THE POLICY IMPLICATIONS OF EFFLUENT COMPLEXITY.

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ABSTRACT

A survey of the chemical composition of industrial effluent discharged to UK coastal and estuarine waters has identified a wide range of contaminants which are neither controlled nor routinely monitored by the regulatory authorities. Monitoring of the waters round our coast show that many of these compounds persist in the environment and may be determined in samples taken some distance from their source.

The discharge of these chemicals is incompatible with environmental protection. The result of licensing the discharge of certain recognised pollutants disguises the discharge of others and the system of regulation is unable deal with this complexity. Improving the system of monitoring alone is likely to be to be of limited efficacy because of our ignorance and of the uncertainties inherent in the assessment of the impacts of these chemicals on the environment. The paper concludes by briefly discussing the role and implications of the Precautionary Principle on a future policy for the protection of the environment.

1. INTRODUCTION

The previous commitments of signatories to the Oslo and Paris Conventions were extended at the 1992 Ministerial Meeting when participating states agreed that (1):

> "as a matter of principle for the whole Convention area, discharges of substances which are toxic,. persistent and liable to bioaccumulate, in particular organohalogen substances, and which could reach the marine environment should, regardless of their anthropogenic source, be reduced, by the year 2000, to levels that are not harmful to man or nature with the aim of their elimination".

Regulatory focus upon an entire chemical group such as the organohalogens constitutes an important departure from the "substance by substance" approach where individual chemicals are targetted for action. In addition, the commitment to elimination as the aim is a novel proposal which will be welcomed by environmentalists but its implementation is ultimately dependent on industry, regulatory authorities and policy makers each making changes to the way in which they address their environmental responsibilities.

This investigation attempted to examine the range of pollutants in effluents and to determine whether current regulation of these discharges is adequate in practice or in principle. Although this paper concentrates upon UK examples, there is no doubt that similar situations will be encountered in other convention states where traditional philosophies of environmental regulation are operated.

2. METHODS

The analysis of effluent samples was undertaken on the basis of an examination of the National River Authority (NRA) monitoring data for the presence of list I and II substances as defined by PARCOM (2). Consents issued by the Regional NRA offices are the UK statutory instruments of regulation and control of industrial discharges. They usually specify a few individual chemicals required to be monitored under the terms of EC Directives or domestic legislation and effect general regulation through the restriction of parameters such as chemical oxygen demand (COD), total organic carbon (TOC) and suspended solids.

Samples of effluent were collected directly from discharge pipelines in 1 litre bottles. These were previously cleaned by acid washing and rinsing in analytical grade hexane. The samples were kept cool at 4°C during transport to the analysing laboratory. Samples were generally received within 48 hours of being taken. Analyses were conducted at Greenpeace Exeter (EX) Laboratories, University of Exeter.

Analysis for purgeable organic compounds was carried out on each sample using a Tekmar LSC 2000 with cryofocusing module. Sequential extraction into hexane was used to prepare samples for analysis of organic extractables and an internal standard of deuterated naphthalene was added to each sample. In both cases chromatography was performed using a dedicated Hewlett-Packard 5890 gas chromatograph with HP-5970 mass selective detector. Solvents were evaluated before use and blank and control tests routinely carried out. Compound identification was carried out by computer matching mass spectra of analytes against the US National Bureau of Standards Spectral Library. Matches at >90% probability and <90% but >50% probability were recorded. Some confirmatory analyses of extractables were conducted by Severn Trent (ST) Laboratories, UK, using broadly similar, National Measurement Accreditation Scheme (NAMAS) GC/MS semi-quantitative extraction and analysis methods.

The screening analyses carried out essentially rely on qualitative/semi-quantitative methods and relate to individual spot samples. Data taken from the NRA register represents a summary analysis of spot samples taken at (usually) monthly intervals during 1991. Hence, direct comparison of data reported here is only possible on a qualitative basis. Nonetheless, Johnston et al. (3) note that the constituents of an effluent are likely to vary considerably both qualitatively and quantitatively with time and that this is in itself an important constraint on the prediction of environmental impact (4). Concentration ranges are shown where available indicating typical concentrations found either by the NRA or other analyses rather than precise levels. This allows results from different sources to be compared as originally reported.

