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ASSESSMENT AND MANAGEMENT OF RISKS TO THE ENVIRONMENT

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This paper will describe the work being sponsored by the Health and Safety Executive; Department of the Environment and National Rivers Authority for the development of computer models and incident database relevant to the assessment of environmental risks from CIMAH installations. Reference will be made to the practical application of developing techniques for the assessment and management of onshore environmental risks.

INTRODUCTION

In the UK it was the Flixborough incident which triggered the Government response to the control of risks arising from Major Chemical Accident Hazards. The Advisory Committee on Major Hazards (ACMH-(1)), who were the architects of the framework of controls - Identification: Assessment and Control and mitigation of residual risk (2) - addressed political concerns primarily to the conventional, direct risks associated with fire, explosion and toxic releases to human kind.

Much of this framework was adopted within Europe in the wake of incidents at Seveso and Manfredonia, both of which had a substantial environmental dimension. The resultant so called "Seveso Directive" (3) addressed both human and environmental hazards, which were carried forward in the UK's implementation of the Directive - the Control of Industrial Major Accident Hazards (CIMAH) Regulations 1984 (4). Many initially interpreted the reference to "the Environment" in terms of indirect harm or risk to man via an environmental vector or medium. However, the need to address the consequences of major accident hazards and impact on the environment has always been a key objective of both the Directive and CIMAH. Central to the latter's requirements; for qualifying activities which meet certain indicative criteria or involve specific dangerous substances in an industrial activity; are the general duties under Regulation 4 for the demonstration of safe operation. This includes requirements for the Manufacturer to provide evidence, including documents, that he has not only identified the major accident potential for his site, but has also taken adequate steps both to prevent such major accidents and to limit their consequences to persons and to the environment. The safety report required by Regulation 7 would normally form part of the evidence to discharge these general duties for "Top Tier" installations.

The environmental dimension was given new emphasis by the major accident which occurred in the Sandoz complex at Basle in Switzerland. A large fire in a warehouse, storing a variety of chemicals led to serious and extensive pollution of the River Rhine, when contaminated fire fighting water drained into it. It was this incident which triggered the second amendment to the Seveso Directive (5) which brought within the control framework the storage of generic categories of dangerous substances, based on classifications including "very toxic" and "toxic" to be found in the European package of Directives generally known as the "sixth amendment Directive" (6). These are carried into UK legislation by packaging and labelling legislation (CPL) (7) and food and environmental protection legislation (FEPA) (8). There is also substantial international pressure for the 'Sixth Amendment' categories to include categories of substances which are dangerous to the environment. Criteria are being established for categories specifically concerned with danger to the water environment based on toxicity and persistence (likelihood of potential long term effects in the water environment). Once finalised these categories, with inventory thresholds are likely to be included in the Fundamental Review of the Seveso Directive.

Over 400 safety reports have been assessed by the HSE and in all cases there has been little or no attempt to address the potential for environmental impact arising from major accidents. In some cases the combination of location, nature of process and dangerous substance were clearly indicative of potentially very significant environmental impacts from major accidents. Up to a point this lack of attention to environmental major accident hazards was to be expected, largely because of the considerable uncertainties and problems associated with the determination and prediction of environmental risk and hazard. These uncertainties arise due to a general absence of ecotoxicological methodologies including poorly developed consequence models; ecotoxicity and persistence data for many chemicals and their translation and extrapolation to harm criteria across the multitude of target species present in terrestrial and aquatic habitats in the natural environment.

Furthermore the Regulations had been in force for some years before more definitive guidance became available, building on the original reference to environmental aspects in the first edition of the "Guide to the CIMAH Regulations - HS(R)21(9). In the revision of this document (10) further guidance was published based on, at the time, a consultative document produced by the Department of the Environment, which was subsequently published in 1991 (11). Within the definition of major accident (Regulation 2(1)) reference is made to serious danger to the environment. Reference (10) provides guidance as follows:-

"A major accident will also have taken place if there has been a serious danger to the environment. The occurrence would be sudden, unexpected and unplanned. The "serious danger", whether realised or potential, would be of significant, sometimes relatively long lasting (but not necessarily irreversible) damage to the natural or built environment. There is the need to consider serious danger to a rare, unique, or otherwise valued component of our man-made or natural environment or widespread loss or damage to the wider environment in general. Thus ecological information about the CIMAH site and its environs will need to be compiled".

CIMAH AND THE ENVIRONMENT

The importance of the environmental dimension of the CIMAH regulations has always been recognised by HSE and initiatives to tackle the conceptual "assessment framework" started soon after the Regulations came into force. Over the years a number of papers have been presented

and published at various conferences and proceedings which emphasised the environmental dimension of CIMAH; discussed the factors to be considered in predictive assessments; reviewed operational standards and identified information sources and research needs (12, 13). Over many years the HSE and others have developed a solid and extensive expertise in risk and hazard assessment techniques including mathematical modelling for predicting the effects of major accident hazards to people (see references in 14). Despite the technical constraints and uncertainties associated with for example dispersion modelling and toxicological effects, well established techniques are now widely available for carrying out "conventional" hazard and risk analysis such that the effects of most hazards, thermal radiation overpressure and toxic effects can be predicted with some albeit uncertain consistency.

However this is not the case for environmental assessments since the quantification of consequences, both short and long term, is complicated by the infinite variability and responses of natural ecosystems; taking into account, habitats; nature of species; vulnerability and importance; population dynamics and suitable methodologies to determine dose effect responses. Much of the underlying fundamental technical data for such assessments including ecotoxicity and persistence data is limited (15, 16). There is a scarcity of ecotoxicological methodologies which require not only ecotoxicity data, but an understanding of the factors controlling the transport and fate of toxic substances in the environment. All of which creates considerable difficulties and uncertainties in the development of predictive mathematical models for major hazard and risk assessments, (although some modelling techniques, for routine impact modelling may be of value (17). Consequence modelling and the attenuating factors for chemical concentration, availability, toxicity and dispersion in the aquatic environment is developing including the sponsored work described later. The situation for terrestrial ecotoxicology is at an even more rudimentary stage, since an adequate number of soil ecotoxicity procedures is not available. However, in both cases a substantial amount of further work may be required over the coming years to develop harm criteria for both acute and chronic effects covering a range of target species in both the terrestrial and aquatic habitats and their interfaces.

This is in addition to the work required to resolve many fundamental technical problems and uncertainties with the assessment of "environmental major accident hazards". Work was initiated by HSE in 1988 to consider the conceptual framework and the significant factors which would need to be addressed. Many of the areas in Appendix 1 are within the scope of our ongoing programme of work which is described in the following sections.

PROGRAMME OF WORK

Under a long standing Agency agreement the HSE set up a programme of environmental work in 1988 with the former Safety and Reliability Directorate (SRD), of AEA Technology, formerly part of the UKAEA. Two projects were set up as follows.

Determination of Severity Scales and Safety Criteria for Industrial Accidents Which Cause Environmental Pollution. The main objectives of this project were to develop a method for assessing the severity of accidents which have an impact on the environment. To meet these general objectives consideration was given to the development of: A severity scale for environmental impact: Methods/models to predict the severity of hypothetical accidents and produce practical guidelines and other information to aid the assessment of CIMAH installations. This work considered such factors as area contaminated; persistence of the contaminating agent; the amount and extent of harm caused; the cost of and time taken to recovery; effects on man; the

public perception of the severity of environmental accidents and the overall effect of such accidents to ecological systems and the balance of nature.

