

BACK TO BASICS: THE CASE FOR AN INTENSIFICATION
IN THE MONITORING OF POINT SOURCE DISCHARGES

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EXECUTIVE SUMMARY: TERMS OF REFERENCE

Monitoring of pollutant levels and effects in the North Sea has been carried out by the North Sea Task Force (NSTF). Trend monitoring for a number of contaminants has been established to validate percentage reductions required by the North Sea Ministerial declaration. Other projects conducted as part of the ICES/IOC Bremerhaven Workshop have focussed on spatial distribution of contaminants and biological indicators of toxicity across transects of the North Sea. The Joint Monitoring Group have been charged with the task of defining a suitable monitoring programme for the PARCOM area to provide a quality status report by the year 2000 and to support present and future legislation.

To date, analytical imprecision and the short study times are limiting the precision with which trends can be determined. Specifically, the magnitude of detectable trends in metals concentrations varies from 10% to 400% per annum. Analytical constraints for organic chemicals not only severely limit the suite of chemicals but in some cases entirely preclude trend identification. Nevertheless, as baseline data accumulates, statistical precision will improve. In the meantime, it will remain impossible to assess the success of measures dictated by the North Sea Ministerial Declaration to incrementally reduce inputs of selected chemicals by these methods alone.

Research based monitoring has highlighted the deficiencies in our understanding of the ecotoxicology of contaminants at ambient concentrations. There is a paucity of data on the effects of the vast majority of chemicals discharged into the Convention area. Further complications arise from the fact that ecosystems are subjected to complex and changing mixtures of pollutants.

Near-field monitoring allows more detailed insight into these identified problem areas. Precautionary action, a driving force underpinning the legislative philosophy of the Paris Convention, can then more rapidly be applied to prevent adverse effects being extended to the wider sea area. Smaller geographical study areas allow more intensive sampling without excessive costs. Pollutant concentrations will be elevated in the vicinity of inputs and thus extended analytical suites can be easily applied and source reconciliation data enhanced. Biological effects will be more easily detectable. Absolute input decreases can be assessed with greater speed and precision, as can resulting alterations in biological indices. This presentation discusses results from source monitoring of one industrial sector distributed across the Convention region as an example of the potential research and control advantages of monitoring selected problem industrial sectors.

1. INTRODUCTION

1.1 The purpose of a contaminant monitoring programme is to provide data on the natural and anthropogenic chemical fluxes of the study area, the physicochemical impacts that the area is subjected to and relate these to the biological status of the study area and the legislative framework in place to protect it. This is a formidable task and one to which a great deal of effort and expertise has been applied. Nevertheless, substantial obstacles to the fulfilment of the aims of monitoring programmes in general remain. These include not only resource and technological limitations but fundamental lack of understanding of many relevant chemical and biological processes in systems that emit pollutants as well as those that receive them. The strength of a monitoring programme therefore depends on the extent to which these limitations are appreciated and taken into account at the planning stage. Inevitably, the integrity of such schemes depends upon the measures that are taken to minimise the impact of confounding factors and variables.

1.2 The most commonly encountered problem relates to the analytical burden entailed in developing an holistic picture of contaminant fluxes and their levels in diverse environmental media. This is most widely appreciated through the resource limitations placed upon government monitoring schemes. Four primary constraints may be identified: the number of samples which can be collected and analysed from both a logistic and fiscal viewpoint; analytical precision and accuracy; relevance of detection limits to environmental levels of contaminants; and the range of analytical determinands actually addressed.

1.3 The North Sea Ministers (MINDEC 1990, Annex 1A) have committed their governments to reducing inputs of 36 toxic chemicals to less than 50% of 1985 levels via rivers and estuaries by 1995. A subset of 17 of these compounds must have their atmospheric inputs reduced by 50% by 1995 or 1999 at the latest. Total inputs of dioxins, mercury, cadmium and lead must be reduced by 1995 to at most 30% of 1985 quantities. The North Sea Ministerial Conference due to be held in 1995 is the last scheduled. Similarly, with the completion of the latest Quality Status Report, the responsibilities of the North Sea Task Force (NSTF) will have been discharged. The monitoring responsibilities of the NSTF will be assumed by the Oslo and Paris Commissions. The Commissions are additionally charged with extending monitoring coverage to the whole maritime area covered by the Convention.

1.4 A stated objective of the Commission is to supplement the preparation and review of the final North Sea Quality Status report with status reports covering the Arctic and Sub-Arctic Zones, estuaries in the region, the Bay of Biscay, the Iberian coast and the Irish Sea. Although some of these areas, notably the Arctic regions and the Irish Sea are subject to existing monitoring plans, the objectives relate to a considerably larger marine area than the North Sea alone. This document examines current monitoring activities in the North Sea in order to identify potential problems with contaminant monitoring of this greatly extended area.

1.5 On the basis of the demonstrable and indeed widely recognised deficiencies in the North Sea monitoring programme, this document advocates an extensive programme of near-field monitoring to supplement

the wider field programmes currently in place. It is argued that particular attention should be paid to identifying and characterising chemical inputs and mass balances from direct discharges. This would constitute a resource efficient programme targeted at source reduction, while allowing the continued accumulation of the medium and long term data sets. Finally this would also be an efficient means of more rapidly assessing the wide range of substances (MINDEC 1990, Annex 1D) listed for potential future priority action.

2. QUALITY OF CURRENT INPUT DATA

2.1 In order for PARCOM to meet its extended surveillance commitments, accurate input data will be required. These will be derived from monitoring programmes implemented by national governments and those organised and coordinated internationally. Unfortunately, existing monitoring programmes are inadequate to provide the necessary information. Moreover, the quality of the analytical data which has been generated in the past is of doubtful utility. The intensity and frequency of monitoring of even the limited number of chemicals contained in the UK "RED LIST" (DoE 1988) is not regarded as sufficient to detect reductions of inputs of chemicals on even a local basis let alone over the North Sea as a whole (Agg & Zabel 1990; Bale 1991). In the case of the Tyne and Tees rivers, metal loadings are computed on the basis of just four samples a year (Hupkes 1991).