3. RESULTS AND DISCUSSION

3.1 The Number of Chemicals Identified

From the preliminary survey of the NRA consent and monitoring data it became obvious that a substantially greater number of compounds are discharged in effluents than are specifically consented for discharge. Samples were taken of 34 different effluents for exploratory GC/MS scans. In 26 samples, one or more organochlorine compound could be identified for which there was no specific consent. In total, 37 different organohalogen compounds were detected to 90% certainty in the samples analysed and with many being found in more than one effluent. The overall environmental concerns attached to the organohalogens have led to the PARCOM (1) phase out initiative. It is clear that very few of this group are being routinely monitored.

Table 1 shows the difference between the number of consented chemicals and the number determined by the NRA for four effluents. It also presents the numbers of chemicals clearly identified in GC/MS analytical scans showing that many escape routine monitoring. The total number of compounds isolated on analysis is somewhat greater than the numbers identified using the computer search facilities. For example, one analysis of effluent A isolated 109 integrated peaks. Of these 20 could be identified to 90% certainty, 35 to 50% certainty, leaving 54 unidentified. This is a common result of GC/MS screening when computer based matching techniques are used. Some chemicals may co-elute from the column, producing a spectral trace impossible to match. Alternatively, no accurate spectral data for the compound in question may be held on the library. The shortcomings of probability based matching procedures in GC-MS analysis are discussed by Millington and Norwood (5).

The concentrations of chemicals found by NRA analyses and reported in the data held on the Public Register are often low. Detection limits of low or sub-microgramme per litre levels apply. Nonetheless, some, including organochlorines, are present at high milligram per litre levels. The presence of high concentrations of contaminants is broadly confirmed by the semi-quantitative analytical results reported here. It is unlikely that these chemicals are contained in the raw process water imported onto the sites. In most cases there is an obvious link between the processes located on a given site and the nature of the unconsented chemicals being discharged where these can be identified.

Table 1 A comparison of the number of consented organic compounds with the number determined by NRA, ST and EX analyses in four different effluents. The final column shows the total number of compounds isolated by the EX laboratory including those isolated but not identified.

EFFLUENT	CONSENTED	NRA	ST	EX	TOT
A	2	14	30	55	109
B	2	11	7	9	12
C	2	7	26	27	44
D	3	4	30	18	120

3.2 The Type of Chemicals Identified

The organic chemicals found in one effluent compiled from analyses by the three different laboratories are shown in Table 2 with an estimate of the concentration range wherever possible. This discharge to the Tees Estuary is around 100,000 cubic metres daily. The consent for the effluent refers specifically to only two organic compounds, phenol and chloroform. However, pentachlorophenol, 1,2-dichloroethane, trichloroethane and carbon tetrachloride, all substances listed as priority hazardous substances by the 3rd North Sea Conference, have been found in NRA analyses (2). In addition the listed substance, trichlorobenzene which is controlled under EC Directive Number 90/415, was found in two GC/MS scans as were two of the dichlorobenzenes and mixed haloforms. The NRA and prospective analyses carried out by GC/MS screen also isolated benzene, toluene and xylene. These were present milligramme per litre quantities but are known to be toxic at much lower levels and are included in the European Commission Priority Candidate list (2).

Table 2 The compounds found in one effluent entering the Tees which have been collated from results of the NRA, ST and EX (to 90% certainty) laboratories. Concentration ranges, where available, are indicated in brackets by; A - >1mg/l; B - 0.1-1mg/l; C - 10-100ug/l; D -<10ug/l; .