Collection of Information About Incidents which had caused environmental pollution. This work was to complement the above project with the objectives of reviewing and establishing a database of past incidents which had caused or had the potential to cause significant environmental pollution or damage; identify and classify the various types of environmental pollution taking into account the nature of contaminant, circumstances of accident and consequences. The information gathered from this exercise was to be used to develop a taxonomy scheme for environmentally significant contaminants and provide a basis for making proposals about safeguards for environmental protection and to be a possible source of case studies in the validation of consequence models.

Attempts to develop severity criteria were superseded by the Department of the Environment's development of consequence criteria for environmental major accident hazards (11). Furthermore it was decided that the programme of work should be taken forward by the development of a risk assessment methodology for contaminants affecting the aquatic environment. A number of factors were key to influencing this decision. Historical records show that the vast majority of significant pollution incidents affect the water environment. Furthermore the safeguards which have been developed to minimise the risk to people from major accidents via the atmospheric vector are well established and inevitably provide a measure of environmental protection. However in many instances precautionary measures for the water environment have received less attention sometimes because of perceptions about the limited direct/indirect harm to people via this vector and the limited priorities to addressing the ecological significance of major accidents.

An environmental incident database (EnvIDAS) has been established which is subject to further ongoing development and is described in the next section.

ENVIRONMENTAL INCIDENT DATA SERVICE (ENVIDAS)

EnvIDAS is a database of World Wide incidents that have caused or had the potential to cause damage to the environment. It is being developed jointly by SRD, HSE and the Department of the Environment to analyse previous incidents which have caused, or had the potential to cause damage to the environment with particular reference to: Frequency, cause, major contaminants and environmental impact. The data are mainly collected from specialised publications in the fields of incident reporting, although some information is derived from newspaper reports. Further relevant information on incidents is actively sought from relevant organisations in the UK and Europe.

The items of data coded under various fields include, amongst others; nature of substance and its form; medium the material is released into; nature of process/storage and use of the substance; cause of the incident; hazards of the material including properties, quantity released and concentrations. Currently the data records are limited to about 400 incidents. Because of the various sources of information and the differences in reporting criteria of incidents, the quality of data is in some cases very limited. Nevertheless, the data found so far represent a very useful resource and provide an albeit limited insight in the nature of environmental incidents.

The following sections describe the preliminary analysis of data and is based on a paper presented by SRD (18).

There are basically two sorts of information that can be obtained from databases of this kind. One relates to the causes of events, their frequency and the probability of their escalation. This information can be used in evaluating the need for measures to prevent the incident and allow identification of what those measures might be including an assessment of the effectiveness of existing measures. The second relates to the consequences of the event and the seriousness of those consequences. Information on the severity of consequences can be used to aid decisions as to whether preventive measures are required and also enables judgements to be made about the required emergency responses and mitigation measures to be identified. The preliminary analysis of the data on EnvIDAS presented in the following sections has not been evaluated against major accident criteria (11), indeed many of the incidents predated the Seveso Directive and CIMAH regulations. However, the fact that they were reported would indicate that they were of sufficient importance and significance using other criteria which may have read across implications in the major accident context.

Activity

The events have been classified into 6 different kinds of activities, namely:

- Transport
- Warehouse
- Waste
- Storage
- Transfer
- Process

"Transport" indicates that the incident occurred during the transport of material external to the plant and includes pipelines. "Waste" indicates that the incident occurred in a waste storage or disposal area. "Storage" indicates that the incident originated in items of storage plant or in the vicinity of such plant as distinct from internal warehouse storage. "Process" relates to an incident occurring in the process itself and transfer would indicate that the incident occurred during loading or unloading operations. Over half of the incidents recorded to date arise from transport activities.

Cause

An analysis of the distribution of initiating events or causes for the different kinds of incidents indicates that in the case of transport impact was the main cause. This produced the highest number of events of any of the combinations of activity and cause. Apart from this, mechanical failure, human error and external causes are the main contributors to the event database. (Figure 1)

Consequences

In the majority of cases water contamination was particularly significant and 87% of the incidents reported affected water courses of one kind or another (Figure 2). A significant number of these incidents also affected aquatic life or the amenity value of a water source. In contrast, less than 20% of incidents affected terrestrial mammals and only about 10% affected vegetation and the soil. The only significant departures from this pattern are transfer accidents of which very few affected vegetation and the soil; and warehouse accidents which had a greater tendency

to affect more than one environmental medium. For example, at Alliance, Ohio, USA in 1974, a chemical warehouse caught fire following a lightning strike. The complex was destroyed and 500 residents were evacuated, 180 were injured and some hospitalised. The fire fighting water affected the Berlin reservoir which was closed for 2 days after the incident and restrictions were imposed on the consumption of fish from this source. The nearby river Mahoning was saved by blocking storm sewers and a small creek to prevent the water reaching it. One foot of soil was removed from the site because of contamination and the total damage to the plant alone was estimated at \$1 million. The incident at Basle, Switzerland in 1986, where fire destroyed a Sandoz agrochemical warehouse, is well known for having grossly polluted the River Rhine with transboundary impacts. This same incident also affected vegetation and animal life around the site. Fish were killed up to 400 km downstream. Emergency water supplies had to be made available in Bonn. Fishermen and market gardeners suffered financially in Holland. Fifty thousand square metres of soil around the site was contaminated, mainly with mercury. Basle itself was affected by a cloud of mercaptans released during the incident.

Dispersion Medium

Over 80% of all incidents resulted in the contaminant being dispersed through a flowing watercourse which tends to support the higher priority given to their protection. Other contributors were dispersion into soil, the air and static water, all of which were affected in about 10% of incidents. This pattern was found in most kinds of incident, the main exception being waste incidents where soil and ground water were the media affected in a significant number of incidents. (Figure 3).

The development of EnvIDAS is ongoing, not only in terms of maintaining the database with new records but also to explore new avenues and contacts to collect better quality and more comprehensive data from relevant environmental agencies. Further work is also underway to improve the structure of the database, remove redundant fields and provide enhanced user interfaces for recording and retrieval including facilities to generate standard reports. Ultimately we would hope that the database will become more widely available.

DEVELOPMENT OF A RISK ASSESSMENT TOOL FOR WATER CONTAMINATION

As indicated in the foregoing sections contamination of watercourses feature heavily in environmental incidents. This supported the view that it was appropriate to focus our collaborative work with the Department of the Environment and NRA, towards the development of assessment methodologies, consequence models and assessment techniques for water contamination. Work commenced in 1990 to produce assessment methodologies for the determination of the nature; extent; severity and overall implications of potential major accidents which may harm the water environment. A key purpose for such an assessment tool was to assist in the predictive analysis of environmental impact from major accidents.

A comprehensive programme of work was undertaken by SRD to develop:

- Databases for ecotoxicity information;
- River specific hydrological data and processes with a relatively high potential to release dangerous substances to the environment by virtue of eg. high operating temperatures and pressures and/or capacity for exothermic reactions.

