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**Concentrations of Industrial Organic
Chemicals Measured in the Environment:
The Influence of Physico-Chemical
Properties, Tonnage and Use Pattern**

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CONCENTRATIONS OF INDUSTRIAL ORGANIC CHEMICALS MEASURED IN THE ENVIRONMENT :
THE INFLUENCE OF PHYSICO-CHEMICAL PROPERTIES, TONNAGE AND USE PATTERN

A. SUMMARY

Various regulatory schemes for the notification of chemicals require the notifier to supply information on possible adverse effects which a chemical may exert when it passes into the environment. To evaluate these effects an estimate of the concentration likely to occur in the environment is essential. In many cases this cannot be made except with the aid of models which oversimplify the complex problems involved. ECETOC therefore decided to see what useful generalisations on environmental concentrations could be made from an examination of actual measured values, and whether such generalisations could provide a more valid means of estimating environmental concentrations.

The approach adopted was to put chemicals into "environmental distribution categories" according to their route of entry and subsequent distribution in the environment, to seek chemicals, representative of each category, for which measured environmental concentrations were available and to look for relationships between categories, tonnage and concentration. The likelihood that the distribution and concentration of a chemical could then be estimated by analogy from its category was examined.

The environmental distribution categories chosen were the 7 possible distributions of a chemical in one or more compartments, i.e. air (A), water (W), solids (S) (sediment and biota), air-water (AW), air-solids (AS), water-solids (WS) and air-water-solids (AWS). A chemical was allocated to its category by assuming that it was present in its entry compartment and in the compartment(s) in which it is distributed at equilibrium. This distribution was calculated using the Mackay Level I model from the molecular weight, water-solubility, octanol-water partition coefficient (P_{ow}) and vapour pressure.

The search for reference chemicals to fill these categories was carried out by the Water Research Centre, UK, who initially scanned the literature on 150 industrial organic compounds for data on the above physico-chemical properties and on concentrations found in the environment. Adequate data were found on 68 chemicals, covering all of the 7 environmental distribution categories.

There was some relationship between the measured environmental concentrations and the environmental distribution categories of the chemicals. Thus, chemicals in categories A and AW occurred at higher concentrations in air than did those in other categories, and the maximum concentrations in sediments and biota were highest for chemicals in categories S and AWS. There were significant correlations between concentrations in air with Henry's Constant, $\log P_{ow}$, and tonnage. There were no correlations between those physical characters and concentrations in other media. With the possible exception of air these relationships were not strong enough to allow reliable quantitative predictions of concentration to be made from any one of the factors involved. In addition it has not yet been possible to determine the influence of degradation which is of major significance in predicting the environmental concentration of chemicals.

In general, the measured concentrations of a chemical in any one compartment covered a wide range (often several orders of magnitude); the rare exceptions were when only one or few values were recorded. With these 68 reference chemicals it was clear that away from points of discharge the concentration of non-ionic organic chemicals does not exceed :

- 15 $\mu\text{g}/\text{kg}$ (15 ppb) in air
- 30 $\mu\text{g}/\text{kg}$ (30 ppb) in water
- 10,000 $\mu\text{g}/\text{kg}$ (10 ppm) in sediment or biota

(with the exception of species which can biomagnify certain chemicals via the food chain).

The 68 reference chemicals covered a wide range of production tonnages, and assuming they are reasonably representative of industrial organic chemicals these figures can be taken, for the purposes of risk evaluation, as the maximum likely concentration of a chemical in the above compartments.

B. INTRODUCTION

Regulatory schemes for the notification of new chemicals, such as the European Communities' Council Directive amending for the sixth time Directive 67/548/EEC require provision of information on various aspects of the production, use, disposal, properties and possible adverse effects of a chemical on humans or the environment. To enable identification of environmental risks it is necessary to compare information on effects with the concentration of the chemical in relevant parts of the environment.