2.2 Unsurprisingly, the published input estimates of chemicals into the North Sea are subject to wide uncertainty. In some cases, the maximum and minimum input estimates differ by a factor of ten. In the 1993 quality status report it is noted the data are more reliable than in the 1987 QSR. However, the uncertainty attached to riverine/direct inputs and dumping is estimated at +/-20% to +/-30%. The reliability of loading figures is therefore still low and recorded changes in annual loads from rivers are seldom of statistical significance (Hupkes 1991). Indeed, examination of input estimates in the 1993 QSR indicates substantial differences between upper and lower estimates. The upper and lower riverine input estimates for PCBs are 2700 and 410 kg respectively. For cadmium, they are 55 and 36 tonnes respectively. Certainly, therefore, little justification exists for regarding cadmium in the North Sea as having reached a steady state, as claimed in a recent study (Kuhn et al. 1992).

2.3 Atmospheric inputs are subject to even greater uncertainty. One of the more important results of the recently reported five year UK Natural Environment Research Council Project was the possibility that in excess of 50% of the input of some metals to the North Sea occurs via atmospheric deposition (Chester et al. (1993). However, the input estimate variance is still between +/-50% to +/-100% according to the 1993 QSR. The lack of truly authoritative input data seems certain to be a key deficiency of any new QSR predicated solely on the basis of wide field, infrequent sampling. Significantly, there are no estimates in the current North Sea QSR for PCDD/F input despite the commitment to a 70% reduction agreed by the North Sea ministers. The majority of the annex 1A compounds scheduled for 50% reduction are also excluded.

2.4 The monitoring programmes fail on both a local and regional level in other respects. On a national level, point sources of contaminants are

controlled through licensing systems. Basic problems in the UK system have been described by Johnston *et al.* (1991a) and these problems are shared by regulatory regimes in mainland Europe. The Belgian system is particularly inadequate (Johnston *et al.* 1991b). In these cases, moreover, the licence conditions themselves often regulate only a small proportion of the chemicals routinely discharged (Johnston & Stringer 1991). According to the UK Royal Commission on Environmental Pollution even licences regulating large industrial discharges may routinely control fewer than 20 physico-chemical determinands (REP 1992). In addition the Commission report also notes the difficulty of evaluating diffuse sources of contaminants.

2.5 Finally, regulation of industrial point sources are carried out by a variety of national regulatory authorities. However, a point source needs to be monitored at least sixty times in a year in order to reliably ensure statistical detection of a fall from 95% compliance on an annual basis. Below this figure, the certainty of ensuring compliance with licence conditions falls off rapidly (Ellis 1986). Very few effluents are monitored so intensively and so the reliability of any derived input budgets will be imperfect.

2.6 The specific problems of deriving reliable input data for the extended area covered by the Paris Convention are, therefore, as follows:

a) In samples collected at sites remote from sources of pollution, concentrations of contaminants may often have fallen below detection limits for routine analysis;

b) The logistic difficulties and expense of collecting samples mean that even in a region monitored as intensively as the North Sea, sampling frequency and intensity will not provide sufficiently resolved data.

c) Full source reconciliation of atmospherically and aquatically transported contaminants will not be possible.

2.7 In short the quality of input data will improve if it is based less on inference and more upon empirical measurement. The degree of empiricism could be improved considerably by an increased intensity of monitoring of contaminant point sources and the geographical areas close to them.

3. IDENTIFICATION OF TRENDS

3.1 The current commitment to percentage reduction of contaminants agreed in the 1990 Ministerial Declaration implies an ability to detect trends in levels of contaminants in the environment over relatively short time scales as well the accurate calculation of inputs. Difficulties in detecting trends are identified in a recent assessment of the ICES Cooperative Monitoring Programme (CMP) of contaminant levels in fish muscle (Fryer & Nicholson 1993). It is stated that accounting for random between-year variation, it would be unrealistic to expect to detect any patterns of change over a two to three year period. The CMP data sets span no more than eight years which would give sufficient power to the programme to detect trends in zinc of 10% per year and of copper and mercury of 20% per year, assuming that analytical data are

reliable. These are large trends. Consequently, validation of reduction commitments will not be possible through far-field analysis alone.

3.2 If large scale pollution incidents are considered, then zinc and copper would need to change by 200% and mercury by 400% to be identified through the CMP. Only by extending the CMP data to cover 20 years does the power of the programme rise to the extent that trends of 5% can be detected. As pointed out by the authors of the analysis, the environmental impact of a contaminant over this period, prior to trends emerging, may well prove unacceptable.

3.3 Moreover serious complications have recently emerged in the use of fish as "sentinel species" for pollution. It has recently been found that for the target species of a US benthic surveillance programme the length of the fish alone accounted for between 19% and 67% of the variability in the data. The study considered only metals and was initiated in response to concerns that size differences alone between fish sampled in different years could fatally confound the identification of spatial differences or temporal trends (Evans *et al.* 1993). These concerns seem amply justified in the North Sea also where a recent report from the Netherlands notes that levels of DDT and PCBs in cod liver were found to be related to the length or age of the sampled fish. A recalibration of the trends data was necessary since average lengths of the fish have decreased considerably during the last decade (RIVO 1993).