- Undertake a review of all prominent water dispersion models and select one or more for further development.

Following a review by SRD of a number of river dispersion models a model developed by the University of Newcastle (DYNUT) was selected for the risk assessment tool. This model uses a one dimensional representation of a non tidal river, where the system is formulated conceptually as a horizontal series of sections (Figure 4). Quality variations occur longitudinally as the water is transported out of one section and into the next. The model is set up to represent short term variations in flow, quality etc. so that inputs can be specified as variables in time/distance matrices. The basic model has been developed further by SRD to incorporate rate equations for processes such as volatilisation, adsorption, photolysis, hydrolysis, biodegradation and the dispersion of ionic species (Figure 5). This model has been incorporated as the river dispersion code into the first version of the risk assessment tool - PRAIRIE (Pollution Risk from Accidental Influxes into Rivers and Estuaries). It is hoped that the full details of PRAIRIE will be published in due course on conclusion of this programme of work. However, the following sections provide an overview of the technical details and specifications for PRAIRIE based on internal communications and reports produced by SRD (19, 20, 21).

About PRAIRIE

This is a newly developed assessment code for predicting the risks associated with accidental releases of hazardous materials into a river or estuary system. (NB. at the moment PRAIRIE does not include an estuarine dispersion model, however, work is currently ongoing to evaluate such a model for possible inclusion into subsequent versions of PRAIRIE). The system consists of the front end Xi Plus knowledge based menus environment which allows the user to create a set of input files which are used to both control and provide input data for the DYNUT aquatic dispersion model and its driver routine.

The tool has been designed to assist river management and of particular interest to HSE is the capability for predictive modelling of pollution incidents to allow objective assessments of possible impacts downstream and as a function of time. The user can define the release of a chemical, organic, molecular or ionic species, into the non tidal section of a defined river catchment which may contain weirs. At the initial stage of data input information is required about; the river system, simulation times, hydrological data, chemical properties, chemical release characteristics, and the optional river suspended solids load. PRAIRIE calculates the concentrations of dissolved, undissolved and adsorbed (to suspended solids) forms of the released chemical as it disperses in the river system. In the case of spills of ionic material the user needs to specify the species of interest ie cation, anion or total chemical concentrations. At the end of a calculation there are graphical and tabular output options.

The spill consequence analysis options for PRAIRIE version 1.0 are as follows:

Deterministic option

Will model the release of a chemical into the river, its subsequent chemical fate and its transport down a specified length of the river. The chemical fate (or sink) processes may be switched off by the user to provide a worst case scenario for the simulation. The inclusion of the chemical sinks gives a best estimate scenario. It is important to note that in many cases the data required for describing chemical depletion mechanisms will not be available for many substances.

A chemicals property database is built into PRAIRIE for access by the user. For selected chemicals the required data may be available to describe the measure of degradation potential, namely; first order rate constants for surface photolysis, hydrolysis, oxidation, adsorption/desorption to sediments and desolved solids and octanol/water partition coefficients.

Stochastic #1

For water quality impact assessments given a known chemical release scenario, the most sensitive river property to consider is the flow rate ($\text{m}^3 \text{hr}^{-1}$). Flow is also the most difficult river variable to measure, particularly at the point and time of release. There is therefore, a large underlying uncertainty in the flow used in the deterministic model. To account for flow variations, the stochastic #1 option has been designed to randomly vary river flows using realistic flow patterns for a specific river system. The user defines a gaussian flow profile in terms of the mean and standard deviations; and the stochastic #1 driver routine randomly samples from this flow distribution and performs a deterministic run using the sample flow and other ancillary, deterministic, data. Flows are continuously and randomly sampled and the final output file contains the results of all the deterministic runs for all flows considered. The number of samples taken are controlled by the stochastic #1 subsidiary options "-approximate" and "exact modes". In the approximate mode 25 random flows are sampled before the simulation ends and the results file is generated relatively quickly to give statistically approximate consequence data. In the exact mode the sample statistics for flow are compared with input data. If they agree to within a predetermined tolerance then the simulation ends. An upper limit of 60 samples has been set to avoid unnecessarily long simulation times. The run times are much longer for this type of calculation but the result in output file will give statistically more accurate consequence information.

Stochastic #2 option

This uses 'live data' for the annual flow variations measured at a particular gauging station to provide real flow distributions. If for example daily flow readings were taken then 365 deterministic runs are needed to compile annual statistics which requires specific and accurate hydrological data.

Each of the above options can be displayed in graphical or tabular formats. Graphical outputs include concentration versus time/distance; 3-D plots of concentration, distance, time variables and risk envelopes showing the frequency of exceeding certain threshold concentration criteria (based on annual frequencies of spills and flow conditions).

Modelling parameters.

Introduction

It is outside the scope of this paper to consider in any detail the methodologies and parameters used to define and predict the environmental fate of chemicals. These are described in the literature, which should be consulted for more specific information, for example an overview can be found in reference 22. However the following sections will describe some of the PRAIRIE modelling parameters and other factors. This information is taken from reference 21, which includes an extensive Bibliography to the work of many researchers (not referenced here) in the

field of environmental science. It is hoped that reference 21 will eventually be published on completion of the Programme of Work.

Numerical Methodology

Finite Difference Solution Scheme

The DYNUT aquatic dispersion model represents the non-tidal section of a river or stream which is formulated as a horizontal series of sections, termed meshes, or nodes (see Figure 4). Temporal water quality variation occurs longitudinally as the water is transported out of one mesh to the next.

An overall material balance for any pollutant can then be constructed by considering the following:

- advective movements into and out of the mesh.
- dispersive movements into and out of the mesh.
- additions (through sources) and removals (through sinks) of the pollutant chemical.

The one dimensional advection-diffusion equation with a source/sink terms:

$$\frac{\partial C}{\partial t} = -U(x,t) \frac{\partial C}{\partial x} + E(U) \frac{\partial^2 C}{\partial x^2} \pm S, \quad (1)$$

where

- x = distance (m),
- U = longitudinal velocity (m hr^{-1})
- E = coefficient of longitudinal dispersion ($\text{m}^2 \text{hr}^{-1}$),

The longitudinal advection term defines the bulk transport of spilled chemical, and the diffusion term defines the transport of the spilled chemical relative to the bulk movement. The terms in equation (1) are converted into finite difference form and the concentration is calculated successively downstream for each mesh point at each time step.

The users defines the number of mesh points (n) and the total river length. The mesh length is then calculated by sub dividing the total length into a series of n-1 stretches. The finite difference time step is calculated automatically using an algorithm based on the maximum river velocity and the mesh length.

There are several mechanisms which contribute to the dispersion of dissolved solutes in rivers, notably velocity shear in the longitudinal direction and diffusion in the vertical direction. These processes have been combined into a single (Mannings) equation which calculates the apparent longitudinal dispersion coefficient. This coefficient is either input by the user or calculated from Mannings Coefficient.

Boundary Conditions

A set of boundary conditions are required to define the finite difference scheme at the beginning of a simulation. These conditions are:

- a Upstream Boundary Conditions - Defines the released chemicals concentration at $x=0$ (over the simulation time duration).
- b Initial Conditions - Defines the released chemical concentration along the stretch of the river to be simulated at the start time of the simulation.

