# COMPLEXITY, ENTROPY AND ENVIRONMENTAL EFFECT

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## INTRODUCTION

The precise relationship between a given substance entering the hydrocycle and its effects upon external ecosystems is one which has over the last three decades attracted increasing attention. In the UK the Industrial Revolution between 1750 and 1830 had led to substantial decreases in the quality of surface waters due to the use by industry of water as a basic raw material and as a medium for the disposal of wastes. By 1863 Charles Kingsley in his work "The Water Babies" was able to write the following about Britain's industrial rivers:

> Dank and foul, dank and foul
> By the smoky town in its murky cowl
> Foul and dank, foul and dank,
> By wharf and sewer and slimy bank,
> Darker and darker the farther I go,
> Baser and baser the richer I grow.

The Mersey and the Yorkshire Don were by about 1850 no longer notable salmon rivers but had reached a deplorable state whilst it was written of the Yorkshire Calder that a page of a report was written by dipping a pen into its water (RPPC 1868).

The first piece of legislation passed to prevent water pollution in the UK was the Gas Works Clauses Act of 1847 which made it an offence to discharge wastes from these works into rivers and streams. 127 years and much legislation later the Control of Pollution Act (1974) was partially enacted in the UK and now constitutes the legislative backbone of water pollution control in this country. One of the more notable features of this Act was the general injunction upon Water Authorities to bring about an end to pollution "injurious to flora and fauna". Whether this will survive the rewriting of the legislation necessitated by the privatisation of the water industry remains to be seen.

Early attempts to restore Britain's polluted waterways centered on reducing the Biological Oxygen Demand (BOD) placed upon them (see eg Isaac 1957), and encouraged the treatment of industrial effluents at sewage treatment works. Reduction of BOD formed the basis for the much lauded Thames rehabilitation in both its phases (Wood 1982) and as a concept is now being applied to the much publicised Mersey Basin cleanup campaign.

The spectacular improvements in the biological quality of rivers managed in this way, for example the return of salmon to the Thames and the alleged return of four regularly caught species in the Mersey, have tended to draw attention away from the chemical aspects of water contamination. By doing so a serious problem has been obscured. Waggot (1981) drew attention to the large number of chemical compounds which could be isolated from a lowland river system while Richardson & Bowron (1985) felt it necessary to evaluate the fate of pharmaceutical residues in river water abstracted for potable supply and used to dispose of sewage effluent. Richardson (1986) at a previous conference held at the Robens Institute considered that the ecotoxicological relationships of the large variety and quantities of substances entering the hydrocycle constituted the greatest single challenge to workers in this field of study. Hence, merely bringing living creatures back into a polluted waterway should not be seen necessarily as a great achievement. After all, it is reasonably easy to ensure that there is sufficient oxygen (a primary ecological determinant) in a water to support aquatic life. What is not so easy is to ensure that such newly established communities constitute a viable component of a natural ecosystem or do not act as a toxicological vector given the presence in the system of a number of other possible materials of toxicological significance. For example, Lewis & Makarewicz (1988) showed that migrating salmon were responsible for importing the pesticide Mirex into an otherwise isolated ecosystem. This is where ecotoxicology traditionally comes to the fore as a rigorous experimental discipline in the evaluation of potential effects. A further, conceptual basis of evaluation is also available, however, which considers processes in terms of entropy changes that they involve. Consideration of both leads to the conclusion that adoption of a precautionary principle is the only certain way to ensure full environmental protection. This paper explores the question of whether discharges to the aquatic environment can ever be wholly justified.

## PROBLEM IDENTIFICATION

The identification of an ecotoxicological problem has often taken place long after the scope of the problem has become too wide to address in simple remedial terms. Such an example is furnished by the polychlorinated biphenyls (PCBs) which went into production in the late 1920s and were eventually discovered to be persistent and bioaccumulative as a result of their interfering with analyses for the earlier identified persistent organochlorine pesticides. From the wide literature on these compounds (Waid 1986; Safe 1984) is now obvious that strict control of egress of these compounds into the wider environment is vital. Tanabe (1988) gives an overview of the potential future problems while Cummins' (1988) extreme view is that if such control is not exerted then the extinction of marine mammal populations is inevitable due to the severe effects of PCBs on reproductive and other physiological processes. This concern is not restricted to xenobiotic compounds. Nriagu (1988) and Nriagu and Pacyna (1988) note that the environmental toxicity of trace metals mobilised annually far exceeds that of organic and radioactive wastes combined as assessed by the volume of water required to dilute them to the in itself arbitrary drinking water standard.