In the near field situation, close to the point of use, a useful estimate of the potential environmental concentration (PEC) may be obtained by using simple dispersion models. The far field situation, i.e. in all compartments of the environment well away from the initial point of use, is much more complicated and although there are a number of sophisticated models which attempt to predict PEC values, these suffer from a number of deficiencies. Firstly, as such models are extremely difficult to validate and, since many of the processes involved are not well understood, it is unlikely that the PEC values produced will always be reliable. Secondly, models of this type produce "average" values which cannot give any indication of the range of PEC's to be expected.

ECETOC therefore advanced the following hypothesis to assist in this far field situation, synthetic chemicals have been in use for greater than 100 years and there exists a large database relating to their concentrations in various environmental compartments. As a consequence these measured concentrations are likely to be more reliable than those derived from complex models. In theory the PEC of a "new" chemical might be estimated by analogy from the data on an already existing chemical with closely matching physico-chemical properties and similar use pattern, production tonnage and degradability. In practice it will often be difficult to find such a close analogue and thus a more general scheme was sought.

In such a scheme all existing chemicals would be divided into classes based on their physico-chemical properties, reference chemicals reflecting various use patterns, production tonnages and degradability would be selected and these would then be matched against the properties of a "new" chemical to provide PEC values by analogy.

To determine whether such a scheme was feasible ECETOC first sought to determine whether any relationships existed between measured environmental concentrations and the physico-chemical properties of the product concerned.

The terms of reference of the ECETOC Task Force examining this topic were :

- a) To define the main categories of distribution patterns of industrial chemicals in the environment.
- b) To define the properties of a chemical which determine into which category it falls.
- c) To select a small number of industrial chemicals that are representative of each category on which environmental measurements have been made.
- d) To collect data on actual environmental concentrations of the selected chemicals, produced from about 1975 onwards but including earlier data if they are adequate.
- e) To assess how useful such data are for making broad generalisations relating actual concentration to tonnage.
- f) To define what further work, if any, would be of value in relating actual environmental concentrations to quantities discharged or disposed and use patterns.

The Task Force set out to achieve these objectives by :

- a) Defining a number of environmental distribution categories based on physico-chemical properties and where these chemicals enter the environment.
- b) Selection of reference chemicals, for which measured concentrations are available and allocating them environmental distribution categories. The Mackay level I model was used to assist this allocation.
- c) Gathering together published information on environmental concentrations for the reference chemicals and reviewing the data to see if there were any broad correlations with environmental distribution category, production and discharge tonnages or individual physico-chemical properties. It was not possible at this stage to incorporate one of the most important variables, namely degradation, into the analysis, and further work on this topic is recommended.

Much of the collection of data on environmental concentrations and physico-chemical properties and the Mackay level I calculations were carried out by the United Kingdom Water Research Centre.

C. ENVIRONMENTAL DISTRIBUTION CATEGORIES

A chemical discharged to one or more environmental compartments, i.e. air, water, soil, sediment or biota, may subsequently be transferred to others. The number of compartments is small and it is possible to derive a limited number of "categories of environmental distribution" characterised by the point(s) of entry into the environment and the compartment(s) occupied subsequently. To simplify the categorisation, the gas and air particulate phases were combined as "Air", the various water phases were considered as "Water" and the three solid phases (soil, sediments and biota) as "Solids". As seen from the Venn diagram in Fig. 1, when 3 compartments (air, water and solids) are considered, there are 7 possible categories of environmental distribution for a chemical. It may be found in a single compartment only air (A), water (W) or solids (S), or it may occur in two compartments simultaneously (A - W, W - S, A - S) or it may occur in all three (A - W - S).