For conditions a) and b) the chemical concentrations are automatically set to zero within the Xi plus operating environment. For simplicity the user is asked to input a chemical concentration which constitutes the background concentration of the released chemical along the river catchment at all times during the simulation. The background concentration is added onto the calculated concentration during graphical and tabular generation at the end of DYNUT simulation. This total concentration is partitioned into dissolved and undissolved forms.

Hydrology

The hydrology of the simulated river stretch needs to be defined by the user. The important hydrological parameters considered by DYNUT are volumetric flow, linear velocity, and depth.

Chemical MethodologyGeneral

DYNUT has been designed to be capable to simulating a variety of river, hydraulic and environmental conditions; to provide an accurate prediction of the aquatic concentration of a chemical species (organic, molecular or inorganic) accidentally spilled into a river. A large number of chemicals can be modelled. However, the physical and chemical data required, may not always be available so the requirements for input data has been kept to a minimum consistent with obtaining an accurate simulation.

Reaction Kinetics

Organic and molecular chemicals in the environment are not only subject to physical processes such as sorption (chemical partitioning) and volatilisation but also to chemical processes such as hydrolysis, photolysis, oxidation and biological degradation. First-order reaction kinetics are assumed for all these processes. Thus the organic or molecular chemical is assumed not to radically change with river environmental or hydraulic conditions such as temperature, pH or flow. Temperature effects on reaction rates are included in the model, but diurnal or natural short term variations in temperature are ignored. To a large extent the high specific heat capacity of water will tend to keep any temperature variation to a minimum in all but the smallest rivers. For inorganic, ionic spills the only depletion process considered is that due to labile cationic exchange with suspended solid clays.

A number of simplifying assumptions have been necessary and use has been made of various correlations for obtaining physical and chemical parameters. Where information on a particular process or parameter is inadequate or not available then a "worst case" scenario is adopted. The

chemical methodology and further, more specific assumptions used in modelling the fate of chemicals spilled into a river as described in the following sections.

INITIAL SPILL ASSUMPTIONSSlick-Forming Spills

When a chemical is spilled into a river it is assumed to be uniformly distributed throughout the water column. No attempt is made to model the spreading and evaporation of low-density, immiscible liquids that form surface slicks. Many models exist that model oil slicks on the open sea and in coastal areas but these focus on spreading and drift phenomena, which determine oceanic spill movement and possible shoreline fouling. Bulk spill movement in rivers is dominated by longitudinal advection with shoreline fouling virtually unavoidable.

High Density Spills

A rapid and large spill of a high density ($>1.0\text{g cm}^{-3}$) immiscible liquid or sparingly soluble solid into a flowing river is likely to cause substantial contamination of the bottom sediments at the spill site. Since the bottom is unlikely to be a smooth surface the material may accumulate in pools or clumps and only slowly dissolve into the flowing water column such a scenario could be simulated by the model by assuming a possibly extended source leaking into the water column at some low rate determined from the solubility of the chemical and the river flow rate. However, in general any spilled chemical is assumed to be intimately mixed throughout the water column and it is assumed that turbulence in the river will break down any "globs" of immiscible chemical to a size that will remain in suspension in the river as it is advected downstream. Similarly, sparingly soluble solid materials in the form of powders or granules are assumed to be maintained in suspension by the turbulent river.

Mixing Zone

Instantaneous transverse mixing across the whole cross-section of the river at the spill site is highly unlikely to occur. There will be a mixing zone extending downstream from the spill site for some considerable distance and there are a number of methods available for determining the length of this zone. A rough rule of thumb is that the length of the mixing zone is approximately 100 channel widths though the effects of bends and lateral currents may allow practically complete mixing to be achieved within a shorter distance.

Dead Zones

In addition to the non-uniformity of chemical concentration across the river cross-section close to the spill there may be localised areas of high concentration caused by the action of eddy pools trapping chemical for a finite time before reentrainment back into the general flow. "Dead-zone" trapping results in a concentration versus time profile at downstream points with a steeper front and longer tail than is predicted in the model though it is not considered to be a source of significant inaccuracy in the model since profile peak concentration will be largely unaffected.

CHEMICAL SOLUBILITY

Once the chemical enters the river it is assumed to divide immediately into either the dissolved or undissolved phase (Figure 6). For a given chemical spill mass released into a river, the initial concentration at the spill site is found by assuming the chemical is uniformly mixed immediately downstream of the release point.

Any undissolved chemical is advected and dispersed downstream with the rest of the material in the river flow. This undissolved fraction then acts as a "reservoir" source of chemical continually replenishing the dissolved fraction as it is removed by various processes. The effect of temperature on solubility is not addressed in the model.

Co-solutes

Solubility may be affected by the presence of dissolved species. Electrolytes present in sea water (35,000 ppm) cause a reduction in solubility in most organic compounds to levels of about 70-80% of their pure water values which may be important in marine or estuarine waters. Rarely does the electrolyte content of inland water significantly affect aqueous solubility except, possibly, near waste outfalls. There is evidence that humic substances can solubilize organic compounds that are otherwise water insoluble and so modify their behaviour and activity. The binding of organic compounds and humic materials may or may not render them innocuous. The presence of dissolved organic carbon (DOC) can significantly decrease the sorption of hydrophobic compounds like DDT, maintaining them in solution and enhancing their aquatic transport properties.

CHEMICAL PARTITIONING.

The binding of a spilled chemical with the suspended solids present within the river environment is modelled in DYNUT as two distinct processes. The first process considers the physical adsorption of organic spills. The second process considers the cationic exchange of cations associated with an inorganic spill and cationic constituent of suspended smectite clays.

Organic Chemical Sorption Model

A dissolved organic chemical partitions into the aqueous phase and the particulate adsorbed phase according to its sediment-water partition coefficient, K_p . Sorption reactions are modelled in terms of a two-step process where the first step, labile sorption, is treated as an instantaneous process. The second step, non-labile sorption, is treated as a first order process where the rate constant, K_{sorp} , is related to the partition coefficient thus:

$$K_{sorp} = \frac{1}{0.03K_p} \quad (1)$$

where K_{sorp} is in units of hr^{-1} .

Labile sorption corresponds to the rapid surface adsorption (or desorption) of chemical onto or from suspended particulate and requires at most a few minutes to a few hours to occur. It depends upon the probability of chemical-particulate collisions and is promoted by the turbulent

energy in the stream. It is assumed to be rapid in comparison with other transformation processes occurring in the dissolved phase and effectively instantaneous.

(i) Partition Equations: The particulate and dissolved concentrations can be calculated from knowledge of the total dissolved concentration and the suspended sediment concentration M_s .

Typical values of suspended sediment loading, M_s , are $10-500 \text{ mg l}^{-1}$. These values are representative of rivers in the United States which tend to carry larger sediment loads than British rivers.

(ii) Desorption from Suspended Sediment: The rapidity of sorption/desorption kinetics is dependent upon there being an amount of chemical present on the labile surface of the particulate. It is estimated that 50% of sorbed organic chemical is labile and hence can instantaneously desorb back into the dissolved phase.