3.4 Determining the biological status of contaminant impacted systems is subject to even greater resource and logistic limitations. This is illustrated by the recent report of IOC/ICES Bremerhaven Workshop which took place in March 1990 (Stebbing *et al.* 1992a). This was only the second intensive study carried out to assess North Sea condition and considered a transect of nine sample points running northwest from the mouths of the Elbe and Weser out to the Dogger Bank. A second transect was designed to investigate a disused oil drilling site off the Dutch coast. The study provided an opportunity to investigate indices of health in dab, conduct bioassays of water and sediment quality and test a system for the integrated measure of benthic environmental quality.

3.5 The results from the various surveys went a long way to confirming suspicions that pollution effects in the North Sea were actually occurring and identified the need for a more exhaustive research programme. Even so, the exercise served to reconfirm the resource limitations inherent in wide field monitoring campaigns. Over 100 scientists took part in the exercise and seven research vessels were deployed. Yet this was sufficient only to obtain a set of data from the nine major stations and the limited survey of the oil drilling site. The major findings have been reported in the scientific literature (Stebbing *et al.* 1992a) together with an overall summary and conclusions (Stebbing *et al.* 1992b) and serve to illustrate well that the detection of significant effects is largely dependent upon the sensitivity of the methods used and the intensity of the research programme.

3.6 Nevertheless, the power of chemical and biological monitoring in the wider field will improve with the extension of data gathering over time. For this reason alone it is imperative that such programmes be maintained and extended over the entire Convention area. In order to

increase the precision of these exercises, there will be a continuing need to develop and refine analytical and sampling methods.

4. QUALITY OF ANALYTICAL DATA

4.1 It is clear that the quality of the data derived from analytical programmes is highly suspect. This may be illustrated by data gathered in a German intercalibration exercise for individual PCB congeners (Rimkus *et al.* 1993). The data show a wide range and extreme erroneous values were generated, but not consistently by any single laboratory. The report concludes that any absolute comparison of the data obtained is only justified if statistical variability is accounted for and that the same PCB congeners are compared.

4.2 The project manager of the latest international Quality Control and Quality Assurance Project (QUASIMEME) notes that it has become quite clear that the measurements made on the same sample by one laboratory often bear no resemblance to the values obtained by another laboratory. More worrying still, this means that the interpretation of the environmental significance of such data sets is no more than an observation on the spread of errors generated by the scientists concerned (Wells 1993). These problems are common both to the North Sea Task Force (NSTF) and to the Joint Monitoring Group (JMG) of the Oslo and Paris Commissions active in the North East Atlantic region.

4.3 In 1992 the JMG reported a great improvement of the mutual comparability of analysis results. The standard deviations for most PCBs in seal- and sediment extracts had diminished to around 20% (RIVO 1993). The QUASIMEME Project is still underway and not due to lead to conclusive results until sometime in 1994 (Wells *et al.* 1993). Hence, even if data do stretch back a number of years (see: Law and Thain 1991) there has as yet been no comprehensive intercalibration exercise carried out to validate them. Therefore, the use of historical data in resolving contaminant trends is strictly limited.

4.4 Even when the QUASIMEME programme is completed, the number of chemicals that it will consider as mandatory determinands are the metals Cd, Cu, Hg, Pb, Zn, hexachlorobenzene, and isomers of HCH and PCBs. Laboratories can select voluntarily from a list of twelve other chemical types. This list includes the dioxins, which are scheduled for a 70% reduction under the terms of the 1990 North Sea Ministerial Agreement (Wells *et al.* 1993). This is an extremely limited subset of the chemicals targeted by legislation for incremental discharge reductions.

4.5 Thus the feasibility of providing the data necessary to police the legislative requirements of the North Sea Ministerial declaration or the Paris Convention must be under serious question, at least in the short term. Consequently, significant changes in the monitoring strategies will be needed. Continuation of the far-field monitoring will in time provide data on contaminant trends in the study area but will be only of limited utility in assessing input trends. A more immediate and meaningful result could be obtained by concentrating investigations more intensively at the site of input.

5. POINT SOURCE MONITORING

5.1 There are a number of potential advantages in intensifying monitoring of point sources as a means whereby the accuracy and precision of input estimates may be enhanced. The power of such an approach would follow in considerable measure from the substantial simplification of analyses conducted on analytes at high concentration as compared to concentrations in open waters. Ease, accuracy and precision of analyte quantification is directly related to concentration and matrix complexity. Similarly, atmospheric and biological monitoring can be expected to be facilitated by focussing of contaminant source areas and concomitant use of all techniques is recommended to provide a complete and coherent data set.

5.2 Analysis of effluents from a wide variety of industrial sectors has demonstrated that they contain a wide range of chemical contaminants, many of which may be isolated using relatively simple extraction and clean-up procedures (Johnston and Stringer 1991). Concentrations may be generally measured at part per million (ppm) and part per billion (ppb) levels in effluents. In open water, while chemicals of clear industrial origin may be found some distance offshore (Law et al. 1991), measurements need to be conducted on part per trillion levels. It is likely that many of these chemicals, although of environmental concern, are present at levels below current limits of detection.

5.3 Law et al. (1991) not only identified a wide range of chemical contaminants of clear industrial origin in offshore waters, but the exact combination varied between estuaries presumably reflecting differing industrial activities within each area. A similar finding of complex chemical mixtures has been made for the Scheldt estuary. This is regarded as heavily polluted. An additional problem is identified in this study. A significant component of the chemicals isolated could not be identified (van Zoest & van Eck 1991). A wide range of organic micropollutants have also been identified in open waters off the Dutch coast (van de Meent et al. 1986). Measurement of these compounds in open waters is comparatively complex and costly yet indicates the wide range of pollutants possibly contributing to the toxic effects detected using bioassay techniques (Matthiessen et al. 1993).

5.4 Many difficulties could be resolved by intensive monitoring of point sources. Analytical suites are currently extremely limited and intensive effluent monitoring would allow a cost effective extension of existing frameworks. Applying effort to monitoring complex mixtures of anthropogenic chemicals at source will be extremely useful in implementing relevant legislation and for subsequently assessing the effectiveness of any measures taken.

