CHEMISTRY AND THE ENVIRONMENT:
PROBLEMS AND ANSWERS

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INTRODUCTION

The industrial development of the world's nations over the last five decades resulted in an exponential increase in the manufacture and consumption of chemicals. For example, the production of methanol, benzene, ethylene, and propylene increased from several thousand tons/year in 1930 to between 10 and 40 million tons/year each in 1980. Parallel to this increase in the volumes of important feedstock and raw materials, a similar expansion of the total number of chemicals known and produced took place. In the chemical literature, there are now described over three million individual compounds and the list is growing rapidly. Moreover, numerous commercial mixtures contain from tens to thousands of individual compounds, many of which have not been isolated in pure form. A point in case is Toxaphene, an insecticide in world wide use. It is manufactured by chlorination of camphene and may contain several hundred components (Saleh and Casida, 1977) each of which has its own chemical, physical, and most important, biological characteristics (Khalifa et al., 1974).

Obviously, the intended or unintended release of large quantities of biocidal compounds into the environment is likely to be of consequence to the balance of species in the aquatic and terrestrial ecosystems. The negative effects of DDT and its metabolites on certain avian species (Carson, 1962) have brought about a public

awareness of some of such consequences. In other areas, the observed environmental effects include severe losses in species diversity, malformations, reductions of fertility, fecundity, hatchability and chick survival (Gilbertson, 1983), susceptibility to disease, growth reduction, severe reduction of populations, species elimination (Ryder, 1968) from certain habitats and even species extinction.

This is not to forget that the controlled application of fungicides, insecticides, herbicides and other specific biocides has brought extensive benefits to mankind. Today's total world population of approximately six billion people would likely not be able to exist without the large-scale use of such compounds in the production and protection of most of our foods. However, indiscriminate applications, high persistence, unknown environmental pathways and such chemicals' potential to bioaccumulate have resulted in severe repercussions, including the loss of food sources, mutagenic and carcinogenic effects to the ultimate consumer, man. This will be shown in more detail on the example of the Laurentian Great Lakes.

GREAT LAKES CONTAMINATION

The Laurentian Great Lakes are North America's largest freshwater resource and their drainage basin is populated by

approximately 35 million people in both Canada and the United States. Concurrent with the exploitation of the Niagara River for large-scale hydroelectric power generation in the 1940's, a number of electricity consuming industries settled in this area. Among those were calcium carbide, fertilizer and chlorine producing operations.

The availability of large quantities of inexpensive raw materials, such as chlorine, in turn fostered the development of new processes and products for their use. Beginning with the invention of the Diels-Alder Synthesis, in the 1940's, a new line of organic compounds came into existence. In particular , I am referring to the preparation of hexachloro-cyclo-pentadiene and its Diels-Alder products with itself and other dienophiles. The resulting compounds, many of which are well-known insecticides (Table 1), were produced in large quantities to satisfy the increasing demand for agricultural biocides. In addition, in the spirit of the times, new uses were sought for some of these compounds as shown for example for Mirex in Table 2 (Kaiser, 1978). Indeed some of these applications became more important, at least in forms of sales, as shown again on the example of Mirex in Table 3 (Kaiser, 1978).

Not unexpectedly, the large scale production of these and similar compounds, together with further developments, resulted in large amounts of waste- and by-products which were dumped in nearby

landfills. For example, in the greater Buffalo area, more than 250 such dumpsites have been identified, some of which contain tens of thousands of highly potent and very persistent compounds, (Figure 1) (Allan et al., 1983). The multitude of such sites, together with urban and industrial expansion, disruption of clay linings by construction, erosion, and frequently loss of knowledge of location and types of materials disposed of led and continues to lead to contamination of the aqueous systems downstream. As the Niagara River itself is rather short, only 38 km, and its flow immense, ca. 6000 m^3/s, the contaminants or their effects on biota rarely manifest themselves in that system. However, the contrary is true for the recipient of the Niagara River, Lake Ontario. There are two major concerns in the minds of residents on both sides of the border, namely:

Is it safe to drink water, taken from Lake Ontario?

Is it safe to eat fish from Lake Ontario?

Both questions have to be answered in light of the present knowledge on the concentrations, environmental pathways and effects of each contaminant. For example, present Food and Drug Directorate (CANADA) guidelines specify action levels for PCB's (2.0 mg/kg), Mirex (0.1 mg/kg), and for other compounds. In the United States, the same or other values are established as "Action guidelines" by the FDA and

various state authorities. In New York State, the possession of fish from Lake Ontario was temporarily banned because of their levels of Mirex. As easily recognized, the question as to whether or not it is safe to eat fish from a contaminated area depends not only on the concentration of the contaminant and its acute and long term effects, such as carcinogenicity , tumorigenicity, and teratogenicity, but also on the frequency and method of preparation of such meals taken, as well as the susceptibility of the individual consumer. It is evident, that standards or guidelines cannot be set for individual consumers and therefore, compromises have to be made to allow for the protection of the "average consumer". In Canada, for example, this means a frequency of one fish meal per week, prepared from filleted fish.