CHLOROFORM (A)	NITROBENZENE (B)
PHENOL (A/B)	1,3,5-TRICHLOROBENZENE (C)
PCP (D)	BENZOIC ACID (A)
1,2-DICHLOROETHANE (C)	NAPHTHALENE (C)
DICHLOROMETHANE (B/D)	3-CHLOROPHENOL (C)
CHLOROBENZENE (B/C)	2,6-DICHLOROANILINE
CCL4 (D)	4-METHYLBENZOIC ACID (B)
CUMENE (D)	2,4-DICHLOROANILINE
BENZENE (A/B)	ACENAPHTHENE (C)
ETHYL BENZENE (B/C)	1,1'-OXYBISBENZENE (C)
TOLUENE (A/B)	2,4,6-TRICHLOROANILINE
XYLENE (A/B)	2-CHLORO-5-NITROBENZAMINE
TRICHLOROETHANE (B/C)	TCPP
TETRAHYDROFURAN (A)	BICYCLOOCTATREINE
METHYLMETHACRYLATE (B)	1-ETHYL-2-METHYL BENZENE
1,2,3-TRICHLOROBENZENE (D)	1,2,3-TRIMETHYL BENZENE
BROMODICHLOROMETHANE	2-PROPENYL BENZENE
DICHLOROACETONTRILE	1-PROPYNYL BENZENE
DIBROMOCHLOROMETHANE	1,4-DICHLORO BENZENE
TRIBROMOMETHANE	[1,1'-BICYCLOPENTYL]-2-ONE
2-METHYLCYCLOPENTANOL (B)	1-ETHYLIDENE- 1H-INDENE
DIETHYLDISULPHIDE	1,1'-BIPHENYL
HEXANOIC ACID (B)	2,3,4-TRICHLOROANILINE
1-ETHYL3-METHYLBENZENE (C)	HEXADECANOL
1,2-DICHLOROBENZENE (B)	2-METHYLBENZALDEHYDE

3.3 The Regulation of Chemicals Discharged

Increasingly, chemicals are regulated according to their performance with regard to three parameters considered to predict their likely behaviour in the environment - persistence, toxicity and tendency to bioaccumulate. Production volume and/or liklihood of environmental release is additionally used to evaluate relative risk. Such procedures have been used to derive the EC List I and II and the UK's Red List (2,6). The complexity of industrial effluents such as those considered here, however, undermines the use of lists derived in this way. Firstly, prioritisation processes driven in part by production volume data as opposed to full environmental audit data will tend to omit chemicals formed as by-products of an industrial process. This problem may be illustrated with reference to chloroform present in the effluent featured in Table 2. This was only recently added to the consent after being found in the effluent. The site processes utilised no chloroform, and it was therefore not expected to be present in the effluent. It was subsequently found to be synthesised in the site drains as a result of chemical reactions between effluent streams. It follows that many other chemicals may escape regulation or control since they are not products, but by-products, with no function in the industrial process.

Secondly, the validity of the available information on the properties of the substances, used for selection is extremely questionable due to the factors termed by Wynne (7) as uncertainty and ignorance. The uncertainty of the assessments made about which chemicals will be regulated can be seen in the scheme used to select Red List substances (8). In this toxicity, persistence, bioaccumulation and input are the primary criteria used which are classified as high, medium or low. The tests used to assess toxicity and the other characteristics rarely bear much resemblance to the actual situation in the wider environment and are coming under increasing scrutiny (9,10). Uncertainties are also encountered in the setting of the ranges for classification whereby the boundaries used by different scientists for a high or low acute toxicity can vary by a factor of 100 (8).

An example of the ignorance which is still inherent after these usual forms of testing is the lack of knowledge of the impact of these chemicals in a complex mixture. Single chemical laboratory tests fail to give information on whether or not a chemical will act in combination with another (or several hundred others) in an additive, synergistic or antagonistic mode (11).

Thirdly many studies highlight the fact that the data available on the persistence, toxicity and tendency to bioaccumulate of the majority of the chemicals identified is extremely limited (4). Large numbers of organic chemicals likely to be of industrial origin have been isolated in water from the mouth of the Tees and other estuaries (12,13). In one study it was found that for 75% of the chemicals tentatively identified by GC/MS no ecotoxicological data could be found while sufficient data could only be found for one chemical (12). In a second study toxicity data was available for 35% and quantitative structure activity relationships were available for a further 33% leaving 32% with no available data (13) although all had fulfilled one of the three criteria by persisting to the mouth of the estuary.

In combination, these chemicals were also found to exert toxic effects on marine biota. Significantly, Matthiessen et al. (13) conducted an assessment of the literature for chemicals identified by analysis. They found none of the chemicals present in the Tees at concentrations expected to be individually harmful. In fact, samples from the Tees were found to be acutely toxic in an oyster embryo bioassay. Therefore, while the chemicals were said to be present in apparently 'negligible' concentrations, the combined impact was a toxic effect assumed to be the result of combined action of some or all of these chemicals. This assumes that the observed effects are not attributable to a chemical analytically intractable by the procedure used.

