UNEP) has its head office in Nairobi, Kenya, but the unit responsible for chemicals (UNEP/CHEMICALS) has their office in Geneva, Switzerland. In 1995 the Governing Council of UNEP invited several international programmes to initiate an expeditious assessment process of POPs, initially beginning with a short-list of persistent organic pollutants that, at that time, was discussed by the UN-ECE. In 1997 it was decided that UNEP should negotiate an international legally binding instrument for implementing international action initially beginning with twelve specific POPs, which constitute a subset of the chemicals found in the UNECE protocol. The

compounds found on the UN-ECE protocol but not in the UNEP priority list are hexachlorocyclohexane, chlordecone, polycyclic aromatic hydrocarbons and hexabromobiphenyl, and I don't know the reason why they were excluded. The negotiations have resulted in a convention signed in Stockholm, Sweden, earlier this year, and it is now known as the Stockholm Convention. Also these substances had to be divided in three groups, and the first of these is shown in the following slide.

Slide 10 Stockholm Convention, Annex A

The parties shall prohibit and/or take the legal and administrative measures necessary to eliminate the production, use and import/export of the substances in Annex A. Except for endrin and Toxaphene it is possible for a party to obtain some specific exemptions for all chemicals, mainly for their use as insecticides. These exemptions are going to be listed in a registry, which will be available to the public. Quantities of the chemicals occurring as unintentional trace contaminants in products and articles are not included, as well as quantities in articles manufactured before the date the convention entry into force. The use of these chemicals as closed system, site limited intermediates are also not covered by the convention, if no significant quantities are expected to reach humans or the environment.

Special attention is paid to the elimination of PCB in use, and "the parties shall make determined efforts to identify, label and remove from use equipment containing greater than 0.05% PCB and volumes greater than 5 litres" and "endeavour to identify and remove from use equipment containing greater than 0.005% PCB and volumes greater than 0.05 litres". The parties have to report every five years on their progress in eliminating PCB.

Slide 11 Stockholm Convention, Annex B

Each party shall restrict production and use of chemicals listed in Annex B, where only DDT is found today. The acceptable purposes to use DDT are for disease vector control, to produce dicofol and as an intermediate. Parties producing and /or using DDT has to notify this and will be registered in a register available to the public. Every three years, each party that uses DDT shall provide information on the amount used, and they shall try to implement suitable alternative products, methods and strategies.

Slide 12 Stockholm Convention, Annex C

Each party shall take several measures to reduce the total release derived from anthropogenic sources of each of the chemicals listed in Annex C, with the goal of their continuing minimization and, where feasible, ultimate elimination. These measures include action plans, source inventories, and promotion of substitutes and the use of best available techniques.

The twelve compounds included in the Stockholm Convention does not include all persistent organic pollutants, and during the negotiations a special group was working on the criteria to be fulfilled by other chemicals to be included in the convention in the future. The result of their work is described in Annex D of the final text, and it stipulates that any party may submit a proposal to list a chemical in Annexes A, B and/or C. This proposal shall contain information on identity and data on the properties persistence, bioaccumulation, potential for long-range transport, and adverse effects of the proposed chemical. The working group also decided on screening criteria for the inclusion of further substances in the convention, and their result can be seen in this slide. To be considered for the inclusion in the convention a chemical has to fulfil the following screening criteria:

Slide 13 Stockholm Convention, Persistence

Persistence: The half-life in water is longer than two months, or longer than six months in soil or sediment, or there is other evidence, such as monitoring data, demonstrating the persistence of the chemical, and

Slide 14 Stockholm Convention, Bioaccumulation

Bioaccumulation: The bioaccumulation factor in aquatic species exceeds 5000, or log Kow exceeds 5. High bioaccumulation in other species, high toxicity or ecotoxicity may also fulfil this criterion, and

Slide 15 Stockholm Convention, LRT

Potential for long-range environmental transport: The chemical is measured at levels of concern far from its sources, or monitoring data showing that long-range transport may have occurred via air, water or migratory species. Also environmental fate properties and/or model predictions demonstrating long-range transport are accepted, and

Slide 16 Stockholm Convention, Adverse effects

Adverse effects: Evidence of, or toxicity and ecotoxicity data indicating the potential for, damage to human health or to the environment.

If all these criteria are fulfilled, a risk profile shall be conducted based on available data. If this profile indicates that it is likely that the chemical may lead to significant effects on human or environmental health (and here lack of full scientific certainty shall not prevent the proposal from proceeding), information on socio-economic considerations are gathered from the parties of the convention. The next step is to prepare a risk management evaluation that includes an analysis of possible control measures for the chemical. Finally the Conference of the Parties shall decide, in a precautionary manner, whether to list the chemical, and specify its related control measures, in Annexes A, B and/or C.