6. A CASE STUDY- THE PVC SECTOR

6.1 The production of dichloroethane and vinyl chloride has been placed on the Reference List of Priority Activities in The North Sea Ministerial Declaration (Annex 1C). PVC production is the largest single end-use of elemental chlorine globally and consequently, the production of the raw and intermediate materials are among the largest bulk production organochlorine chemicals. The incidental by-production of numerous organohalogens, some of which are known to be toxic, persistent and bioaccumulative, has been documented. These include the

STENUNGSUND (SW)

WILHELMSHAVEN (FRG)

ERLLE (FRG)

MIDDLESBOROUGH (UK)

ROTTERDAM (NL)

HURTH (FRG)

ANTWERP (BGM)

BARRY ISLAND (UK)

TESSENDERLO (BGM)

MARZINGARBE (FR)

JEMEPPE (BGM)

NAMUR (BGM)

TAVAU (FR)

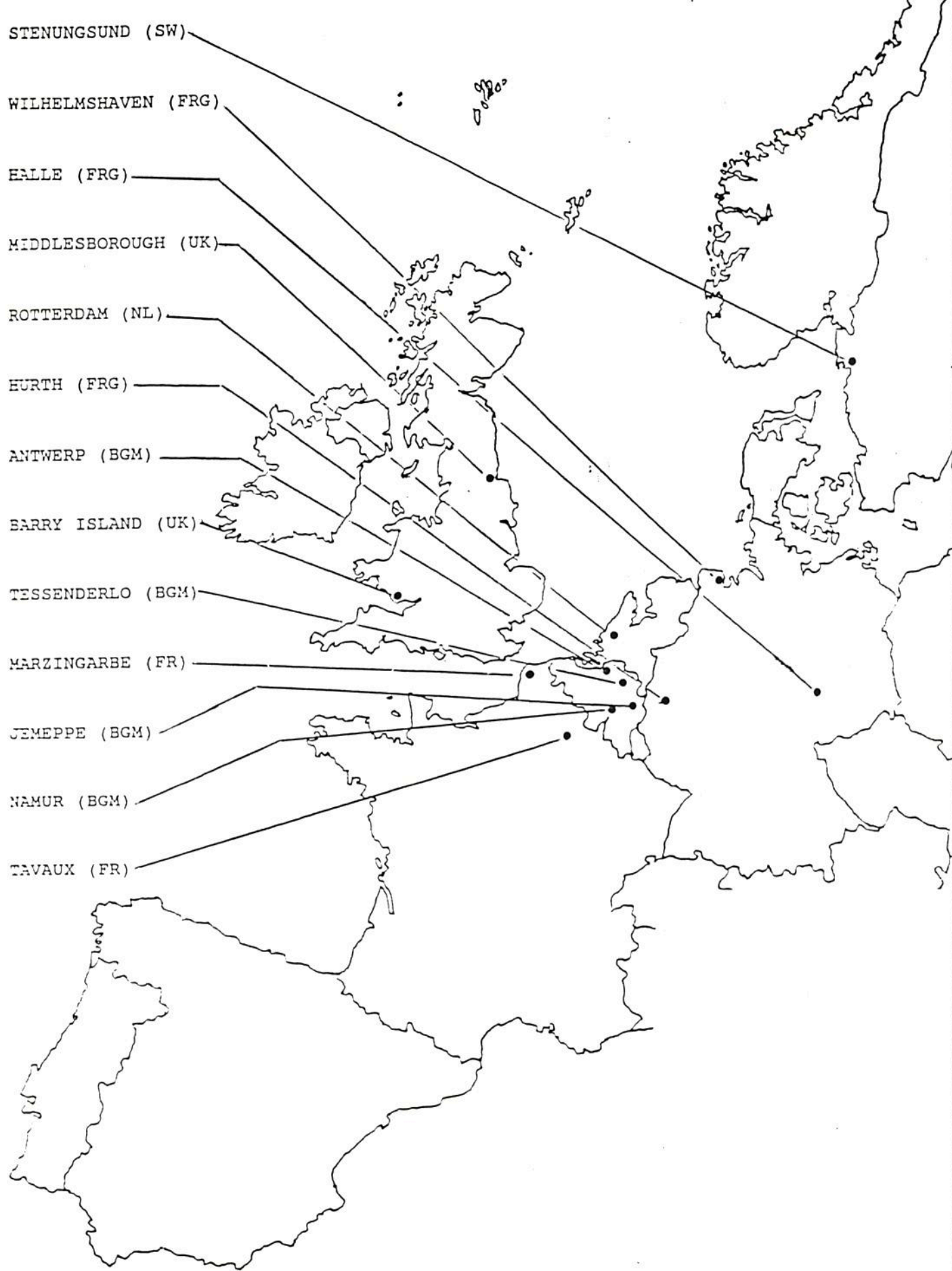


Figure 1. Locations of PVC manufacturing facilities sampled.

chlorinated dioxins and dibenzofurans. Such compounds have been selected for priority action by PARCOM. The release of other chemicals from PVC-related production facilities has been poorly researched to date. As an illustration of the potential power of point source monitoring, results from a recent Europe-wide survey of discharges from the PVC industry are presented below. Locations of sample sites are given in figure 1. The countries where samples were taken were Belgium, France, Germany, the Netherlands, Sweden and the United Kingdom. Amongst those Convention countries from which samples were not taken is Ireland, which, although it has chlor-alkali capacity, does not as yet manufacture vinyl chloride or PVC.