A chemical can be assigned to its environmental distribution category as follows. If it is initially discharged, for example, to air (A), it will remain substantially in the air if this is its equilibrium compartment. Otherwise, it will begin to be transferred to those compartments which represent its equilibrium distribution, i.e. to water (W), or solids (S), or one of the combinations A-W, W-S, A-S or A-W-S. It is doubtful whether any chemical ever reaches a true equilibrium in the environment, and the environmental distribution category therefore includes its entry-compartment and the compartment(s) in which it would occur at equilibrium. The possible distribution categories are therefore as shown in the final column below :

<u>Input Compartment</u>	<u>Equilibrium Compartment</u>	<u>Environmental Distribution Category</u>
A	A	A
	W	A-W
	S	A-S
	A-W	A-W
	W-S	A-W-S
	A-S	A-S
	A-W-S	A-W-S

This reasoning can be extended to chemicals discharged to the remaining input compartments (W, S, A-W, A-S and AWS) to give the complete categorisation scheme shown in Table 1.

It is important to recognise that this categorisation is concerned with distribution compartments and not concentrations. The concentration of a chemical in a compartment will depend upon the tonnage discharged to the environment, its transfer between compartments and its stability, i.e. rate of degradation by processes such as biodegradation, hydrolysis, oxidation, phototransformation, etc. Unstable chemicals may never survive to reach their equilibrium compartment(s) in any significant quantity but may be found, for varying periods, in non-equilibrium compartments.

A somewhat more comprehensive categorisation scheme which took greater account of inter-compartmental transfer was considered (see Appendix 1) but it proved to be of no more value than the above scheme.

D. SELECTION OF REFERENCE CHEMICALS

Allocation of chemicals to their environmental distribution category required two pieces of information, the input and equilibrium compartments. The input compartment was defined by the pattern of use (Table 2). The equilibrium compartment is independent of point of entry, tonnage and degradability, and can be calculated using molecular weight, vapour pressure, and octanol-water partition coefficients. The Mackay Level I model (1979) was used for this purpose. Although more sophisticated Mackay models exist for predicting environmental concentrations it was considered that the Level I model, based solely on physico-chemical properties, was adequate to predict the environmental distribution at equilibrium.

The following types of chemicals could not be handled within the scheme, namely :

- a) Ionised organic chemicals. The sorption of such chemicals by sediments and biota cannot be predicted from their partition coefficients.
- b) Ionised inorganic chemicals. These may occur in air as particulates, in water as a solution or suspension, in sediments (by sorption or ion-exchange), or in biota via bioaccumulation. Their concentration in suspended particulate matter in air or water is not governed by partition coefficients, which are not measurable. Similarly, the distribution of water-soluble inorganic chemicals between water and sediment or biota is not governed by passive partitioning between the aqueous phase and organic matter or fatty tissue, and is thus not predictable from the partition coefficient. The equilibrium distribution of such materials cannot therefore be estimated. Within this category lie the inorganic compounds of heavy-metals.
- c) Chemicals in the environment derived from sources other than industrial production and use (eg. synthesis via chemical reactions in situ or by living organisms).

It was considered desirable to include among the reference chemicals some which are environmentally widespread, such as agrochemicals and solvents, and some of

which only a small proportion reaches the environment, e.g. chemical intermediates in factory effluent.

No attempt was made to collect degradability data (bio-degradability, photodegradability, oxidation, hydrolysis, etc.). Thus only non-ionised organic compounds on which the following information was available were considered suitable as reference chemicals:

- molecular weight,
- vapour pressure,
- solubility in water,
- octanol-water partition coefficient (P_{ow}),
- measured environmental concentrations in appropriate compartments,
- the input compartment.

Knowledge of world-wide production tonnage was also considered desirable so that any relationship between this and environmental concentration could be explored.

E. COLLECTION OF DATA ON PHYSICO-CHEMICAL PROPERTIES
AND CONCENTRATIONS FOUND IN THE ENVIRONMENT FOR REFERENCE COMPOUNDS

During the past few decades increasing concern about the environment has led to the collection of a large amount of information on concentrations of substances occurring in the environment. Unfortunately the greater proportion of this is on a few compounds of particular scientific, medical and regulatory interest, e.g. some pesticides, chlorinated products, and heavy metals. There is a limited amount of data on a larger number of other chemicals but it is rare to find adequate data on the concentrations of these chemicals in all compartments of the environment in which it might occur.

