



Environmental modelling of antifoulants

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Environmental modelling of antifoulants

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Antifoulants are widely used in paints on ship and boat hulls to prevent the growth of fouling organisms. Their physicochemical properties and toxicity mean that they pose a potential risk to biota in the surrounding environment. An assessment of the potential for exposure of biota to antifoulants is therefore an important part of the environmental risk assessment of antifouling products carried out by the Health and Safety Executive's Pesticide Registration Section.

Estimation of the environmental concentrations of antifouling chemicals requires a mathematical model that uses data on the leaching rate, physicochemical properties and fate of the chemical(s) and on the properties and processes of a particular environment. The available models reviewed during the course of this work were found to be unsuitable for the requirements of assessment of antifoulants for regulatory purposes and a new software model called REMA (Regulatory Environmental Modelling of Antifoulants) has been developed and validated.

The REMA software developed is based on a QWASI (Quantitative Water, Air and Soil Interaction) model using the fugacity concept. It can predict environmental concentrations of antifouling chemicals in marinas and estuaries using only leaching rates and physicochemical property data. The model was validated using existing antifouling chemicals (copper, zinc, Irgarol 1051 and diuron) and produced reasonable agreement between predicted and measured concentrations for water and sediment for two UK estuaries.

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SUMMARY

I BENEFITS

Antifoulants prevent the growth of organisms on boats and ships. A wide range of active ingredients are used including inorganic, organometallic and organic substances. Antifouling biocides are by their very nature toxic so could potentially impact other organisms. An assessment of the potential for exposure is therefore important in assessing the likelihood of environmental impact.

II OBJECTIVES

This study was performed by WRc for the UK Health and Safety Executive and Environment Agency, with the objective of developing, testing and ultimately validating a predictive model which estimates concentrations of antifouling biocides arising from boats in a variety of environments. The study was performed in three phases:

- 1) assessment of currently available models;
- 2) development of a new model; and
- 3) model validation.

III REASONS

The Pesticides Registration Section (PRS) of the Health and Safety Executive are responsible for approval of non-agricultural pesticides under the Control of Pesticides Regulations (COPR). Currently, PRS are committed to reviewing the booster biocides presently approved for use in the antifouling paints in the UK under COPR. There is therefore a need for the development of transparent and validated risk assessment strategies for antifouling products which are acceptable to the ACP, industry and other interested parties.

The Environment Agency has an interest in the potential to model concentrations of chemicals resulting from the use of antifoulants in order to target their monitoring programme. The Agency have therefore provided additional funds for this project.

IV CONCLUSIONS

The fate of antifouling biocides in the environment is dependent on a wide range of environmental and chemical properties and a variety of processes. None of the currently available models that were identified modelled these processes satisfactorily. A new model (REMA – Regulatory Environmental Modelling of Antifoulants) was therefore developed from first principals to provide predictions of antifoulant concentrations in marinas and estuaries, based on the principle of fugacity and using partitioning data obtained from laboratory experiments. Four specific estuaries were chosen and model outputs validated against monitoring data. The model has been shown to produce predicted environmental concentrations that are close to measured values for the selected antifoulants.

V RECOMMENDATIONS

It is recommended that when using the REMA model for other antifoulants or estuaries, particular attention is paid to ensure critical input parameters such as leaching rate, partition coefficients and estuarine flows are as accurate as possible to ensure best possible predictions.

The model has been validated using a limited dataset drawn from monitoring of two estuaries. If the model is applied to other estuaries, which have distinctly different characteristics, then it is recommended that further validation is carried out.

1. INTRODUCTION

1.1 Environmental Risk Assessment of Biocides

The assessment of the impact of chemicals on the environment uses data on the likelihood of exposure of organisms to the chemical and the likely effects of the chemical on an organism. This assessment is usually achieved using data obtained from a combination of experimental investigations and models that simulate the environment of interest.

The Pesticides Registration Section (PRS) of the Health and Safety Executive (HSE) is the regulatory authority in the UK with responsibility (on behalf of the Ministers) for the assessment of non-agricultural pesticides under the Control of Pesticides Regulations, 1986 (COPR). PRS has a commitment to evaluate and review environmental hazard data and produce risk assessments for consideration by the Advisory Committee on Pesticides (ACP).

Non-agricultural pesticides include wood preservatives, surface biocides, public hygiene insecticides and antifouling products. PRS have a commitment to evaluate and review environmental hazard data and produce risk assessments for consideration by the Interdepartmental Secretariat (IDS) followed by the Advisory Committee on Pesticides (ACP) prior to Ministerial consideration. Currently, PRS are committed to reviewing the booster biocides presently approved for use in the UK. Booster biocides are used in small quantities in the antifouling paints applied to the hulls of boats and ships to enhance the antifoulant properties of the paint. There is a need for the development of transparent and validated risk assessment strategies for antifouling products which are acceptable to the committees, Ministers, industry and other interested parties.