6.2 Results presented were obtained by using two analytical methods; dynamic headspace and simple hexane-water extraction followed by gas chromatography coupled to low resolution mass selective detection. In one case, effluents were not obtainable so instead soil samples were taken from the site to give an indication of point source contamination. Soil samples were extracted by sonication with hexane/acetone followed by sulphuric acid cleanup. Chromatography and analyte identification were carried out as for effluent samples. These are extremely quick and cost-effective analytical methods which moreover eliminate many of the cleanup stages which are major contributors to the analytical uncertainty which compromises analytically derived input estimates.

6.3 Quantification of priority compounds can easily be carried out using external standards whereas semiquantitative determination on non-priority compounds or unknowns can quickly be achieved by comparison with labelled internal standards. It may be anticipated that some fractionation of the raw extract may be necessary to enhance chromatographic separation of compounds, but again, the simplicity of the matrix means that this can be achieved with a relatively low loss of analytical accuracy and precision. Moreover, using high resolution GC/MS techniques, an empirical formula can be derived from the considerable number of compounds which remain unidentified following analysis.

6.4 The results of the survey provide an interesting insight into releases of regulated chemicals into the marine environment directly and via riverine systems. The tables below list those substances which were identified to greater than 90% against the NBS and Wiley Spectral Libraries. Those chemicals which are included in Annexes 1A and 1D of the Third Ministerial declaration and are therefore scheduled for 50% input reduction or are recognised as priority substances for future measures, are highlighted. Also highlighted are organohalogenes, chemicals which are under close scrutiny by the Paris Convention. Annex 2 of the revised Paris Convention lists criteria for setting priorities and states: "The above criteria indicate that substances which shall be subject to programmes and measures include: ... (b) organohalogenes compounds (and substances which may form such compounds in the marine environment).

Key to results tables: Compounds listed have been identified to >90% certainty.

1AW: compound is listed in annex 1A of the Final Declaration of the Third International Conference on the Protection of the North Sea (MINDEC 1990) as a priority hazardous substance in water; scheduled for >50% reduction

1AA: compound is listed in annex 1a of the Final Declaration of the Third International Conference on the Protection of the North Sea (MINDEC 1990) as a priority hazardous substance in air; scheduled for >50% reduction in air

1D: compounds is listed in Annex 1D of the Final Declaration of the Third International Conference on the Protection of the North Sea (MINDEC 1990) for consideration for prioritisation

HHC: halogenated hydrocarbon

BELGIUM

BASF, Antwerp

SAMPLING DATE: 20/10/93; LAB CODE: MI3287; SAMPLE TYPE: EFFLUENT

TOTAL COMPOUNDS ISOLATED: 31

				furan, tetrahydro-2-methyl-
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SOLVAY & CIE, Antwerp

SAMPLING DATE: 20/10/93 LAB CODE: MI3289 SAMPLE TYPE: EFFLUENT

TOTAL COMPOUNDS ISOLATED: 17

			HHC	ethane, bromodichloro-
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SOLVAY & CIE, Namur

SAMPLING DATE: 19/10/93; LAB CODE: MI3290; SAMPLE TYPE: EFFLUENT

TOTAL COMPOUNDS ISOLATED: 60

1AW			HHC	1-butanamine, N-butyl- 3-pentanone, 2,2,4,4-tetramethyl- benzene, 1-methyl-3-(1-methylethyl)- benzene, 1,2,4,5-tetramethyl- naphthalene, 1,2,3,4-tetrahydro- 1,3-butadiene, 1,1,2,3,4,4-hexachloro- ethanone, 1-(2,5-dimethylphenyl)- benzene, 1,1'-oxybis-
1AW			HHC	methane, trichloro-
1AW	1AA		HHC	ethene, trichloro- benzene, 1-methyl-2-propyl-

SOLVAY & CIE, Namur

SAMPLING DATE: 19/10/93 LAB CODE: MI3291; SAMPLE TYPE: EFFLUENT

TOTAL COMPOUNDS ISOLATED: 60

1AW	1AA		HHC	ethene, tetrachloro- 1-butanamine, N-butyl- 3-pentanone, 2,2,4,4-tetramethyl- benzene, 1,3,5-trimethyl- benzene, 1,2,3,5-tetramethyl- naphthalene, 1,2,3,4-tetrahydro-
1AW		1D	HHC	1,3-butadiene, 1,1,2,3,4,4-hexachloro- 1,1'-biphenyl benzene, 1,1'-oxybis-
1AW	1AA		HHC	ethane, 1,1-dichloro-
1AW	1A		HHC	methane, tetrachloro-
1AW	1A		HHC	ethene, trichloro- 3-pentanone, 2,2,4,4-tetramethyl- benzene, 2-ethyl-1,4-dimethyl- 1H-indene, 2,3-dihydro-5-methyl-

LIMBURGSE VINYL, Tessenderlo

SAMPLING DATE: 19/10/93 LAB CODE: MI3281; SAMPLE TYPE: EFFLUENT

TOTAL COMPOUNDS ISOLATED: 5

			HHC	methane, dibromo-
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LIMBURGSE VINYL, Tessenderlo

SAMPLING DATE: 18/10/93 LAB CODE: MI3283; SAMPLE TYPE: EFFLUENT

TOTAL COMPOUNDS ISOLATED: 18

			HHC	methane, tribromo-
			HHC	methane, bromodichloro-

LIMBURGSE VINYL, Tessenderlo

SAMPLING DATE: 18/10/93 LAB CODE: MI3284; SAMPLE TYPE: EFFLUENT

TOTAL COMPOUNDS ISOLATED: 29

1AW	1AA	1D	HHC	ethane, 1,1-dichloro-
			HHC	methane, bromodichloro-
			HHC	ethane, 1,1,2-trichloro-
			HHC	ethene, tetrachloro-
			HHC	methane, tribromo-