After a potential toxicological effect has been identified for a material then a wide evaluation generally follows. This effectively takes the form of a determination, tabulation and subsequent supplementation of the available literature related to the quantitative interactions and the dose/effect relations between environmental compartments. FIGURE 1 is a schematic representing a putative cycle for naturally and anthropogenically mobilised selenium in the environment. As with most such schematics, it will overall inevitably be biased in the direction of perceived research needs and available information. Different priorities, moreover will inevitably be attached to different identified toxicants and the data bases consequently evolved will suffer from varying degrees of incompleteness according to the way in which the priorities are set. Indeed this prioritisation in itself has tended to be a subjective process.

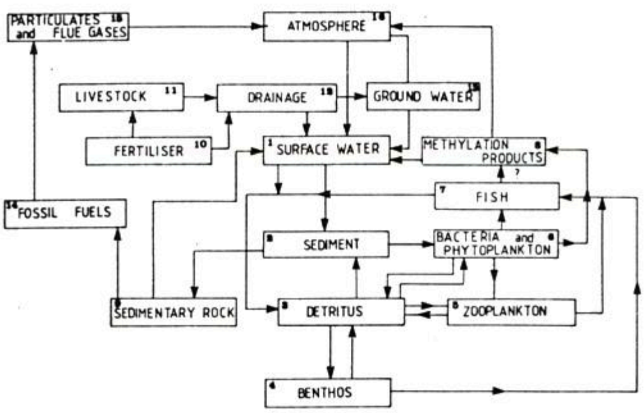



FIGURE I: A putative scheme for the cycling of selenium in water. Such schemes tend to reflect the information available for a particular substance and generally require continuous revision in the light of evolving knowledge.

The above superficially comforting ascription of environmental relationships then is inevitably based on limited information. It may include little quantitative information concerning levels or fluxes of a contaminant without which no assessment of dynamic equlibrium processes can be reliably made. Hence such schemata can never be regarded as absolute but liable to extensive revision in the light of evolving knowledge. For example, in the case of selenium recent dramatic development of the literature related to the compartments covering drainage, surface water, and ground water has taken place due to toxicological problems in the San Joaquin Valley, United States, associated with irrigation schemes (see eg Saiki & Lowe 1987; Saiki & May 1988).

Of course, initially, a toxicological problem needs to be identified as such before the process of data gathering can even begin. Selenium toxicosis was probably first recorded by Marco Polo in 1414 but the problem was not recognised in agriculture until the twentieth century (see: Rosenfeld and Beath 1964). The overall picture was complicated by the discovery that selenium was an essential trace element as a component of the enzyme glutathione peroxidase. Interest in anthropogenically mobilised selenium cycling through aquatic systems was first generated by Copeland (1971). A time lapse between anthropogenic mobilisation of contaminants into the wider environment, the perception of associated environmental effects and general admission of a necessity for alleviation was common to all pollutants currently identified and presumably this will also apply to the many contaminants whose polluting effects have still to be recognised.

## TOXICOLOGICAL EVALUATION

The delay between identifying a pollutant and taking action to deal with it arises principally as a result of current pollution control philosophy failing to embrace the precautionary principle which can be simply stated as: If in doubt don't pump it out. Even when a problem has been identified regulatory action often seems to be governed less by scientific principles than by economic and political ones. The major arguments often centre on the thesis that since society has benefitted considerably from, for example, the chemical industry, society must bear the costs of any cleanup or alternatively that cleanup will be carried out to the extent that society demands. In the first case the argument is economic but ignores the fact that industry is in business to generate profits for its shareholders and is effectively maximising these profits at the expense of the greater number of shareholders in the wider environment. In the second case the argument is effectively political, deploying notions of democracy while taking little part in the educative process upon which accurate democratic expression depends.