1.2 Fouling

Fouling is the successive development of a community of bacteria, protozoa, algae and invertebrates on surfaces exposed to water. When a clean surface is placed in natural water, macromolecules that are dissolved in the water form a layer on the surface; this organic layer facilitates the attachment of bacteria. Protozoa and algae then settle on the bacterial layer where they attract larvae of macroalgae, mussels, barnacles and other invertebrates.

Fouling occurs on all surfaces which are below the water line, including:

- ships hulls
- offshore constructions
- buoys and other small static objects
- mariculture equipment
- sluice doors
- harbour constructions
- inlet pipes of cooling systems
- marine sensors

Fouling occurs in both salt and fresh water but the fouling process is more rapid and intense in salt water than in fresh water. Fouling is a process with negative economic consequences; for example, fouling of ships causes an increase in water resistance and a consequent

increase in fuel demand. Biocides are therefore applied to surfaces in the form of antifouling paints in order to prevent the growth of fouling organisms.

1.3 Antifoulants

Antifoulant biocides are applied in paints as a protective top layer on a surface and the paint is formulated to release the biocide(s) slowly over an extended period of time, thus minimising fouling. In general, the majority of antifoulant paints applied are used on ship and boat hulls.

A large number of biocides are used in antifoulant paints including inorganic substances, organometallic and organic chemical compounds (Table 1.1). Antifoulant paints often contain more than one biocide, for example tributyltin oxide and copper can be combined to give good protection during sailing and mooring.

Table 1.1 Biocides used in antifoulant paint

Biocide type	Examples
Inorganics	copper cuprous oxide cuprous sulphide cuprous thiocyanate copper bronze powder copper resinate
Organo-metallics	tributyltin methacrylate tributyltin oxide (TBTO) zinc pyrithione zinc ethylenebis(dithiocarbamate) (zineb)
Organics	2,4,5,6-tetrachloro isophthalonitrile (Chlorothalonil) 4,5-dichloro-2-n-octyl-isothiazolin-3-one (Kathon, RH 287) 2-methylthio-4-tert-butylamino-6-cyclopropylamino-triazine (Irgarol 1051, Irgarol 1051) 3-(3,4-dichlorophenyl)-1,1-dimethylurea (Diuron) 2-(thiocyanomethylthio)benzothiazole (TCMTB) N-(dichlorofluoromethylthio)-N,N'-dimethyl-N'-phenyl-sulfamide (dichlofluanid)

The major types of antifouling coatings together with a brief description of their properties are outlined below. These coating types will be used when considering efficacy evaluations for antifouling products. This list is not an exhaustive one into which all product applications must be categorised. Applicants may submit novel coating types not covered in this list or they may, in some cases, wish to submit a reasoned case in support of their product application if a product cannot be readily categorised into one of these groups.

Coating type**Description and Properties****Soluble matrix
(conventional)**

In coatings of this type the biocide(s) have been physically mixed ('freely associated') into a rosin matrix. Upon exposure to seawater the slightly acidic matrix slowly dissolves releasing the biocide(s) into the water. (Seawater is slightly alkaline (pH 8) and the acidic matrix readily dissolves). Continuous dissolution of the coating surface occurs resulting in fresh biocide(s) being released until eventually the film is exhausted. The soluble matrix coatings have poor mechanical properties which limit film thickness and hence the coating lifetime is attainable to approximately 12-18 months. As the matrix rosin is a natural product, batches differ and therefore coating lifetime is unpredictable

**Insoluble matrix
(contact leaching or
long-life)**

Within this type of coating the binder or matrix is insoluble, the biocide(s) is physically mixed into the matrix (often at higher concentrations than is the case with the conventional coatings). As seawater enters the paint film the biocide(s) is released by dissolution and diffusion from within the insoluble matrix. This type of coating has a high initial release rate, which decreases exponentially with time as the biocide(s) has further to travel through the paint film. This release process continues until exhaustion of the coating. The higher mechanical strength obtained with these coatings allow applications of thicker systems and coating lifetimes of approximately 24 months are attainable.

**Ablative
(self polishing
copolymer) TBT
coatings**

In this type of coating the TBT biocide is chemically bound to the binder of the paint, a methacrylic acid/methylmethacrylate copolymer matrix into which other biocides can be incorporated. The copolymer hydrolyses at a predictable rate in seawater (depending on temperature, pH and rate of movement of a vessel through water) releasing the biocide(s) into the surrounding water, creating a localised concentration at the paint surface discouraging the growth of settling organisms. This hydrolysis results in a softening of the surface layer of the copolymer and, together with the physical wearing away of the binder by the action of passing seawater, 'polishing', exposes fresh surface layers. This mode of action with biocide release and polishing rate are both dependent on the same (chemical) process. The paint film thus smoothes, reducing drag and turbulence until eventually, through these processes, the whole of the coating is exhausted. After initial rapid release, a steady biocide release is achieved; the life of the coating is proportional to its thickness and is accurately predictable. The copolymer has a high mechanical strength, allowing build up of very thick systems and hence correspondingly long coating lifetimes, typically up to 5 years.