LIMBURGSE VINYL, Tessenderlo

SAMPLING DATE: 18/10/93 LAB CODE: MI3285; SAMPLE TYPE: EFFLUENT

TOTAL COMPOUNDS ISOLATED: 38

		1D		benzaldehyde
				cyclohexane
			HHC	methane, bromodichloro-
			HHC	benzene, chloro-
			HHC	benzene, 1-chloro-2-methyl-
			HHC	benzene, 1,3-dichloro-2-methyl-
			HHC	benzene, dichloromethyl-
			HHC	benzene, 1,2-dichloro-4-methyl-
			HHC	benzene, 1-chloro-4-(chloromethyl)-

FRANCE

SOCIETE ARTESIENNE DE VINYL S.A., Marzingarbe

SAMPLING DATE: 12/10/93 LAB CODE: MI3313; SAMPLE TYPE: EFFLUENT

TOTAL COMPOUNDS ISOLATED: 10

		1D	HHC	ethene, chloro-
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SOLVAY & CIE S.A., Tavaux

SAMPLING DATE: 13/10/93 LAB CODE: MI3273 SAMPLE TYPE: EFFLUENT
IN SETTLING LAGOON

TOTAL COMPOUNDS ISOLATED: 90

1AW	1AA	1D	HHC	ethane, 1,1-dichloro-
			HHC	ethene, trichloro-
1AW	1AA	1D	HHC	1-propene, 2,3-dichloro-
			HHC	ethene, tetrachloro-
			HHC	cyclobutene, 3,4-dichloro-
1AW		1D	HHC	benzene, chloro-
				hexanal, 2-ethyl-
			HHC	1,3-butadiene, 1,1,3,4-tetrachloro-
				benzene, 1,2,3,4-tetramethyl-
				1H-Indene, 2,3-dihydro-1-methyl-
				naphthalene, 1,2,3,4-tetrahydro-
			HHC	benzene, 1,2,4-trichloro-
	HHC	1,3-butadiene, 1,1,2,3,4,4-hexachloro-		
		HHC	benzene, 1,2,3,5-tetrachloro-	

GERMANY

BUNA AG, Halle, near Leipzig

SAMPLING DATE: 27/10/93 LAB CODE: MI3317 SAMPLE TYPE: EFFLUENT

TOTAL COMPOUNDS ISOLATED: 4

			HHC	methane, tribromo-
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HOECHST A.G., Hurth, Northrhine Westphalia

SAMPLING DATE: 23/10/93 LAB CODE: MI3309 SAMPLE TYPE: EFFLUENT

TOTAL COMPOUNDS ISOLATED: 17

1AW			HHC	methane, trichloro-
				benzene, 1-methyl-3-nitro-
				phenol, 4-methyl-2-nitro-
		1D	HHC	benzenamine 3,5-dichloro-

HOECHST A.G., Hurth, Northrhine Westphalia

SAMPLING DATE: 24/10/93 LAB CODE: MI3311 SAMPLE TYPE: EFFLUENT

TOTAL COMPOUNDS ISOLATED: 7

1AW	1AA		HHC	benzene, 1-methyl-3-nitro-
				ethane, 1,2-dichloro-

ICI, Wilhelmshaven

SAMPLING DATE: 26/10/93 LAB CODE: MI3314 SAMPLE TYPE: EFFLUENT

TOTAL COMPOUNDS ISOLATED: 3

1AW	1AA		HHC	ethane, 1,2-dichloro-
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NETHERLANDS

AKZO, Rotterdam Harbour

SAMPLING DATE: 22/10/93 LAB CODE: MI3300 SAMPLE TYPE: EFFLUENT

TOTAL COMPOUNDS ISOLATED: 19

		1D	HHC HHC	ethane, 1,1,2-trichloro- methane, dibromochloro-
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LVM, Jemeppe, Limburg

SAMPLING DATE: 21/10/93 LAB CODE: MI3292 SAMPLE TYPE: EFFLUENT

TOTAL COMPOUNDS ISOLATED: 1

				none
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SHELL, Rotterdam Harbour

SAMPLING DATE: 22/10/93 LAB CODE: MI3293 SAMPLE TYPE: EFFLUENT

TOTAL COMPOUNDS ISOLATED: 40

		1D	HHC	pentane, 2-methyl- propane, 1,2-dichloro-
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SWEDEN

NORSK HYDRO, Stenungsund

SAMPLING DATE: 26/03/93 LAB CODE: MI3090 SAMPLE TYPE: SOIL
NEAR CONTAINER ON FACTORY SITE

TOTAL COMPOUNDS ISOLATED: 142

1AW		1D	HHC	ethane, 1,1,2,2-tetrachloro-
			HHC	ethane, 1,1'-oxybis[1-chloro]-
			HHC	1-propene, 3,3,3-trichloro-2-methyl-
		1D	HHC	ethane, hexachloro-
			HHC	benzene, 1,3,5-trichloro-
			HHC	butane, 1,2,3,4-tetrachloro-
			HHC	1,3-butadiene, 1,1,2,3,4,4-hexachloro-
			HHC	ethanone, 1-(4-chlorophenyl)-
			HHC	benzene, 1,2,3,4-tetrachloro-
			HHC	1,3-cyclopentadiene 1,2,3,4,5,5-hexachloro-
		1D	HHC	phenol, 4-nitro-
			HHC	benzene, pentachloro-
		1D	HHC	1-propene, 1,2,3,3-tetrachloro-
			HHC	benzene, hexachloro-
		HHC	oxazole, 5-bromo-4-phenyl-	