It is obvious that setting of guidelines for compounds with proven tumorigenic or carcinogenic effects are much more difficult. Apart from questions such as dose/response relationships, threshold values, cocarcinogens and latency periods, which are generally unresolved for such chemicals, any setting of guidelines as standards requires a risk assessment that involves not only chemical, physical, and biological considerations but also socio-economic evaluations in a cost-benefit analysis. It is outside the frame of this paper to address this analysis which usually requires a considerable effort by various disciplines working together. Rather, I intend to discuss the

directions of analytical and biological research which may be able to stave off any future contamination problems. Two major thrusts of ongoing research activities which are meant to provide some of the information needed. They are: (i) sensitive and inexpensive analytical measurements providing quick results on the levels and trends of known contaminants, and (ii) simple and effective tests to help predict potential environmental behaviour and biological effects of old and new contaminants. These two points will be addressed in more detail below.

ANALYTICAL REQUIREMENTS

In the last few years, the development of capillary columns for gas chromatography (GC) together with that of new small dead volume detectors has brought a great increase in analytical sensitivity. Computerized retention time and integration systems with background slope and peak overlap corrections have further improved the speed of identification and quantification of contaminant peaks in gas chromatograms. The resulting speed in chromatographic resolution and accuracy of analysis has greatly increased both the number of compounds which can be measured and the number of analyses which can be made per laboratory manhour. However, the increased chromatographic resolution has also brought the need for more measurements on

each sample and the identification of new compounds hitherto not detected. Other developments in that direction are new and highly sensitive gas chromatographic-mass spectrometers (GCMS) with computerized data acquisition and manipulation. Several suppliers now offer GCMS systems with multiple MS choices, such as positive and negative ion chemical ionization methods. Also here, the increase in sensitivity has resulted both in better and faster determination of previously known compounds and in a significant increase of newly identified compounds. For example, recent GCMS studies of sediment samples from Lake Ontario indicate the presence of highly chlorinated, authracene, phenanthrene, and pyrene derivatives, none of which appears to be commercially produced (Kaminsky et al., 1983). In fact, many of the possible isomers are not even described in the literature and their sources are not known. In other words, each step in the improvement of our analytical capabilities appears to be accompanied by a further opening of Pandora's Box resulting in more questions and concerns about such contaminants.

Many of the aquatic contaminants are found in sediments and biota, primarily fish, long before they are observed in the water itself. This is a result of environmental processes known as bioconcentration and bioaccumulation (Kaiser, 1979). For lipophilic contaminants, such as PCB's, the observed increases in concentrations from water to fish to avian predators, for example, the herring gull,

are in the order of 10^5 to 10^8 fold. Not surprising then, such compounds are observed in fish or gulls at part per billion ($1:10^9$) to hundred part per million ($1:10^4$) levels while the corresponding concentrations in the water ($1:10^{15}$ to $1:10^{12}$) are well below our routine analytical detection limits. This fact has been made use of by agencies for the determination of long-term contamination trends in the Great Lakes. For example, routine monitoring of salmonid and other fish species is undertaken by laboratories in both the United States and Canada. In addition, regular monitoring of comtaminant residues in herring gull eggs is underway by the Canadian Wildlife Service. Many of those long-term investigations have shown declining trends in PCB and DDT type contaminants in the last years. However, the benefit of measuring comparatively high concentrations of a contaminant in say coho salmon for this purpose is also accompanied by several drawbacks. For example, the mean age of a fish species in a lake may vary from year to year due to fishing pressure, natural changes in food, spawning and hatching, or simply to sampling variations. Even if corrections are made for age or weight of individual specimens, considerable contaminant variations can exist between specimens from one school or sample collection (Kaiser, 1982). Furthermore, the relative longevity of species such as coho salmon, rainbow trout, or lake whitefish, makes it difficult to discern contamination trends in a period of less than a few years. We developed a theoretical model, using intra- and interspecies

contaminant ratios and quotients from two fish species, one of which is the predacious sea lamprey (<u>Petromyzon</u> <u>marinus</u>), and which allows a much faster recognition of such contaminant trends (Kaiser, 1982).

Unfortunately, the recognition of a contaminant in a fish from a large lake, such as Lake Ontario, is only a very first step in the long process of identifying its source(s) and to eliminate such. Contaminant concentrations in the water are frequently too low to be directly measured. This has led us to develop a new approach for the determination of lake currents and movements of tributary water in nearshore zones (Comba and Kaiser, 1983a). Our highly sensitive GC method for the analysis of a set of volatile halocarbons in water (Comba and Kaiser, 1983b; Kaiser and Oliver, 1978) allows both the identification of water subjected to municipal or industrial outfalls and the tracking of water movements in a large lake. In short, the presence and relative concentrations of a total of approximately 20 volatile halocarbons provides clues as to the location and types of their sources. Examples for such have been shown earlier for Lake Erie (Fig. 2) (Kaiser and Valdmanis, 1979) and have recently been analyzed for the Niagara River - Lake Ontario area (Fig. 3) (Kaiser et al., 1983) and the Welland River tributary (Kaiser and Comba, 1983). As certain of these contaminants are indicative of industrial type effluents, their presence is also of concern with respect to those other contaminants which are frequently found in industrial

discharges, but which are not directly detectable by this method, such as, for example, PCB's.