(iii) Desorption from Bed Sediments: Chemicals sorbed to suspended sediment particles may be deposited onto the river bed through the process of sedimentation and hence be removed from the mean current flow that is carrying the dispersed chemical downstream. Under these conditions there will be a tendency for the labile fraction to desorb into the surrounding pore-water as a result of the new equilibrium conditions.

It has been shown that strongly sorbed chemicals that settle out of suspension onto the bed tend to be captured by the benthic sediments, whereupon their release to the overlying water column is controlled by benthic exchange processes. These exchange processes, such as the activities of burrowing organisms, filter feeders and disturbance by demersal fish are relatively slow and effectively lock the chemical into the sediment for weeks. Since the model is intended for short simulations it is safe to assume that desorption and resuspension from bed sediments is insignificant.

(iv) Partition Coefficients: The partition coefficient K_p in equation (1) is only for sorption due to the hydrophobicity of an organic chemical and does not include any ion-exchange phenomena or coulombic attraction that may additionally contribute to sorption of the organic chemical to sediments. The ionisation or dissociation of the organic chemical is not considered. For neutral organic chemicals the degree of sorption to suspended sediments is dominated by the interaction with the organic carbon content (oc) of the particulate, which varies with the particular sediment type (ie. silts > clays > sands). Normalising the partition coefficient, K_p , with respect to organic carbon content one obtains:

$$K_{oc} = \frac{K_p}{\text{fraction organic carbon}}$$

However, neutral compounds are also sorbed by sediments with little or no organic carbon content such as sands or inorganic clays.

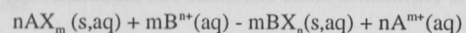
K_{oc} is correlated to the octanol-water partition coefficient, K_{ow} , which is available for many organic chemicals.

Inorganic Cationic-Exchange Model

Suspended solids in rivers and estuaries tend to have negatively charged surface sites associated with them; this means positively charged cations have the potential for being adsorbed onto the solid surfaces, whereas negatively charged anions will tend to remain in solution.

A model has been developed for cation exchange phenomena onto the clay mineral smectites (aluminosilicates), chosen because they have high ion-exchange capacities and are common in soils, sediments, and the suspended matter found in aquatic environments.

The ion exchange process is given by an equation of the chemical equilibrium type for binary exchange between a cation in the smectite and a cation in solution:



where A and B are cations of valency m+ and n+ respectively, $AX_m(s, aq)$ is a smectite-polymer exchanger with exchange cation A,

$BX_n(s, aq)$ is a smectite-polymer exchanger with exchange cation B,

and X is the exchanger surface.

The equilibrium constant for this exchange reaction can be written as

$$K_{ex} = \frac{[BX_n]^m [A^{m+}]^n}{[AX_m]^n [B^{n+}]^m}$$

The implementation of the model within DYNUT itself relies upon a number of assumptions including the following:-

- (i) The ionic strength of the river remains the same throughout the equilibration process.
- (ii) In contrast to organic adsorption the ion exchange process is very fast, hence it is assumed that equilibrium is reached instantaneously.
- (iii) There are no other cations present in the river environment that may compete for surface sites.
- (iv) The activity coefficients of all solid smectite phases found in solution are assumed to be unity.
- (v) All of the suspended material in the river, once corrected for organic carbon fraction, is assumed to be smectite or clay like. Thus adsorption mechanisms arising from the interaction of metals with oxide material (as favoured by heavy metals and iron oxides) are excluded.

Sedimentation

Suspended sediment particles and therefore any chemicals sorbed to them are transported downstream at roughly the mean current velocity. In addition, they are transported vertically

downward by their mean sedimentation velocity. Generally it is the washload (fine silt and clay-sized particles and fine sand) that carries most of the mass of adsorbed chemical.

Sediment Transport in the Model

Clay and silt particles are responsible for almost all the adsorption of dissolved chemical and hence the degree of sedimentation must be known accurately when evaluating highly hydrophobic chemicals. Sedimentation rates in the model are inferred from actual river gauging station data. The model interpolates linearly between the suspended sediment concentrations M_s , from each gauging station or sampling point.

Thus the accuracy of simulating the sedimentation process is dependent upon obtaining good field data at as many points along the river as possible. This is considered to be a more acceptable basis for modelling the process than relying on largely unvalidated empirical formulations.

CHEMICAL TRANSFORMATIONS ON PARTICULATES

Pollutants adsorbed on, or contained within, particulate solids behave quite differently - chemically, biochemically, hydro-dynamically and toxicologically - from dissolved pollutants. Sorbed chemicals may be judged to be in a micro-environment that is both less polar and a better hydrogen donor than water. Since the understanding of chemical and biochemical transformation processes by sorbed chemicals is inadequate to predict or measure the rates of such reactions for use in modelling, then it should be assumed that no transformation processes occur on particulates. Such an assumption would lead to the maximum expected chemical. Such an assumption would satisfy the requirement that a "worst case" scenario should be adopted where inadequate data exists to make an accurate judgement.

Toxic Reaction Products

The above assumption of no transformations on particulates violates the worst case scenario only when the transformation product is more toxic than the original chemical and occurs preferentially on particulate (eg the methylation of mercury). It may result in a significant overestimation of the concentration in the dissolved and particulate phases when there is significant reaction on particulates, particularly if reaction on particulate is faster than in solution.

The role of sorption is to reduce the chemicals potential for reaction by "trapping" it in a less - or non - available form. Purely in terms of the accuracy of the model, however, it is important to know whether there are reactions occurring on particulates.

Effect of Sorption on Volatilisation

Sorption will prevent a chemical being removed by volatilisation since, in inland waters where loss from aerosol formation can be neglected, only the unionised, unsorbed molecule can be volatilised across the air-water interface.

Effect of Sorption on Hydrolysis

Reactions like the neutral hydrolysis of carboxylic acid esters, in which the water molecule participates in the reaction, should be substantially inhibited by residence of the target molecule in a sorbed state.

Effect of Sorption on Oxidation

Oxidation reactions involve the formation of chemical oxidants such as the alkylperoxyl radical and singlet oxygen primarily via the interaction of sunlight, humic materials and dissolved oxygen. Except for a few substances it appears that there are no definitive studies in the literature on what effects residence in the sorbed state has on chemical reactivity.

Effect of Sorption on Photolysis

Suspended particulates influence photolysis by absorbing light and adsorbing dissolved contaminants. Sorption onto sediment may retard photolysis by quenching excited states of the molecule or may enhance photoreaction through an indirect catalytic effect (eg. photocatalysis by TiO_2).

Effect of Sorption on Biodegradation

The importance of biodegradation reactions are very difficult to assess for an acute, accidental spill scenario. Phthalate esters are highly sorbed onto sediment, thus any microbial degradation reactions occurring on sediment would be important. This is not as a result of the formation of more toxic products, since there is no evidence to support this, but simply in terms of model accuracy. However, measurements of the effects of sediment sorption on microbial degradation of phthalate esters and other non-halogenated industrial compounds indicate that sorption of toxics to suspended sediments renders the compound unavailable for biodegradation in the absorbed state.

REACTION KINETICS AND RATE CONSTANTS

The mechanisms outlined in the following sections apply to organic or molecular chemical spills only.