NORSK HYDRO, Stenungsund

SAMPLING DATE: 26/03/92 LAB CODE: MI3091 SAMPLE TYPE: SOIL NEAR
CONTAINER ON FACTORY AREA

TOTAL COMPOUNDS ISOLATED: 125

1AW		1D	HHC	ethane, 1,1,2,2-tetrachloro-	
			HHC	ethane, 1,1'-oxybis[2-chloro]-	
			HHC	1-propene, 3,3,3-trichloro-2-methyl-	
			HHC	benzene, 1,3,5-trichloro-	
			HHC	1,3-butadiene, pentachloro-	
			HHC	butane, 1,2,3,4-tetrachloro-	
			HHC	1,3-butadiene, 1,1,2,3,4,4-hexachloro-	
			HHC	benzene, 1,2,3,4-tetrachloro-	
			1D	HHC	benzene, pentachloro-
				HHC	benzene, hexachloro-
1AW	1AA		4-methoxy-2-methylaniliniumbromide		
		HHC	benzamide, 2-chloro-N-(4-hydroxyphenyl)-		
		HHC	1-propene, 3,3,3-trichloro-2-methyl-		
		HHC	4-fluorobenzoylcarboxylic acid		
		HHC	benzene, pentachloro(trichloroethyl)-		

NORSK HYDRO, Stenungsund

SAMPLING DATE: 26/03/93 LAB CODE: MI3092 SAMPLE TYPE: SOIL
NEAR CONTAINER ON FACTORY SITE

TOTAL COMPOUNDS ISOLATED: 142

1AW		1D	HHC	ethane, 1,1,2,2-tetrachloro-
			HHC	1-propene, 3,3,3-trichloro-2-methyl-
		1D	HHC	ethane, hexachloro-
			HHC	butane, 1,2,2,4-tetrachloro-
			HHC	1,4-butadiene, pentachloro-
			HHC	benzene, 1,2,4-trichloro-
			HHC	butane, 1,2,3,4-tetrachloro-
			HHC	1,3-butadiene, 1,1,2,3,4,4-hexachloro-
			HHC	benzene, 1,2,3,4-tetrachloro-
			HHC	1,3-cyclopentadiene, 1,2,3,4,5,5-hexachloro-
1AW	1AA	1D	HHC	phenol, 3-nitro-
			HHC	benzene, pentachloro-
			HHC	benzene, hexachloro-
				phenol, 2,4-dimethyl-
			HHC	benzamide, 4-chloro-N-(1,1-dimethyl)-
			HHC	1-propene, 3,3,3-trichloro-2-methyl-
			HHC	2-butene, 1,4-dichloro-
			HHC	1,3-diphenyl-2-pyrazoline-[1-15N]
	HHC	benzene, pentachloro(trichloroethenyl)-		

NORSK HYDRO, Stenungsund

SAMPLING DATE: 19/10/93 LAB CODE: MI3265 SAMPLE TYPE:
SOIL/GRAVEL FROM BENEATH OXYCHLORINATION REACTOR

TOTAL COMPOUNDS ISOLATED: 14

1AW	1AA	1D	HHC	benzene, pentachloro-
			HHC	benzene, hexachloro-
			HHC	benzene, pentachloro-(trichloroethyl)-
			HHC	benzene, 1,2,3,4-tetrachloro-
1AW		1D	HHC	1,3-butadiene, 1,1,2,3,4,4-hexachloro-
			HHC	benzene, 1,2,4,5-tetrachloro-

UNITED KINGDOM

EVC, Barry Island, South Wales

SAMPLING DATE: 11/11/93 LAB CODE: MI3316 SAMPLE TYPE: EFFLUENT FROM
SETTLING LAGOON

TOTAL COMPOUNDS ISOLATED: 152

	1D	HHC	ethene, chloro-
	1D		benzene, methyl-
	1D	HHC	ethane, 1,1,2-trichloro-
	1D		benzene, ethyl
	1D		benzene, 1,3-dimethyl
			1,3,5,7-cyclooctatetraene
			4-heptanone, 3-methyl-
	1D		benzene, 1-ethyl-2-methyl-
	1D		naphthalene
			styrene
			2-furancarboxaldehyde, 5-methyl-
			benzene, (1-methylethenyl)-
			phenol
			3-cyclohexene-1-carbonitrile
			benzaldehyde, 2-hydroxy-
			cyclobutane, 1,2-diethyl-
			furan, 2,2'-methylenebis-
			phenol, 2-methoxy-
			phenol, 2,6-dimethyl-
			phenol, 2,4,6-trimethyl-
			1-decanol
			decanoic acid
	1D		1,1-biphenyl
			9-tricosene, (Z)-
			1,2-benzenedicarboxylic acid,
			butyl-2-methylpropyl ester
		HHC	benzene, 1-chloro-2-[2,2-dichloro-1-
			-(4-chlorophenyl)ethenyl]-
		HHC	benzene, 1,1'-(2,2,2-trichloroethylidene),
			bis[4-chloro]-