This process seems rather complex, but there are probably a number of compounds fulfilling the criteria, so it will be very interesting to see how difficult it is to add new substances to the protocol.

Slide 17 Stockholm Convention, Research recommendations

In Article 11 of the Stockholm Convention it is said that the parties shall encourage and/or undertake research, development and monitoring pertaining POPs. The areas for these activities include sources, monitoring, fate, effects, socio-economic impacts, reductions and inventories of the chemicals covered by the convention. It is therefore most encouraging to hear that the Japanese government now is initiating a new monitoring programme for POPs.

The evaluation of the effectiveness of the convention shall start four years after its entry into force, and this evaluation will then be done periodically. The Conference of the Parties shall, at its first meeting, initiate the establishment of arrangements to provide itself with comparable monitoring data on the presence of the chemicals covered by the convention. The production of comparable monitoring data is not easy, especially as the comparisons will be used to disclose possible geographic and temporal trends. This implies that data with small differences have to be compared, which means that the analytical

accuracy has to be high. The most effective way to obtain that is probably to do all the analyses in one laboratory, but this would not distribute the awareness of the POPs problem effectively to the different parts of the world. Training activities may be needed to improve the analytical skill in some regions, and if a distributed system is chosen, there is a need for intercalibrations of the laboratories to investigate the comparability.

Regionally-Based Assessment of Persistent Toxic Substances

Slide 18 RBA-PTS

The evaluation of the effectiveness of the convention has to be based on the situation before the convention came into force, and UNEP has, with economical support from the Global Environment Facility, started a project called "Regionally-Based Assessment of Persistent Toxic Substances". The overall objective of this project is to deliver a comprehensive regionally based assessment of the damage and threats posed by persistent toxic substances, and to evaluate and agree the priorities between chemical related environmental issues at the regional level in order to focus subsequent interventions on the most important and pressing issues. The twelve regional reports will include assessment of the sources of persistent toxic substances in the environment, their concentrations and impact on biota, their transboundary transport, and an assessment of the root causes of the problems and capacity to manage these problems. Consolidation of the results of the regional analyses will provide an assessment of global priorities.

Slide 19 RBA-PTS regions

The twelve regions the project is working with are given in this slide. The scope of the project is somewhat wider than just the twelve POPs presently covered by the Stockholm Convention, and the reason for that is to try to find out if there are persistent compounds of high concern in any of these regions. There are teams of experts set up in all regions except for the Arctic and Antarctic that will be treated in another way, and these teams are encouraged to include more chemicals than the twelve currently in the Annexes A, B or C. The work is ongoing and is now in the data collection phase. This project will give a good base for the evaluation of the effectiveness of the Stockholm Convention, and furthermore disclose areas where the present knowledge is limited. Most of the studies on POPs so far have been performed in the OECD countries and to some extent in the Arctic region, and there will probably be a need for increased activities in several other regions.

UNEP is now also initiating several Internet based discussion groups where monitoring of chemicals in the environment will be the focus. Initially these discussions will be mainly focussed on POPs, but will also expand to other chemicals. UNEP is also discussing the possibility to organize an international conference on monitoring of chemicals in the environment, something that would be very welcome as there is not any good opportunities for people active in this field to communicate their findings at the international arena.

POPs as endocrine disrupters

I was not asked to discuss the endocrine disrupting effects of the POPs, but as this is the first lecture of a meeting focussed on these effects, I'll end my lecture with a short description of some observations regarding POPs from this point of view. The European Commission has recently published

“List of Priority Substances for further evaluation of their role in Endocrine Disruption”, and the POPs covered by the UNEP and the UN-ECE conventions can be found in this list.

Slide 20 ED effects of POPs (1)

The drins (aldrin, dieldrin and endrin) are all found to potentially be endocrine disrupters both in the environment and in humans. Heptachlor has not been found to disrupt endocrine systems in wildlife, but may do it in humans. Chlordane and Chlordecone are potential environmental endocrine disrupter, and shows hormone activity in humans. Mirex and Toxaphene are both potentially interacting with hormone systems in the environment, and were classified as endocrine disrupters in humans.

Slide 21 ED effects of POPs (2)

Both brominated and chlorinated biphenyls, as well as the polychlorinated dioxins and furans, were found to interact with human hormone systems, but were not classified for environmental effects. Hexachlorobenzene has been found to interact with human endocrine systems, but not with those in wildlife. DDT is causing a number of endocrine effects in both environmental species and in humans. Lindane, one of the HCH isomers, was classified as an endocrine disrupter in humans and potentially also in wildlife. The effects of PAHs were not classified for neither environmental nor human effects.

Thus many of the POP substances are also interfering with the endocrine systems. This is another reason to decrease the emissions of these substances as far as possible and hopefully the Stockholm Convention will be able to improve the situation globally. the situation globally.