A number of physical and chemical processes have been identified as being important in removing or transforming a chemical that has been spilled into the aquatic environment. These are: sorption or desorption to or from particulates and subsequent sedimentation or resuspension; volatilisation into the atmosphere; chemical transformations such as hydrolysis, oxidation and photolysis; biological degradation. Sorption, or chemical partitioning is treated as a quasi-equilibrium process and has been described earlier along with sedimentation. The other removal processes are assumed to only occur to the dissolved chemical and obey first-order reaction kinetics such that:

$$\frac{dC_w}{dt} = K_{\text{tot}} C_w$$

where K_{tot} is the sum of all the removal rate constants.

Volatilisation

The transfer of pollutants from water to air is an important fate process to consider when modelling organic chemicals in aquatic environments. Volatilisation is a transfer process; it does not result in the breakdown of a substance, only its movement from the liquid to the gas phase. The methodology employed in the model assumes an unstratified well-mixed water body, which is probably valid for flowing streams. The partial pressure of the organic contaminant above the river is assumed to be zero. Although in most cases this is probably an accurate assumption but there may be certain atmospheric conditions that, along with a chemical's high vapour density, may invalidate it.

The overall volatilisation rate constant, K_v (units h^{-1}), is expressed in terms of individual rate constants for the diffusion through the liquid-film and gas-film at the gas-liquid interface:

$$\frac{1}{K_v} = \frac{1}{K_{\text{liq}}} + \frac{1}{Hk_{\text{gas}}}$$

$$\begin{aligned} K_{\text{liq}} &= \text{liquid-film rate constant, h}^{-1} \\ K_{\text{gas}} &= \text{gas-film rate constant, h}^{-1} \\ H &= \text{Henry's constant (non-dimensional form)} \end{aligned}$$

Henry's constant is the ratio of a chemical's vapour pressure to its solubility and is a measure of the fugacity of a chemical or its escaping tendency from water into the air and is thus directly proportional to volatility.

The main environmental parameters that effect volatilisation rates from flowing streams are river depth and velocity and wind speed. Two-film theory predicts that the volatilisation rate is inversely proportional to the depth and directly proportional to the turbulence in the liquid and gas phases. Liquid and gas phase turbulence are of course related to river velocity and wind speed.

The rate of volatilisation of highly volatile compounds (H greater than 0.1) tends to be dominated by the effect of diffusion of the molecule through the liquid-film. The volatilisation of these pollutants is analogous to the reaeration of oxygen in surface water. The ratio of the chemical and oxygen liquid-film transfer rates is related to their diffusivities in water.

The only unknown factor in estimating volatilisation rates of toxic organic pollutants is likely to be the value of Henry's constant, H . A great deal of information is available in the literature on Henry's constant and much of it has been compiled into data sources. It can be calculated but care must be taken that the solubility and vapour pressure values are both obtained at the same temperature and physical state.

(ii) Temperature Effects: The influence of temperature on volatilisation rates is simulated by modifying a reference reaction rate at 20°C by a temperature adjustment factor.

(iii) Effect of Weirs: The effect of weirs or small dams is to enhance the volatilisation of the chemical at that point in the river. It is a transitory effect and is modelled as a discrete process separately from river volatilisation. Only rapidly volatile compounds that are liquid-film

controlled are likely to undergo significant loss from this mechanism. It is therefore analogous to reaeration of oxygen to which considerable research has been directed.

The concept of the deficit ratio, r , is used in the model. This can be considered as a measure of the amount of liquid-film mass transfer of a relatively volatile chemical and is determined from an empirically derived equation taking into account the water quality, weir type and height. Since weir volatilisation is being modelled as a liquid-film controlled process the dissolved concentration downstream of the weir can be related to that upstream, through the deficit ratio and the water diffusivities of chemical and oxygen.

Hydrolysis

Hydrolysis refers to the reaction of a chemical with water, usually resulting in the introduction of hydroxyl function (-OH) into the molecule therefore represents one of the most important mechanisms for chemical transformation/degradation. Rates of hydrolysis are independent of many rapidly changing factors that influence other degradative processes such as the amount of sunlight present, microbial activity and extent of oxygen supply. Hydrolysis rates are influenced by pH and temperature but these change slowly and seasonally in the aquatic environment.

Oxidation

Oxidation of a compound may take place through the presence of naturally occurring oxidants in the river. These oxidants are formed photochemically in sunlit waters at low equilibrium concentrations. The important ones for oxidation of organic chemicals are alkylperoxy radical, RO_2 , at a maximum concentration of $10^{-9}M$ and singlet oxygen, 1O_2 , at a mean annual concentration of $10^{-12}M$. No information is available for the range of RO_2 concentrations, expected over the duration of a spill. This is likely to vary with concentration and origin of humic-fulvic materials present in the water and sunlight intensity.

Photodegradation

Where relevant, photolysis of organic chemicals can be modelled in PRAIRIE. However, in general photodegradation is a less significant degradation mechanism in soil and water systems because of the limited opportunity for exposure of the substance to sunlight. (See Reference 22).

Biodegradation

Biodegradation results from the enzyme catalysed transformation of organic chemicals by microbes naturally present in the environment. The complex factors influencing the biotransformation of a chemical include pH, temperature, dissolved oxygen, available nutrients, the presence of other organic chemicals (synthetic or naturally occurring) that may serve as cometabolites or alternative energy sources, and the population and type of organism capable of transforming the chemical.

Biodegradation does not necessarily occur immediately the chemical is introduced into the river. Organisms must already be present in large enough numbers to significantly degrade the toxicant (a lag often occurs if the population is too few). In addition, adaptation is necessary for the organism to produce the required enzyme to break down a newly introduced chemical.

Furthermore, a shock load of a previously unknown toxicant may kill the very organisms that would degrade it if they had time to adapt.

The assumption is made that the spilled chemical is new to the river and the environmental level of the chemical in the river prior to the spill is zero. Therefore there will be a significant acclimation time of the order of days or weeks. Since the model is intended for short simulation periods biodegradation may be neglected. Such an assumption can be considered slightly pessimistic resulting in a "worst case" scenario in terms of the expected concentration profile of the chemical.

Further work

PRAIRIE will be a useful tool to assist in the assessment of water contamination risks. Further development including the collection of additional chemical data and inclusion of an estuarine dispersion model will be progressed. There are other crucial elements which need to be considered further but separately from this development tool for example it will be essential to determine harm criteria in order to interpret the significance of outputs from the river dispersion model and in addition methodologies will be required to enable the prediction of source terms and the associated collection of event frequency data.

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The views expressed in this paper are those of the author; and except where the context indicates otherwise, are not necessarily those of HSE or any other Government Department or Agency.