Scientific demonstration of direct causal effects is often difficult and of necessity retrospective. To the cynical observer science appears often to be used as part of a formidable armoury of delaying tactics against environmentally protective legislation which, it is claimed, is unnecessary or would be unnecessarily economically damaging.

Such dialogue is an inevitable consequence of a system which avoids action until environmental harm is proven, compounded with the sheer complexity of fully evaluating any single compartment represented in FIGURE 1. Taking, for example, the zooplankton component in freshwater and evaluating the effects of inorganic selenium, then *Daphnia magna* constitutes a suitable test organism. The first step is to devise an experimental system to test acute and then sub-acute concentrations of selenium to this species supplied as selenite and selenate, two ions of importance. Such a testing procedure is described by Johnston (1987) and leads to the determination of toxicity curves which in turn are used to derive such parameters as the 96H LC50 and the incipient lethal level where the latter is defined as the threshold of acute toxic effect. FIGURE II (a-f) shows the graphical output of such a study and it is apparent from FIGURE II (c & d) that a comparative difference exists between the toxicological behaviour of selenate and selenite as evident in the split probit line. This is of uncertain environmental significance although there is a tendency by selenate to be metabolised to selenite *in vivo*. Selenite is more toxic than selenate both in terms of lethal concentration values and rapidity of action. Further experimental work reveals that selenium as selenate at a sub-acute level results in significant alteration to physiological parameters of *D. magna* such as egg production and growth and maturation (FIGURE II e & f). These parameters are of primary importance in the population dynamics of daphnids and hence the structure of the community of which they comprise part. An explanation for any deleterious effects upon physiology is difficult. It may be in this case that changes described by Johnston (1989) in the gut diverticula as a result of selenium exposure are related since these organs are involved in the assimilation and digestion of food. These gross and ultrastructural changes are shown in Figure III(a-d). X-ray microanalysis of the mitochondrial granules in FIGUREIII