CHARACTERISTICS

Under the Organization for Economic Cooperation and Development (OECD) guidelines, new compounds, when produced in quantities exceeding certain limits, require a number of physical, chemical, and biological data to be given to the respective authorities. Such characteristics include, for example, information as to melting and boiling points, water solubility, octanol/water partition coefficients, resistance to hydrolysis and other forms of chemical degradation, and last, but not least, acute toxicities to a few key species including rats and fish. Manufacturers or importers of chemicals are required to produce that information to allow decisions as to transport hazards, spill cleanup and for an indication of the likely environmental hazard which can be described as a function of each of its bioaccumlation potential, persistence, and toxicity (Fig. 4). For example, HCN or the cyanide ion are highly toxic, but degrade quickly and do not accumulate in the food chain (Fig. 5). As a result, their release to the environment would result in strong effects of short duration in a localized area. In contrast, Mirex is extremely persistent, bioaccumulates and has low acute toxicity.

However, because of the first two properties, it is of great environmental concern as they enable it to exercise its <u>chronic</u> toxic effects, as subtle as they may be, over entire generations of species at the upper levels of the food chain. It is obvious then that, from an ecological point of view, not only the (acute) toxicity but also the other environmental properties are of prime importance.

Unfortunately, our environment has already received many compounds for which information on such properties is lacking or entirely absent. I have already mentioned the chloro-phenanthrenes and -pyrenes. Other examples in that category include chlorinated styrenes, including octachlorostyrene, and fluoro-substituted compounds such as difluoro-diphenylmethanes (Kaminsky <u>et al</u>., 1983) and trifluoro-toluenes (Yurawecz, 1979) in the Great Lakes. Some of these compounds are not available in commerce nor are they described in the chemical literature. Their presence in biota or sediments may arise from the disposal of manufacturing by-products of other chemicals of from formation in processes inadequately known. The point to stress here is that for some of the known contaminants, no or only totally inadequate information exists on their physical and chemical properties. Furthermore, if there is inadequate physico-chemical information, there is as a general rule, even less known on the biological properties of such compounds.

Obviously, not every man-made chemical, when released to the environment, presents an acute problem. Even persistent compounds can be quite safe if they do not bioaccumulate (nor their biochemical transformation products) and have low toxicity. However, in the absence of sufficient information as to their safety, how can the hazardous compounds be screened out from those of less concern? I believe that the answer lies in the science of quantitative structure-activity correlations (QSAR). The last part of this paper addresses the need for and potential benefits of QSAR research in environmental toxicology.

QUANTITATIVE STRUCTURE-ACTIVITY CORRELATIONS (QSAR)

Although comparatively little known, and rarely part of university curricula, the application of QSAR for the <u>development</u> of new drugs and other pharmaceutical products has had a major impact in the last two decades. It has not only led to much lower costs for the development of new compounds, but has also significantly increased their potency and frequently their selectivity. In short, it is a mathematical approach to the solution of equations with several independent variables. For example by measuring the biological effects (activities) of a relatively few compounds, both the magnitudes and directions of substituent contributions to the effect of the

parent molecule can be determined. Frequently, these enhancing or negating effects can be described quantitatively in the form of a mathematical equation. This equation, in turn, may be used to predict the effects of many other derivatives of that parent compound.

The question is how can QSAR be applied to environmental contaminants, where compounds of different structure and various biological effects need to be investigated?

In general, there appear to be no limitations on the type of biological effects which can be correlated and predicted. Numerous examples exist for equations for acute and chronic toxicities for plants, aquatic and terrestrial species of all sorts. In particular, acute lethality to mammalian and fish species have been studied. Most challenging, and so far of limited success, are the numerous attempts to predict carcinogenic effects of compounds based on structure. Large data sets have been analyzed with substructure recognition methods (Craig and Enslein, 1980), but a satisfactory system of evaluation has not yet emerged. Apart from lethality studies, a wealth of information exists on very specific interactions between agent and receptor. For example, a variety of enzymes have been studied as to the exact position, stereochemical and binding requirements to develop highly specific agents of high potency.

Each of contaminant toxicity, bioaccumulation potential, and persistence can, in principle, be predicted from those of related compounds. So far, best progress appears to have been made in correlations of bioaccumlation potentials and bioconcentration factors with the lipophilicity of compounds, commonly expressed as the n-octanol/water partition coefficient, P_{Oct/H_2O} (Veith et al., 1979). The lipophilicity of compounds also is strongly related to their water solubility (Hutchinson et al., 1979) and fugacity (Mackay and Paterson, 1981), hence also to toxicity.

Comparatively less research has been done on the persistence of organic compounds in aquatic systems. Certain experimental systems, such as the Japanese "artificial river" and a few field experiments in North America, are restricted to lotic environments, with unknown applicability to lakes. As the three major processes of degradation, biochemical, photochemical, and hydrolytic (chemical) decomposition depend strongly on climatic conditions and on other lake dependent parameters, the prediction of persistence in lakes will continue to be difficult.