Extending the scope and intensity of monitoring and testing is unlikely to provide a solution to the problem of effluent control. In the absence of supporting data, simply knowing the name of the chemical is of little value. In a resource limited environment, moreover, testing of chemicals for harmful properties is likely to prove a slow process. Even listed chemicals have deficiencies in the supporting data which impede hazard assessment. Byrne (8) considers that this is true of about half of the substances in EC List I & II.

3.4 The Precautionary Principle

The conventional response to identified toxic effects such as those observed by Matthiessen et al. (13) is to attempt to establish causality by isolation of the chemicals causing the effect. This is effectively a reworking of the assimilative capacity approach to environmental regulation. This approach has as a basic tenet that the environment is a resource which can 'be quantified and utilised' and further that its use should not lead to 'unacceptable consequences' (14). Inherent in this philosophy is the notion that unacceptable effects can be quantified prior to the release of the polluting substance(s) in order to avoid those consequences.

Stebbing (14) attempts to address problems associated with the proof of causality and quantification of effect. He acknowledges that in the case of multiple pollutants with multifactorial impacts in the environment it is not possible to predict the impact in advance of environmental evidence and that even once that evidence is available it is difficult to attribute it to a particular cause. His answer to this is to develop 'operational criteria for establishing causality' which provide a basis for decisions about taking action prior to actual damage occurring. His criteria involve extensive monitoring of contaminants in the environment and tissues, assessing toxicity thresholds, increased use of biomarkers and introduction of matrices which make identification of causal agent possible.

Not only does this solution fail to address the inherent risk but it also brings us back to the first question. If the identity of the chemicals in the environment are not known then how can the informational criteria needed to establish causality be satisfied? Assimilative capacity as a concept is therefore flawed because it is excessively reliant upon unavailable information, undeveloped or poorly developed techniques and a restricted ability to satisfactorily characterise industrial discharges to be assimilated. Indeed, continuing to seek simple cause and effect relationships excludes from consideration the multiplicity of interactions which may take place in the environment which will never be replicated in toxicity tests.

Recognition of the limitations of an assimilative capacity approach have led to increasing acceptance of the Precautionary Principle of Environmental Protection in scientific and political fora. The definition of the principle of precautionary action is that action should be taken to prevent damage to the environment even in cases where there is no absolute proof of a causal link between emissions or activity and detrimental environmental effect. Embedded in this is the notion that there should be a reversal of the burden of proof whereby the onus is on the operator to prove that his action will not cause harm rather than on the environment to prove that harm is or will occur.

In order to apply the precautionary approach it is essential that the limitations of science are made obvious to and understood by all involved. In view of the inherent complexity of effluents from the chemical and other industries and the failure of the assimilative approach to predict the impact of even single chemical releases it is not possible to foresee their impact on the environment. Hence a precautionary approach can be used to inform decisions with scientific analysis of the problems but demands elimination of these pollutants as the end result (15). This is succinctly stated by Sprague (16) and is worth quoting in full:

> "The objective of regulations for controlling industrial water pollution is to protect natural communities of organisms. If done, that will include protection of humans as part of the general ecosystem. The ideal and ultimate goal must be no discharge of effluent, since plants and animals in the natural communities are adapted through millenia to conditions without human industrial input. On the other hand humans are now part of the system and cannot live without producing some sort of waste. Hence, any regulation of industrial discharges will always be a compromise between the ideal and whatever is possible at the moment. Regulations should be considered as temporary resting places on the road to a goal of zero discharge."

4. CONCLUSIONS

In the light of the recent Paris Commission agreement to aim for the elimination of discharges of organohalogen pollutants a new approach to pollution control is going to be required. Current control mechanisms which permit the discharge of certain pollutants, by default, also accept the discharge of a wide range of other, often similar, pollutants. The complexity of these effluents is such that it is too great for an assessment of their impacts to be sensibly undertaken. Assessments which are undertaken for even the 'known' pollutants involve uncertainties and ignorance which are fundamental flaws which simply increasing effort will not overcome. It is important that environmental scientists accept these inherent difficulties which fatally flaw regulatory frameworks based on the assimilative capacity.

The implementation of the precautionary principle will require that the goal of future pollution regulation is the elimination of these pollutants which are likely to be toxic, persistent and liable to bioaccumulate because it is not possible to furnish absolute proof of detrimental impacts or otherwise.

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