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EVENTS ANALYSED BY CAUSE WHERE KNOWN

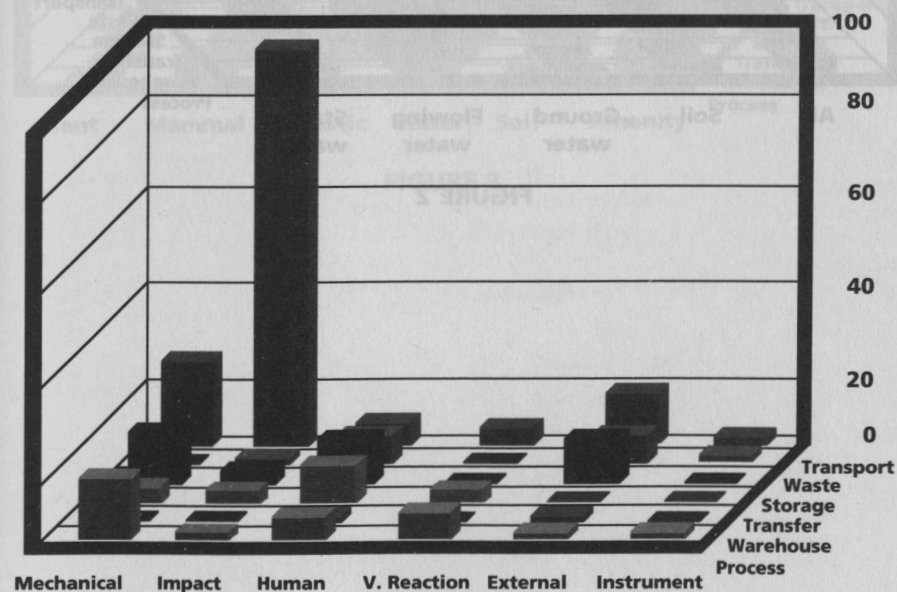


FIGURE 1

EVENTS ANALYSED BY DISPERSION MEDIUM

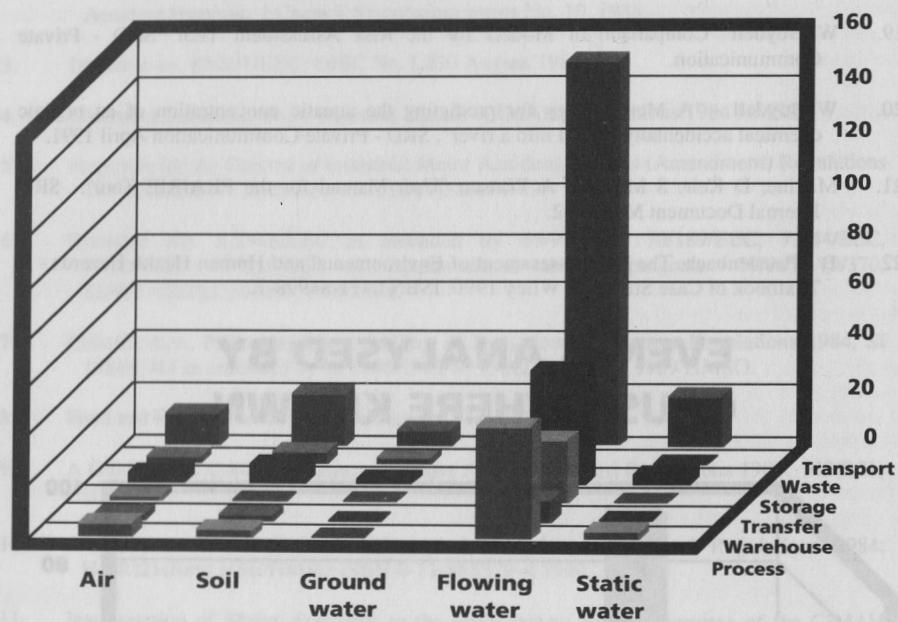


FIGURE 2

EVENTS ANALYSED BY ELEMENT AFFECTED

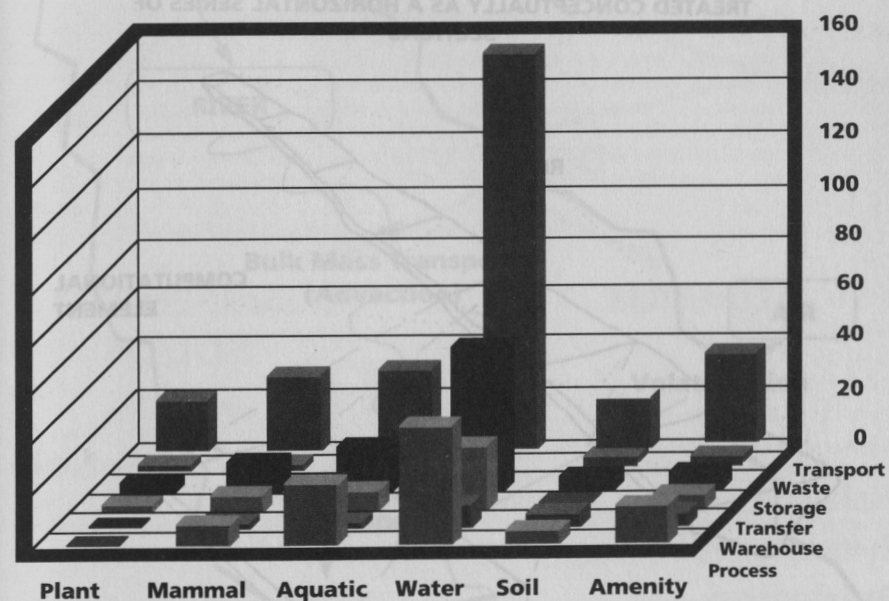


FIGURE 3

MODEL STRUCTURE

ONE DIMENSIONAL REPRESENTATION OF A RIVER -
TREATED CONCEPTUALLY AS A HORIZONTAL SERIES OF
SECTIONS

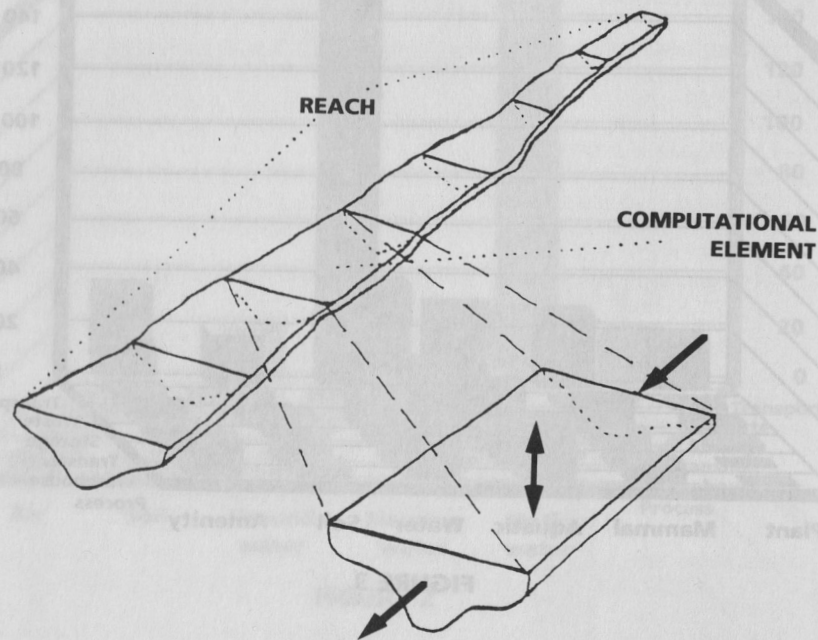


FIGURE 4

RELEASES TO SURFACE WATERS

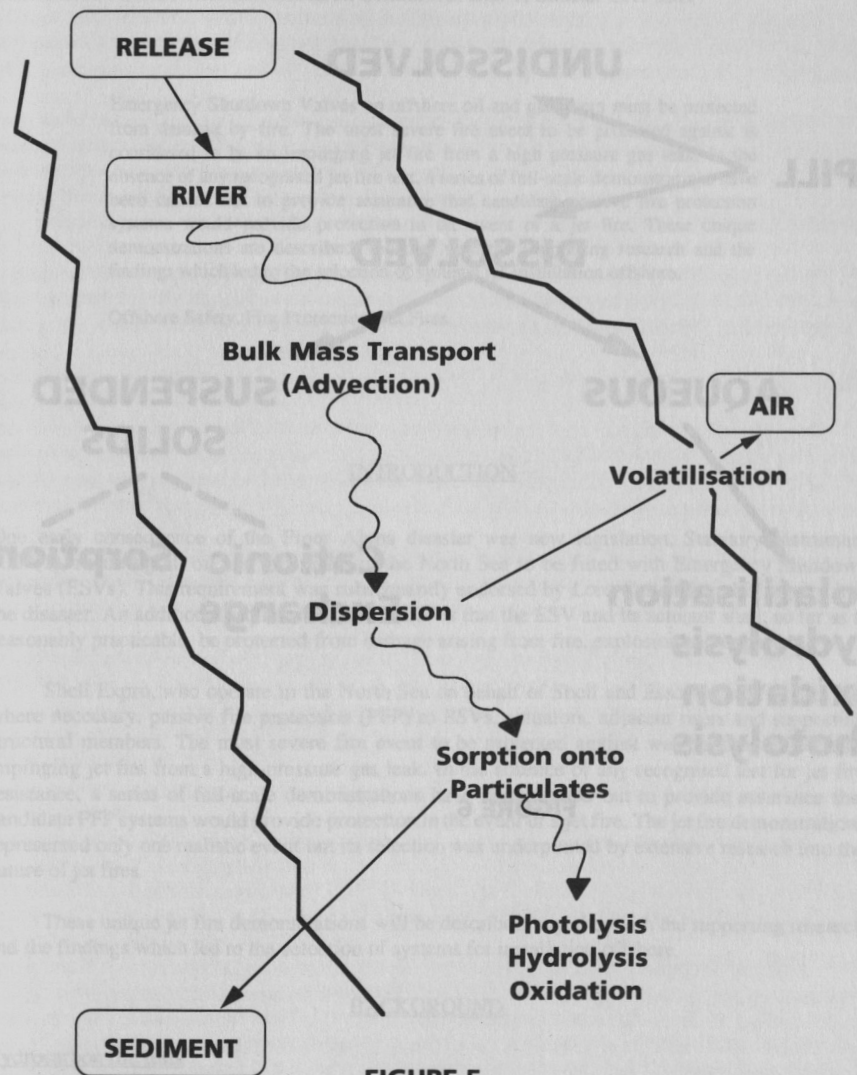


FIGURE 5

POLLUTANT FATE

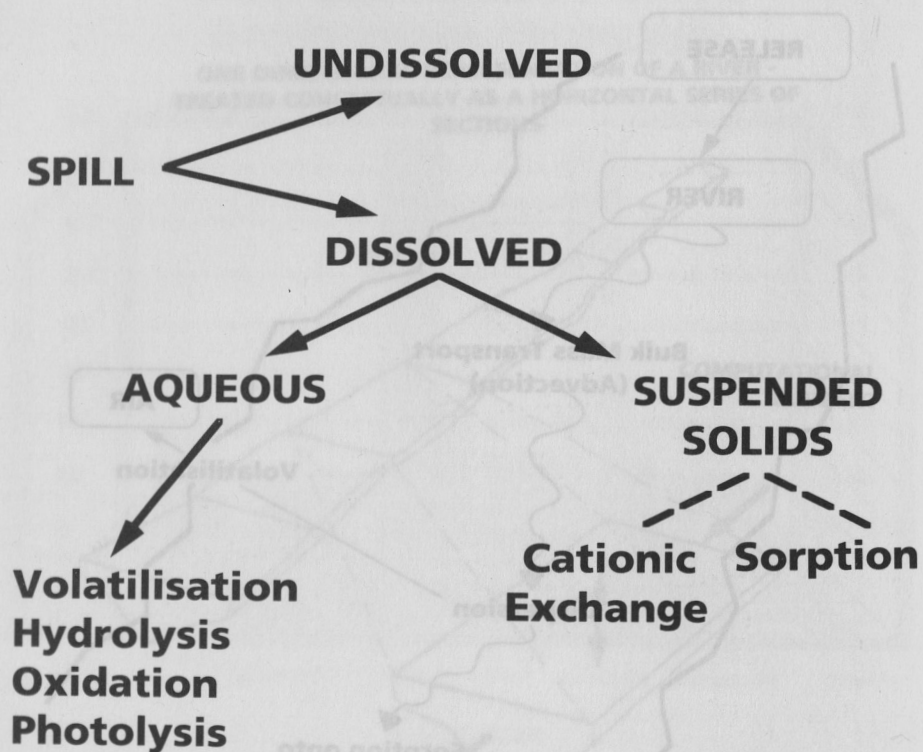


FIGURE 6

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Emergency Shutdown Valves on offshore oil and gas risers must be protected from damage by fire. The most severe fire event to be protected against is considered to be an impinging jet fire from a high pressure gas leak. In the absence of any recognised jet fire test, a series of full-scale demonstrations have been carried out to provide assurance that candidate passive fire protection systems would provide protection in the event of a jet fire. These unique demonstrations are described, together with the supporting research and the findings which led to the selection of systems for installation offshore.

Offshore Safety, Fire Protection, Jet Fires

INTRODUCTION