There are general and specific research needs in aquatic contaminant research which can be addressed by QSAR. Of general importance is the selection of good test systems and the intercorrelation of acute and chronic toxicity data. For example, hundreds of

investigations are availabe with small sets of compounds tested on various fish and invertebrate species. With few exceptions, however, test conditions vary too much to allow combination of results for QSAR investigations. In other words, a "normalization" of test conditions is desirable, including such variables as flow conditions, water quality, temperature, route of administration, control of exposure levels, etc. Even more important is the selection of effect and biota to be tested. For example Daphnia magna is a frequently used organism, but is not native to the Great Lakes. Rainbow trout (Salmo gairdneri) however, while an important and sensitive species in the Great Lakes, are more difficult and expensive to work with. The question then arises, as to whether or not toxicity to Daphnia magna and rainbow trout can be correlated. Furthermore, it is important to determine whether intraperitoneal LD_{50}'s, food exposure LD_{50}'s, 96-hour LC_{50}'s and chronic exposure "no effect" levels for just one species (such as rainbow trout) are correlated with each other and whether the correlations are consistent between different species. Given the biological test results, those questions can be answered by QSAR analysis; at present research in that direction is underway (Hodson et al., 1983).

Other specific research needs are to be found in the area of trace contaminants in test chemicals. All too often, large studies have been undertaken without due consideration of the chemical and

physical variables of the test compounds. For example, there are results showing that the toxicity to certain organisms of the three possible tetrachlorobenzene isomers differ by more than one order of magnitude. Standard purity of those chemicals is in the order of 95 to 98%, so that the remaining constituents (2 to 5%) could create erroneous results. A well known example of extreme proportions is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), which has been found at the part per million level in certain commercial chlorobiphenyl (PCB) mixtures. The acute toxicity of TCDD is approximately 10^6 times higher than that of some of the PCB isomers, showing that even impurities at such trace levels can be of major importance. Frequently, of course, neither the existence nor nature of impurities in commercial products are known.

Other specific research needs are the selection of test compounds with low colinearity of physico-chemical parameters, of compounds with equal modes of action, and the assurance of avoiding kinetically-controlled effects by developing proper dosage, exposure and statistical controls.

One of the most pressing needs and also very promising applications of QSAR is the development of correlations for the prediction of the toxicity of organic contaminants to important aquatic species. Initial results on the toxicity of a few closely

related phenols to Daphnia magna (Carlson et al., 1975) appear interesting and promising. Unfortunately, comparable data sets, particularly on sublethal effects of contaminants on important fish species, are not available from the literature. This will require a large number of compounds to be tested under identical conditions before QSAR work can begin to show results on new contaminants. At present, the development of a useful short-term test as an indicator for chronic toxicity is under investigation (Kaiser et al., 1982). Successful completion of such would allow the analysis of a wide variety of toxic compounds with a minimum of cost and time. Another, very promising tool appears to be the recently developed Microtox test (Bulich, 1979). We have used this test to determine toxicities of chlorophenols, chlorobenzenes, and para-substituted phenols. Correlations of these test results with acute and sublethal effects of these chemicals on various fish, shrimp, and bacteria as well as with structural parameters (Fig. 6) were all significant (Ribo and Kaiser, 1983).

There is no a priori limit on what type of compounds are amenable to QSAR analysis and prediction. Virtually all classes of compounds have been tested in one system or another, albeit with varying success. For example, recent work showed good results on the mutagenicity of organo-platinum compounds as measured by the Ames test (Hansch et al., 1980) and on metal salt toxicity (Fig. 7) to Daphnia magna (Kaiser, 1980). Organic compounds with no functional groups,

such as polynuclear hydrocarbons or those with several different functional groups, or heterocyclic compounds, and those with fused rings are more complicated to work with due to their ambiguity and/or multiplicity of bioactivity mechanisms. For practical reasons, compounds with extremely high or low toxicities should initially be avoided due to the obvious problems with handling and administering such chemicals. In addition, labile compounds subject to rapid hydrolysis, oxidation, or reduction should be omitted because of the likelihood of obtaining toxicity data on mixtures with their respective degradation compounds. Those restrictions on the type of compounds which can or should be investigated, however, do not pose any serious limitations on QSAR work in environmental toxicology.

CONCLUSION

I hope to have demonstrated the need for intensive research in the area of environmental toxicology. As seen on the example of the Laurentian Great Lakes, many contaminants found to be present in sediments and fish have unknown biological effects. There is ample evidence that similar situations exist in many European water systems. Scienctific efforts have to be directed towards an understanding of the pathways and effects of such compounds. In order to cope with the already large and rapidly increasing number of known

contaminants, the most promising scientific approach appears to be the field of Structure Activity Correlations combined with a yet to be defined fast and inexpensive biological test such as the Microtox test. Research in both directions is under way in the Environmental Contaminants Division of the National Water Research Institute of Canada.

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Table 1. Some chlorinated biocides with dates of U.S. patent registrations

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Aldrin (Shell 1953)

Chlordane (Velsicol 1952)

Dieldrin (Shell 1954)

Endosulfan (Hooker Electrochem. 1961)

Heptachlor (Velsicol 1959)

Kepone (Chlordecone), (Allied Chem. 1952)

Mirex (Declorane), (Hooker Electrochem. 1955)

Toxaphene (Hercules 1951)

Table 2. Proposed uses for Mirex from selected U.S. patent registrations (from Kaiser, 1978).