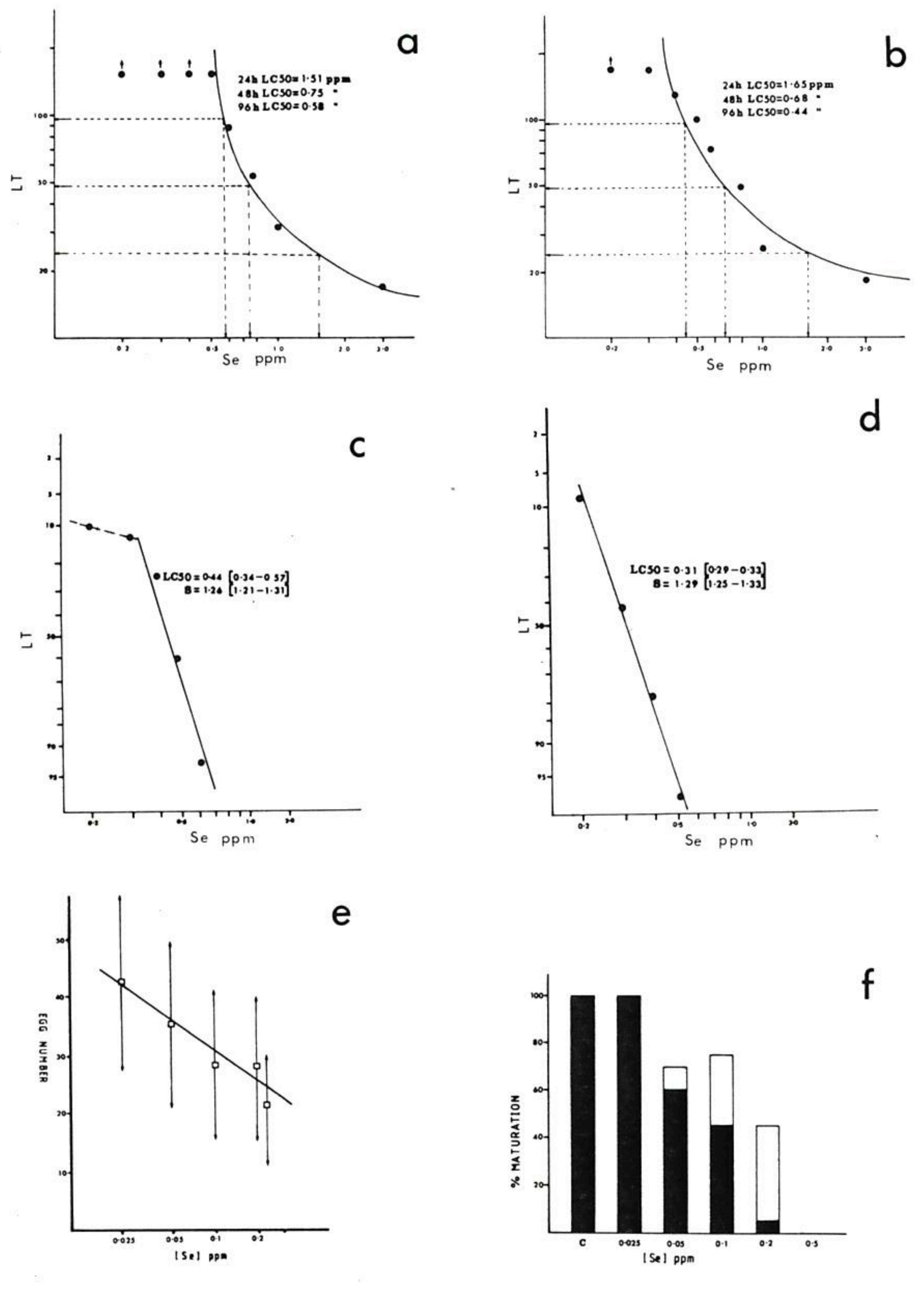
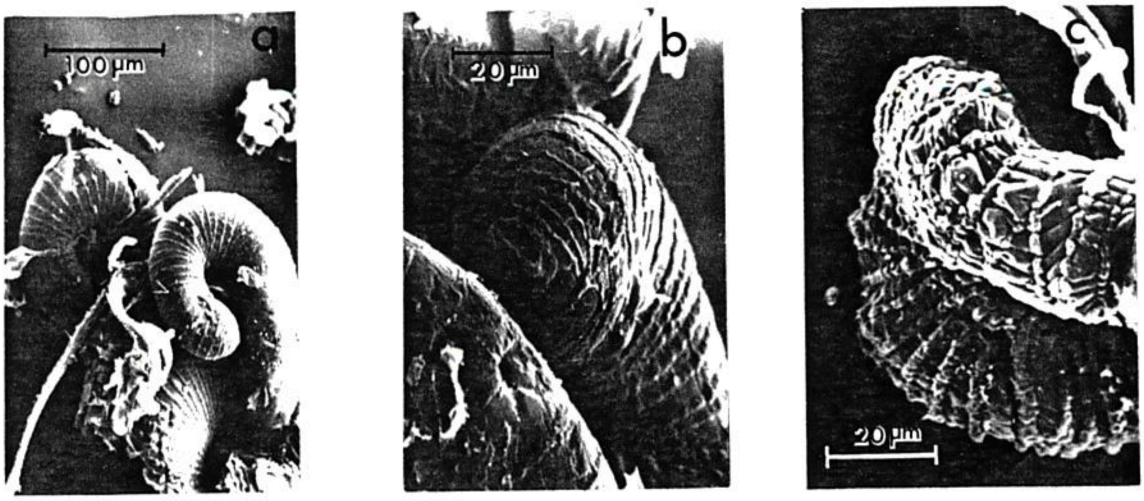



FIGURE II: The graphical output from a basic toxicity test for sodium selenite and sodium selenate to Daphnia magna. a & b show the toxicity curves constructed by plotting the median lethal times at each test concentration for selenate and selenite respectively. An estimation of the asymptotic portion of the curve is then used to derive the probit