One early consequence of the Piper Alpha disaster was new legislation, Statutory Instrument 1029(1), requiring all oil and gas risers in the North Sea to be fitted with Emergency Shutdown Valves (ESVs). This requirement was subsequently endorsed by Lord Cullen(2) in his inquiry into the disaster. An additional requirement of SI 1029 is that the ESV and its actuator shall, so far as is reasonably practicable, be protected from damage arising from fire, explosion and impact.

Shell Expro, who operate in the North Sea on behalf of Shell and Esso, decided to provide, where necessary, passive fire protection (PFP) to ESVs, actuators, adjacent risers and supporting structural members. The most severe fire event to be protected against was considered to be an impinging jet fire from a high-pressure gas leak. In the absence of any recognised test for jet fire resistance, a series of full-scale demonstrations have been carried out to provide assurance that candidate PFP systems would provide protection in the event of a jet fire. The jet fire demonstrations represented only one realistic event but its selection was underpinned by extensive research into the nature of jet fires.

These unique jet fire demonstrations will be described, together with the supporting research and the findings which led to the selection of systems for installation offshore.

BACKGROUND

Hydrocarbon fire tests

Passive fire protection materials for use on offshore facilities are currently subjected to fire resistance tests carried out in a furnace operating under time-temperature conditions defined by a fire