Insecticide

Insecticide-bait compostion

Marine fouling retardant

Smoke generating composition

Cross-linking composition

Flame-retardant composition

Fire-retardant additive

Rodenticide

Antioxidant

Ablative composition

Table 3. Mirex sales by Hooker Chemicals and Plactics Corp. between 1959 and 1975 (from Kaiser, 1978).

	Insecticidal	
	Uses	Other Uses
Year	(kg)	(kg)
1959	–	45
1960	–	800
1961	90	3 900
1962	5 400	35 500
1963	11 500	128 000
1964	12 000	208 000
1965	24 000	243 000
1966	31 000	149 000
1967	32 000	71 000
1968	28 000	125 000
1969	46 000	32 000
1970	27 000	20 000
1971	14 000	37 000
1972	60 000	54 000
1973	51 000	–
1974	36 000	1 200
1975	18 000	4 600

0 2 4 6 8 km

LAKE ONTARIO

NIAGARA-
ON-THE-LAKE

□ DUMP SITES CONTAINING
MORE THAN 20,000 TONS
OF WASTES

CANADA

U.S.A.

NIAGARA FALLS

THE FALLS

BUFFALO

LAKE ERIE
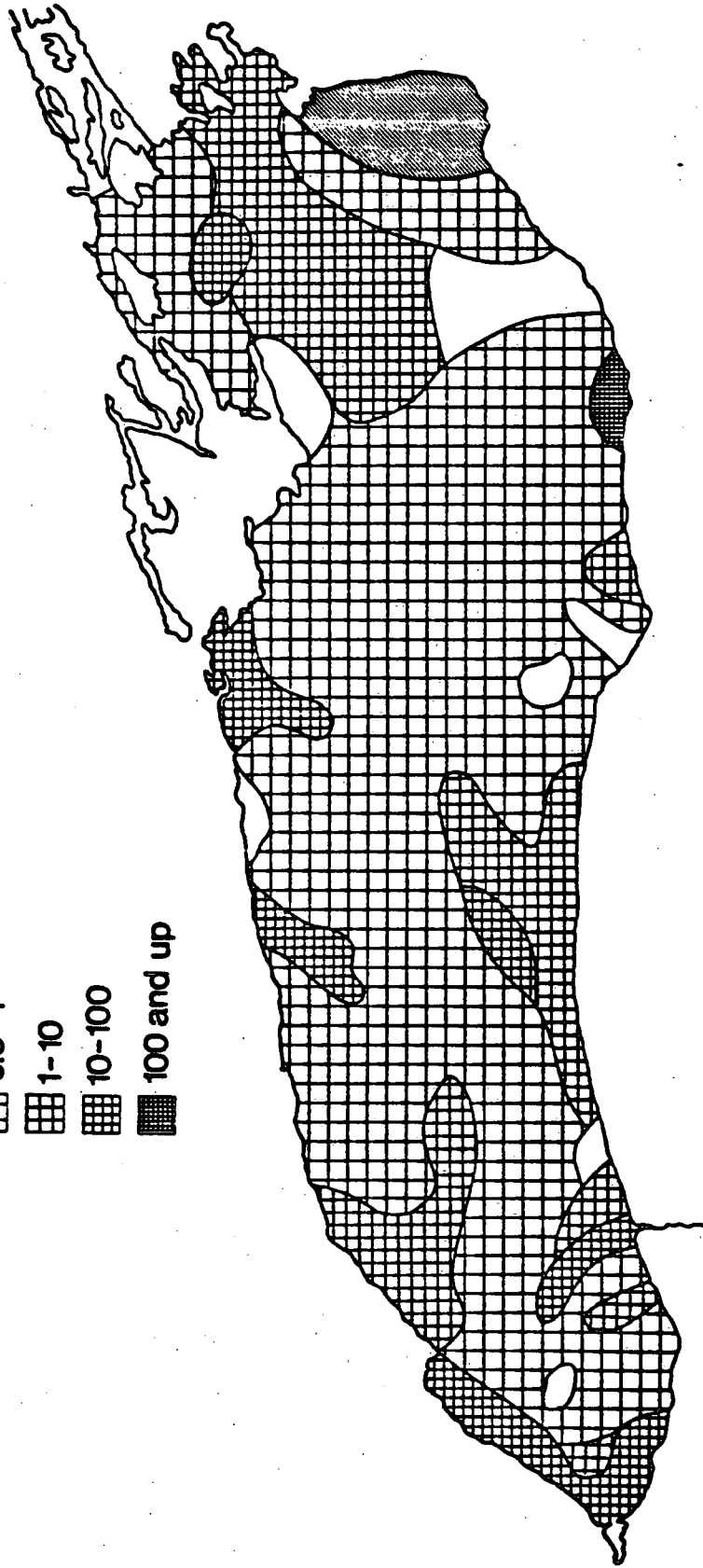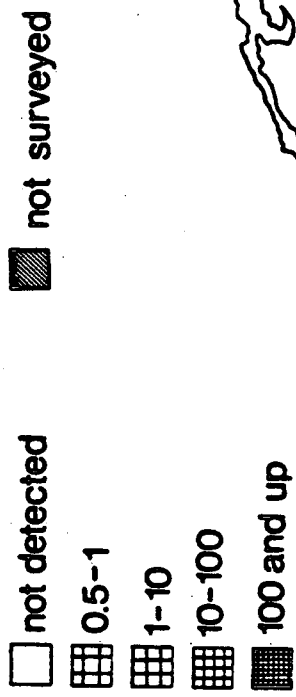
POTENTIALLY HAZARDOUS DUMP SITES AS IDENTIFIED
BY THE NEW YORK INTERAGENCY TASK FORCE ON
HAZARDOUS WASTES