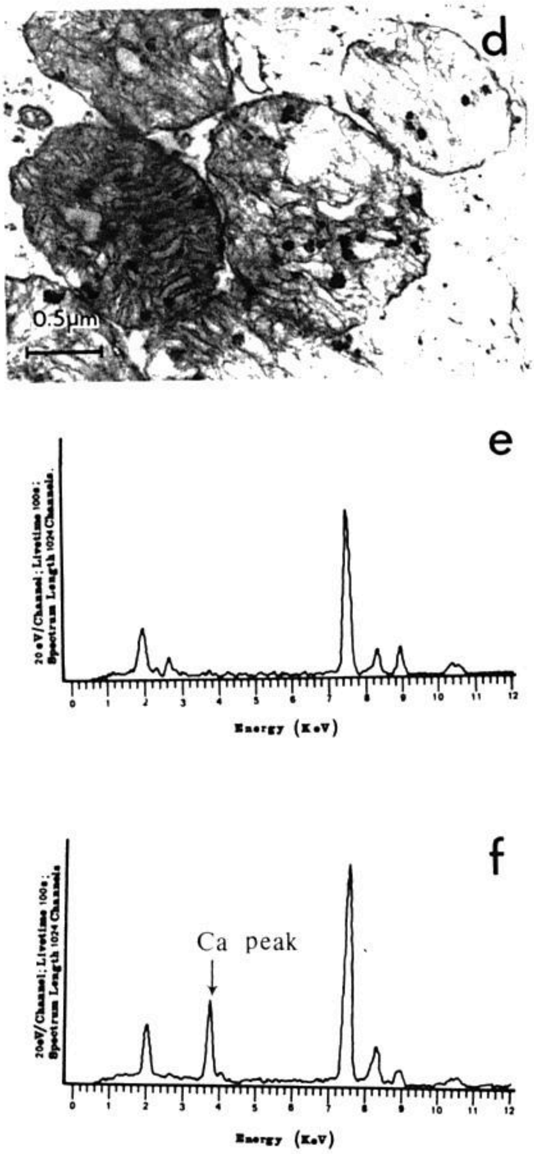




FIGURE III: Morphological effects in <u>Daphnia magna</u> exposed to a subacute level <u>of selenium as</u> sodium selenate. IIIa shows the appearance of the gut diverticula of a control animal while figure IIIb shows a single organ at the same magnification as IIIc. This latter scanning electron micrograph shows a diverticula from an animal exposed to 0.4ppm of selenium as selenate for 30 hours prior to processing. The organ has become markedly distorted due in part to tetanic contraction of the spiral muscles. IIIb shows mitochondria from an experimental animal exposed to 0.25 ppm of selenium for 30 hours. The dark deposits were analysed using energy dispersive X-ray microanalysis and proved to contain calcium as indicated by the peak in IIIf. Intramitochodrial bodies in untreated animals gave no calcium signal. The peaks appearing were attributable to the osmium fixative and nickel grids used to support the specimens.

Given the role of these organs in holocrine digestion, any interference with their function would be expected to result in decreased food assimilation efficiency and be reflected in growth and reproductive parameters. These in turn are primary determinants of daphnid population dynamics and species competetive success.

relationships in c & d. IIc for selenate shows a split probit line indicative of phasic toxic action. These graphs are then used to derive the incipient LC50 which in turn is used to derive a sub-acute range for testing. IIe shows the effect of sub-acute concentrations upon egg production and 1SD of the mean. IIf shows the effect of sub-acute concentration upon sexual maturation with the shaded portion of the bar denoting those animals maturing one instar later than normal for the test strain in instar 6.

cont)...... (f) shows the presence of calcium and is indicative of severe disturbance of the metabolism of this element.

Thus, a considerable amount of time-consuming work is necessary to partially evaluate the effects of two forms of a single toxicant upon one component of a single compartment of the aquatic ecosystem. Considerable further work is required to extend a toxicological study based upon a single species and a single toxicant to the natural environment with all of the many possible synergistic, antagonistic and additive phenomena. This is a basic and crucial failing of all studies of toxicological phenomenology. Whether they purport to elucidate effects upon single organisms or whole communities they can never be regarded as holistic. It is therefore unlikely that full environmental protection can be achieved by retrospective monitoring and management. It is incidental that the potential costs of such measures will preclude their ever being implemented. It seems clear that considering these factors and the environmental damage that results whilst research is progressing, application of the precautionary principle is the only realistic environmental protection option.