1. Quality of Data

Many problems arise when attempting to draw valid general conclusions from environmental concentration data. The factors which effect the reliability and applicability of such measurements are discussed below; these were taken into account when the environmental concentration data were collected and evaluated (see section E.2, below).

1.1 Location of sampling. Environmental concentrations have been measured at various stages of the distribution of a chemical within the environment; data in general relate to three locations :

- i) Close to a point of discharge from a production, use or disposal site e.g. factory air, factory gaseous and aqueous effluent, sewage-sludge and sewage-treatment waters and domestic discharges.
- ii) After significant distribution has occurred following initial discharge (dilution in a river/sea; partial or complete transfer to another compartment; etc.) but before equilibrium has occurred, e.g. locations near to, or not-too-remote from, centres of population and industry : air over or near towns and over coastal or near-coastal regions ; rain water, groundwater, river/lake/coastal waters and drinking water ; top soil, river/sea sediments and biota.
- iii) Sites remote from any source of input, e.g. locations comprising

the non-coastal oceans, the Arctic, the Antarctic and certain desert regions.

A chemical will usually be at its highest concentration close to the point of discharge where its dilution and transfer to other compartments will only just have begun. Its concentration can often be estimated accurately from information on manufacture, use and disposal, or can be directly measured. It is at the point of discharge that the emission can be, and often is, controlled; once a chemical has begun to move away from the point of discharge, further action to reduce environmental concentrations is usually impracticable and much of the regulatory concern relates to possible concentrations and effects at type ii) and to some extent, type iii) locations.

1.2 Adequacy of measurements. The sensitivity, accuracy, precision and reliability of analytical methods for detecting and measuring small amounts of chemicals in the environment have increased very rapidly in recent years. When searching for data on environmental concentrations a suitable cut-off date should be imposed to eliminate much data of indeterminate value. Such a cut-off date means data will be more relevant to modern industrial practices.

Ideally, reports of environmental concentrations should include information on the adequacy of sampling and storage methods, the number of samples, any method used for concentrating the sample, the number of replicates and the recovery, reproducibility specificity, and limit of detection of the analytical method. Many analytical results are reported only as concentration ranges, sometimes covering orders of magnitude, with no indication of whether the highest and lowest values were outliers or part of a continuous spectrum.

1.3 Bias in Availability of Data. Selecting as reference chemicals those for which adequate data on environmental concentrations were available inevitably produced bias against :

- i) degradable chemicals, which are less likely to be found in the environment than poorly degradable chemicals;
- ii) chemicals sought but not found in the environment, since

- negative findings are infrequently reported;
- iii) chemicals present in the environment for which an adequately-sensitive analytical method is not available.

When a chemical is reported as "not detected" all that can be inferred is that the chemical might be present at a concentration below the detection limit. Such information was of no value in the present exercise, since the true concentration could be slightly below or orders-of-magnitude below the limit of detection.

1.4 Concentrations in biota. P_{ow} (octanol-water partition coefficient) has been used as an index of accumulation in biota. Only organisms that take up organic chemicals directly from water into fatty tissues have been considered, even though birds and mammals may accumulate chemicals via the food chain, i.e. not directly from water. Concentrations in biota can be reported as concentrations in the whole-body or in specific organs or tissues, and on a dry-weight or wet-weight basis. It is often not clear from reports on which basis the concentrations are calculated, and this sometimes makes such information difficult to use and interpret.

2. Collection of Data

The task of scanning the voluminous literature and collecting data on physico-chemical properties and measured environmental concentrations was carried out for ECETOC by the Water Research Centre (WRC) Medmenham, UK. The data are reproduced in Appendices 2 and 3.

2.1 * Criteria for collection and selection of environmental concentration data.

The WRC applied the following criteria and restrictions when collecting and selecting the data.

- a) Ionic and naturally-occurring chemicals were omitted.
- b) The validity of the concentration measurements was assessed from the the analytical and sampling methods used. In this WRC relied upon its own considerable experience. It was assumed that analytical measurements had been corrected for blanks.