C_2HCl_3-1978

CONCENTRATION $ng \cdot L^{-1}$
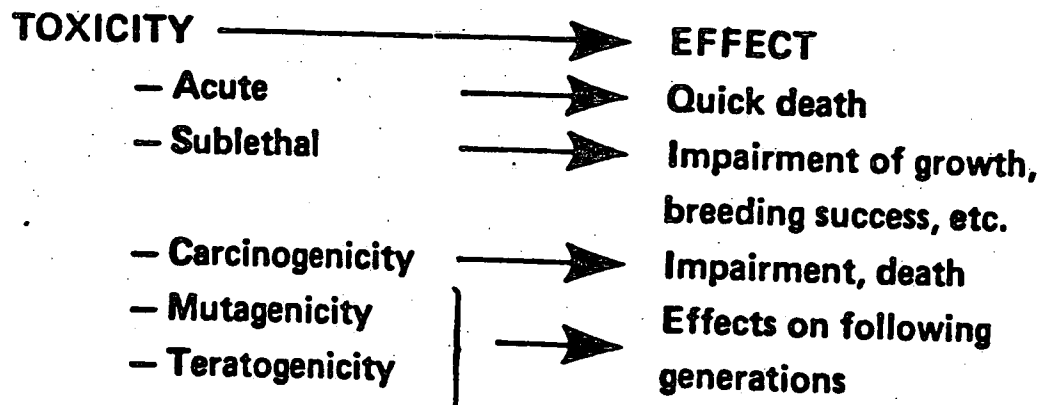
2-9
10-19
20-29
30-49
50-69
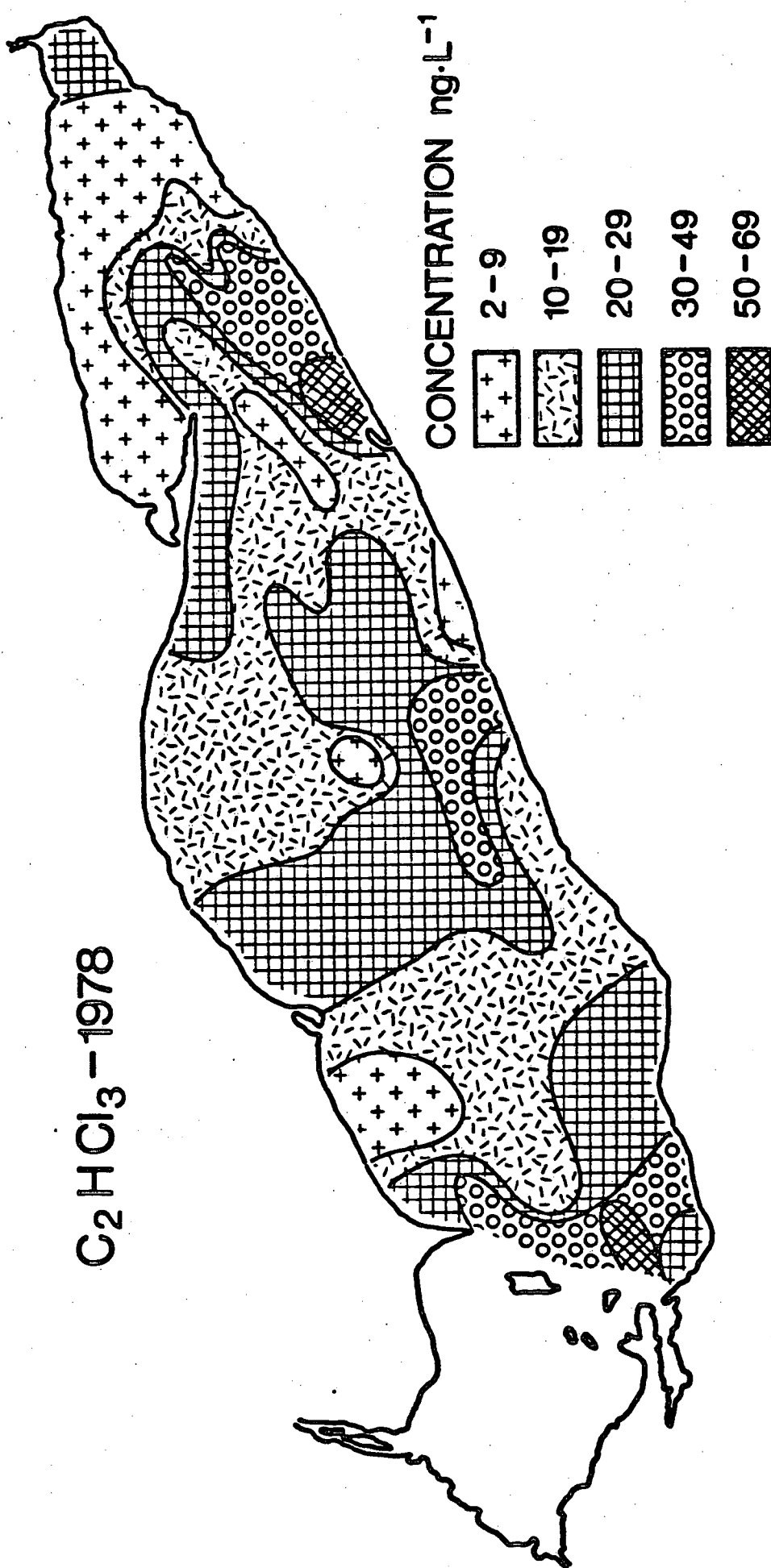
CHCl$_3$, Total