## CONCEPTUAL EVALUATION

Conceptual evaluation of the problem leads to much the same conclusion. Recently, several workers have attempted to examine the degradation of the biosphere in broad, universally applicable terms (see: eg Glasby 1988). These consider the biosphere as an open system to which the laws of thermodynamics can be applied. Their primary considerations are energy flows through the system under scrutiny and between its constituent compartments. Of fundamental importance to these arguments is the concept of entropy. Simply, the thesis is developed that human use of energy will inevitably be associated with environmental degradation and that this can be regarded as an increase in entropy.

Entropy can be qualitatively defined as a measure of disorder, or of thermodynamic probability. Spontaneous processes always result in an increase in entropy (or decrease in organisation), whereas an input of energy will always be required to bring about a decrease in entropy (or increase in organisation). Increases in the entropy of a system are equivalent to the lessening of organisation in that system. Whether an ecosystem is considered or, indeed, the entire biosphere, this lessening of organisation is directly related to degradation of that environment. It is not simply entropy increases which result in such degradation, however, entropy decreases too are associated with deleterious environmental effect in some cases global.

It must, of course, be recognised that the complexity of the biosphere makes the rigorous application of thermodynamic laws to the whole or to compartments a highly complicated process. Also, understanding of thermodynamic concepts, especially entropy, is not complete. These facts, however, do not diminish the extreme usefulness of these ideas in considering the state of the environment in broad and qualitative terms.

One particular attraction of these ideas is that they can be applied at any level; that is to say, they are equally relevant in discussing molecular reactions, biochemical changes occurring in a single organism, or the recently observed changes in the atmosphere. This is the concept of "scaling" and the system (or "control volume") under examination will behave in fundamentally the same way, no matter what its size or complexity may be. The applicability of the concept to a variety of systems may be demonstrated by example. One such is that of the single chemical reaction while another considers the related case of the single animal. Both are discussed below.

An organic chemical process is designed in order to maximise the yield of the product(s) and nearly always involves a decrease in entropy in relation to the starting material. Energy is usually required to facilitate this decrease in entropy (increase in organisation). No industrial process is, however, 100% efficient; energy input is never sufficient to cause the total conversion of starting materials to desired products. Further, the greater the increase in entropy in any given reaction, then the greater its chances of occurrence. This probabalistic function may be expressed in numerical terms in that spontaneous side-reactions may occur and frequently do, to give rise to a wide range of by-products with a random distribution of reactions having the same energetic relations.

The end products of such reactions may be very diverse. As an example, a gas chromatograph trace of a chemical effluent from the UK is reproduced as FIGURE IV. Mass spectrometric analysis of the dominant components revealed a wide range of chlorinated and brominated aromatic compounds at least ten of which are regarded as priority pollutants by the US Environmental Protection Agency. Many of the minor constituents proved impossible to reliably identify using the extensive NBS Spectral Library. If such an effluent proves impossible to evaluate in chemical terms then it will be equally impossible to evaluate in ecotoxicological terms beyond the level of the single organism using the crude parameter of lethality.