ICI Wilton, Middlesborough

SAMPLING DATE: 24/11/93 LAB CODE: UK3116 SAMPLE TYPE: EFFLUENT

TOTAL COMPOUNDS ISOLATED: 258

	1D		benzene, methyl- 1,3,5-cycloheptatriene
	1D		benzene, ethyl- benzene, 1,2-dimethyl- cyclohexanol styrene benzene, cyclopropyl- benzene, 1-ethyl-3-methyl- benzene, 1,2,4-trimethyl- benzenamine pyridine, 3-methyl- benzene, 1-ethenyl-3-methyl- 1H-indene, 2,3-dihydro- benzene, 1,2-propadienyl- benzene, 1-propynyl- benzaldehyde, 4-methyl- benzene, nitro- benzene, 1,3-diethenyl- benzene, (2-methyl-1-propenyl)- benzene, 2-ethenyl-1,4-dimethyl-
	1D	HHC	benzenamine, 2-chloro- 1H-indene, 1-methyl- naphthalene, 1,2-dihydro- azulene naphthalene, 1-methyl- cyclohexane, 1,1'-oxybis-
	1D	HHC	phenol, 2,4-dibromo- 1,1'-biphenyl tetradecane benzene, 1,1'-oxybis- 1-octanol, 2-butyl- cyclododecane diazine, diphenyl-
		HHC	2,4,6-tribromo-phenol 1-ethyl-2-methyl cyclododecane pyrrolo[1,2-a]-1,3,5-triazine-7-carboxylic acid, benzene-
	1D	HHC	acetonitrile, dichloro-
	1D		benzene, 1,3-dimethyl- bicyclo[4.2.0]octa-1,3,5-triene
	1D		benzene, 1-ethyl-2-methyl- aniline benzene, ethenylmethyl benzene, 1-methyl-4-(1-methylethyl)-
	1D		naphthalene benzene, (1-methyl-2-cyclopropan-1-yl)- cycloprop[a]indene, 1,1a,6,6a-tetrahydro-

6.5 Inspection of the results tables indicate that a great majority of PVC-related production facilities emit chemicals subject to specific regulation under the North Sea Ministerial Agreement. It would seem logical that wide spectrum analysis of effluents should serve not only as a primary tool in the control of these substances but also as a means of source reconciliation and confirmation that agreed input reductions of specified chemicals are actually being achieved. A further clear advantage to approaching analytical activities in this fashion is that it provides valuable and unique data on the identity of compounds being emitted in the Convention area. The data can also be used in the initial evaluation of Annex 1D chemicals with a view to future legislation and prioritisation as required by the Action Plan of the Oslo and Paris Commissions, 1993.

6.6 Further important benefits accrue from a sectorally focussed analytical programme. For example, elements of the PVC sector emit a wide range of chlorine substituted benzenes and other aromatics. Certain of the chlorobenzenes have been identified as priority pollutants. It may prove more effective in regulatory terms therefore to treat these chemicals as a group irrespective of likely or known differences in toxicological properties of closely related members of a single chemical group. A further example is the presence of several chlorinated butadienes in some PVC effluents. Two chlorinated butadienes (chloroprene and hexachlorobutadiene) are listed in the annexes of the North Sea Ministerial Declaration. Again, for the purposes of environmental protection, it may be beneficial to regulate on a group basis. Similar considerations apply to the regulation of volatile halogenated organic materials. For example, brominated and chlorobrominated methanes were found in a number of PVC industry effluents and could usefully attract regulation as part of a group including the chlorinated methanes and ethanes. Overall, this approach of aggregating organohalogenes with similar chemical and physical properties for regulatory purposes would facilitate the regulation of the class of organohalogenes as a whole and could be applied to other classes of chemicals.

6.7 Considerable differences in overall effluent quality are also visible in the results. For example, effluents sampled in Germany were found to be substantially less complex than effluents in France and Belgium. Here too a point source approach coupled to chemical group regulation could well be beneficial. In many cases improvement in effluent quality is achieved by the use of settling lagoons and forced aeration treatment processes. Many of the chemicals isolated from the two treatment lagoons sampled are volatile and therefore significant losses to atmosphere may be anticipated from effluents subjected to such treatment. Point source monitoring of effluents before and after treatment could provide valuable data on atmospheric emissions of contaminants.

6.8 The analytical results reported have identified a number of common elements in the effluents discharged from PVC-related industries. Additionally, the results have also revealed extensive differences in the range of identified compounds likely to be emitted by the sector as a whole. This suggests severe limitations to regulatory instruments predicated on the basis of a limited subset of the chemicals discharged with respect to achieving true environmental protection. Indeed, the results provide a clear illustration of the permissive nature of current

regulation. A key deficiency is the reliance upon controlling only those chemicals for which conclusive data have been derived. This is antithetical to the precautionary approach to environmental protection which has been endorsed and embraced by the Paris Commission. The Commission is well known as a leading proponent of the principle and therefore influential in its acceptance globally. In consequence the issue of point source monitoring is crucial to both the implementation of the precautionary principle and the credibility of the Commission itself.

7 CONCLUSIONS

7.1 Examination of current monitoring programmes in place in the PARCOM area, in particular those carried out under the auspices of the North Sea Task Force, reveals a number of problems which inherently limit the quality of the data they generate. In particular, the ability of current programmes to estimate input figures and detect contaminant trends is strictly limited. Uncertainties are attributable to detection limits above ambient contaminant levels, poor analytical reproducibility, insufficient intensity and frequency of monitoring. These problems stem in large measure from over-reliance upon wide field analytical projects to generate data.

7.2 As a consequence, it is impossible to reliably assess the impact of regulatory measures. Measures such as those agreed at the Third International Conference on the Protection of the North Sea and which are based upon an international commitment to percentage input reductions are particularly vulnerable to procedural difficulties. They are, therefore, impossible to verify using only far field analysis. Nonetheless wide field monitoring activities are necessary to assist understanding of ecosystem impacts, and establish on a long term basis fluxes and behaviour of contaminants.

7.3 Calculation of input trends and hence verification of existing international agreements requires an increase in both the intensity and scope of point source monitoring. The advantages of supplementing existing monitoring activities in this way include the easier identification of a wider range of contaminants present in effluents due to reduced analytical constraints. Further, it would provide source data on identified priority chemicals and chemical groups and greatly assist in the evaluation of those chemicals selected for priority action at the North Sea Conference and the Paris Commission. This approach would also help identify critical elements in prioritised industrial sectors and assist in the actual selection of the priority sectors themselves.

7.4 The potential of this approach has been illustrated using qualitative results obtained from effluent samples from PVC-related chemical production facilities. These indicate, moreover, that in this sector, regulation is on a highly permissive basis. Evaluation of point source discharges is also, therefore, a vital step in formulating a regulatory framework based upon a precautionary approach to environmental protection.

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