Concentration ng·L^{-1}

- ☐ not detected
- 0.5–1
- 1–10
- 10–100
- ■ 100 and up

■ not surveyed

DEFINITIONS

TOXIC SUBSTANCES have one or more of three properties:
- Toxicity
- Bioaccumulation
- Persistence

TOXICITY ⟶ EFFECT
- Acute ⟶ Quick death
- Sublethal ⟶ Impairment of growth, breeding success, etc.

- Carcinogenicity ⟶ Impairment, death
- Mutagenicity ⟶ Effects on following
- Teratogenicity } generations

BIOACCUMULATION
- Capacity to enter foodchain

PERSISTENCE
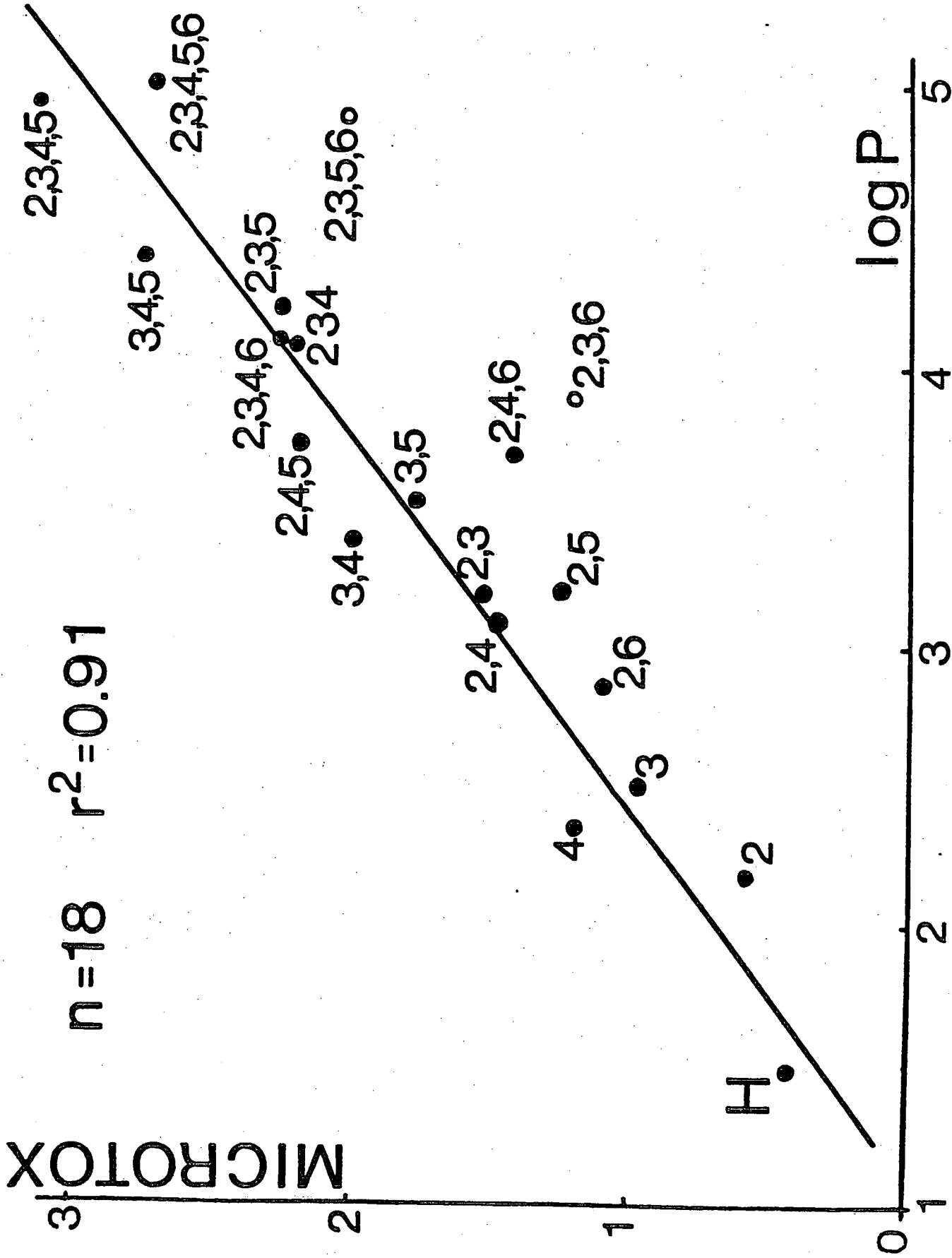- Resistance to degradation under environmental conditions