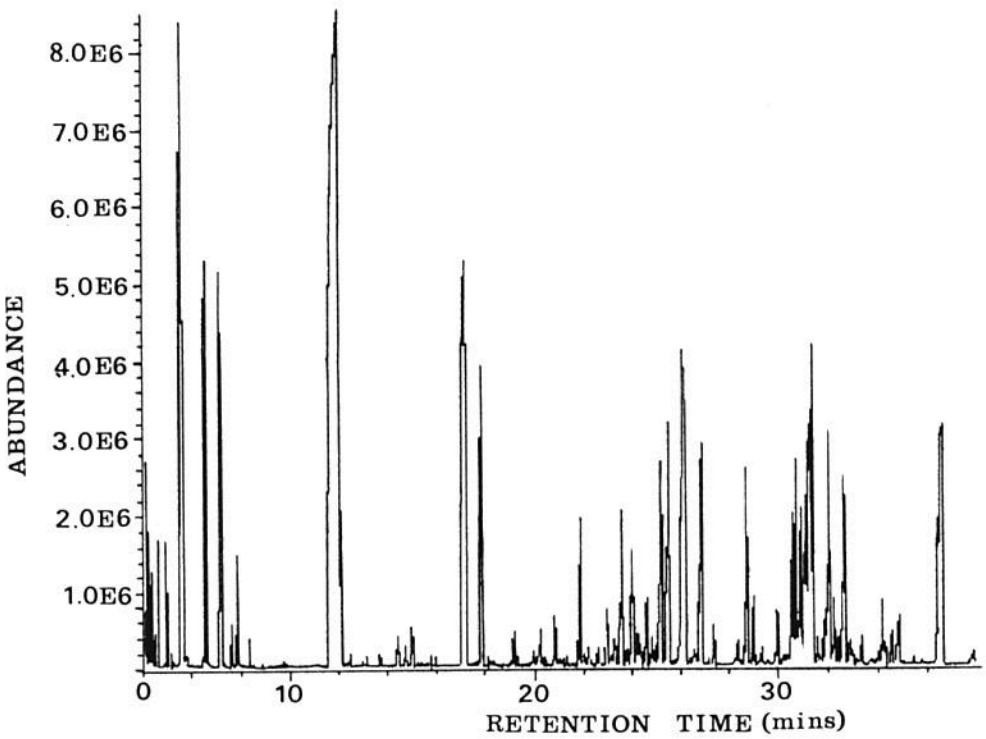



FIGURE IV: Gas chromatograph of a hexane extract of a UK chemical plant effluent. Subsequent analysis using mass spectromemtry showed this extract to contain at least ten compounds regarded by the US EPA as priority pollutants.

Not all effluents are chemically complex. In processes primarily concerned with minerals and metals, such a wide range of chemical recombinations not are possible although the same rules apply. The major perceptible entropic process however, to which all effluents are subject is that resulting from discharge to the wider environment.

Effluents have historically been released to water with the aim of preventing pollution problems by allowing the contaminants to disperse. This policy of dilution and dispersal of wastes is an attempt to use entropy to economic advantage. However, arguments for this philosophy have not considered energy flows in compartments of the wider system.

Anthropogenically mobilised contaminants tend not to become evenly distributed throughout the environment as assumed by dischargers. They instead selectively partition into environmental or biological compartments with which they have an affinity as a result of free energy considerations or undergo entropy decreases as a result of biological energy input.

Hence, the bioaccumulative potential of lipophilic materials is reasonably described by the octanol/water partition coefficient (Mailhot & Peters 1988). This is essentially a process governed by free energy resulting in a highly undesirable entropy decrease. This has been described for a wide variety of compounds, the best known being organochlorine pesticides and PCBs. Similarly, the sequestration of contaminants by sediments results in an entropy decrease which in ecosystem terms is undesirable. The seriousness of the sediment problem is now becoming recognised as reccommendations are made to establish sediment quality criteria based upon partition coefficients (Shea 1988).

Biological energy input can result in other undesirable effects. Many polynuclear aromatic compounds are now known to chemically combine with DNA to form DNA adducts (see Dunn et al 1987). In the case of some chemicals this may well result in a carcinogenic effect (see Bailey et al. 1988).

## CONCLUSION

Whilst specific effects may not be foreseeable, simple thermodynamics should lead to at least an appreciation of potential deleterious effects. It is clearly naive to hope that materials discharged to the environment will not interact in some way, either on a global basis or upon compartments of the global system. In ecotoxicological terms it equally naive to hope that the many potential interactions can ever be fully evaluated. Given that we are unable to asssign on a predictive basis the degree to which an ecosystem will be compromised by interaction with any given contaminant or to evaluate the degree of compromise once it has been established it seems obvious that discharge of any materials to the wider environment should consider the precautionary principle axiomatic to the formulation of environmental legislation.

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