EXAMPLES

SUBSTANCE	TOXICITY	BIOACCUMULATION	PERSISTENCE
Cyanide-ion	X	—	—
Freon	—	—	X
Organo-phosphates	X	?	—
Organo-tins	X	?	?
Methyl-mercury-ion	X	X	?
PCB's	X	X	X
Mirex	X	X	X
Chloro-dioxins	X	X	X
Chloro-styrenes	?	?	?
Hexachlorobutadiene	X	X	X
Chloro-phenols	X	?	X

CHLOROPHENOLS

MICROTOX vs logP

n=18   r² =0.91
$r^2 = 0.91$

2,3,4,5

2,3,4,5,6

3,4,5

2,3,5,6

2,3,5

2,3,4,6

234

2,3,6

2,4,5

2,4,6

3,4

3,5

2,5

2,4

2,3

2,6

3

4

2

H

pT CALCULATED

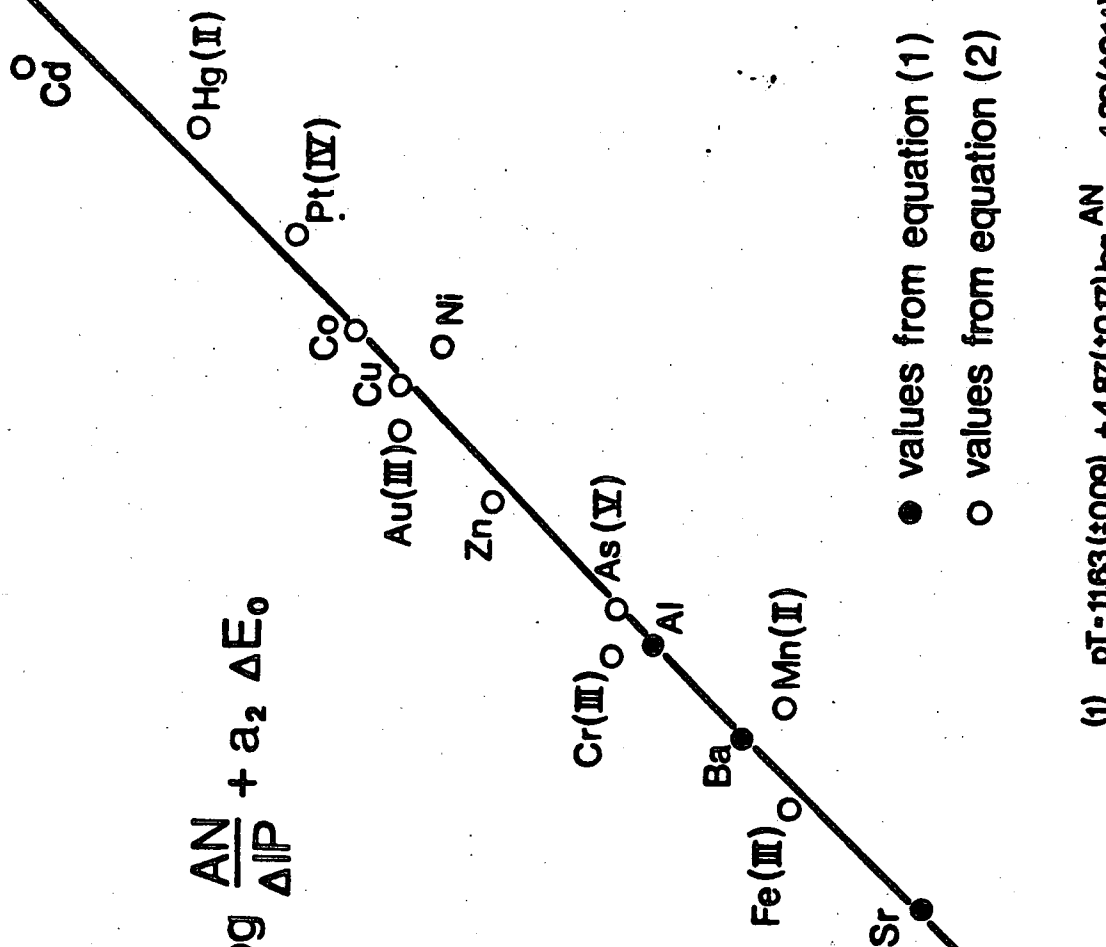pT MEASURED

$$pT = a_0 + a_1 \log \frac{AN}{\Delta IP} + a_2 \, \Delta E_0$$

- ● values from equation (1)
- ○ values from equation (2)

(1) $pT = 11.63(\pm 0.09) + 4.87(\pm 0.17)\log\frac{AN}{\Delta IP} - 4.29(\pm 0.14)\Delta E_0$

(2) $pT = 4.80(\pm 0.32) + 6.15(\pm 0.45)\log\frac{AN}{\Delta IP} - 3.11(\pm 0.32)\Delta E_0$

Cd
Hg(II)
Pt(IV)
Co
Cu
Ni
Au(III)
Zn
As(V)
Cr(III)
Al
Ba
Mn(II)
Fe(III)
Sr
K
Ca
Mg
Na

9799