**Ablative
(polishing copolymer)
Tin-free coatings**

Coatings of this type rely on soluble medium, such as rosin, in combination with insoluble polymers to form a matrix which wears away *physically* at a controlled rate. The biocide(s) is mixed into the matrix and released by dissolution at a rate determined by the rate of physical ablation of the polymer. The physical ablation process is less controlled and predictable than the chemical ablation process. Therefore the steady release rate, predictable life, smoothing and recoating properties of the TBT copolymer coatings are difficult to achieve with this group of coatings. These tin-free copolymer coatings have to date demonstrated that dry docking intervals of 3 years can be achieved by the better performers within this group of coatings.

1.4 Environmental Exposure

Whilst the distribution of some antifoulants has been studied in some detail (e.g. Gough *et al.*, 1994; Thomas *et al.*, 1999), for others there is a distinct lack of usage and monitoring data. Consequently, regulators currently assess the likelihood of exposure to antifoulants using environmental fate models. Environmental fate models use mathematical equations that relate environmental input concentrations to chemical fate and transport processes in order to predict environmental concentrations, fate, transport and persistence. By making simple assumptions regarding the processes that occur in the environment and using a set of parameters that describes the environment of interest, the models can estimate the fate and behaviour of a compound in that environment.

In the UK, the fate of antifoulants is currently modelled using an approach developed by Luttk *et al.* (1992); this model is detailed in Appendix A. The input data for the model includes:- information on the flux of active ingredient over a period of time, number of yachts in a basin, mean ship deck area, volume of paint per yacht and a number of properties of the active ingredient. Results to date indicate that the model grossly over-estimates exposure concentrations for active ingredients in antifoulant paints. Possible reasons for this over-estimation include: inaccurate or unsuitable input parameters; important fate processes are ignored; the influence of environmental factors is not adequately considered.

WRc have therefore been commissioned by the UK Health and Safety Executive (with additional funding from the Environment Agency) to develop, test, modify and ultimately validate a predictive model which will calculate environmental concentrations of antifoulants arising from boats in a variety of environments. The project is being performed in three distinct phases, namely:

1. assessment of models that are currently available and are suitable, at least in principal, for modelling the fate of antifoulants;
2. adaptation of existing models or development of new models; and
3. model validation.

This final report describes the work carried out over the course of the project. The major factors that affect the environmental fate of active ingredients from antifouling paints were reviewed as well as a number of available environmental fate models. The identified models were assessed to determine their suitability for predicting exposure concentrations for active ingredients in antifoulants. On the basis of the results of the model assessment, a new model (REMA; Regulatory Environmental Modelling of Antifoulants) was developed from first principles. Experimental data was obtained using laboratory and field studies, in order to validate the developed model.

2. ENVIRONMENTAL FATE OF ANTIFOULANTS

On entering an aquatic system a chemical will be transported and distributed between the major compartments within the system, namely: sediment; water; suspended sediment and biota. The transport and distribution of the chemicals in the environment is dependent on a range of factors including the nature of the chemical and the characteristics of the receiving water.

Antifoulants cover a diverse range of chemical classes (including inorganics, organometallics and organics) and are used in a wide range of scenarios including freshwater, marine and estuarine environments. To accurately determine the fate of antifoulants, it is necessary to consider the effects of a wide range of variables and processes. A number of the important processes are detailed below.

2.1 Leaching

Antifouling biocides leach out of the paint into the water over time. The rate at which this occurs (see above) is dependent on the characteristics of the biocide and paint matrix. The amount of antifouling biocide that enters the aquatic environment will, therefore, be dependent on the leaching rate of the biocide from a particular paint type.

2.2 Evaporation

For many organic compounds, evaporation can be an important environmental pathway. Volatilisation is dependent on a number of factors including the compound's vapour pressure and solubility (which are used to derive the Henry's Law Constant, a measure of partitioning between air and water) and the hydrodynamic characteristics of a particular environment. Compounds with low aqueous solubility and a high vapour pressure will have a much greater tendency to partition to the gas phase than soluble compounds with a low vapour pressure.

Liss and Slater (1974) developed a simple model that describes the process of evaporation from the aqueous phase, through the air-water interface to the atmosphere. The model calculates fluxes of chemicals based on concentrations in the water and air phases and the Henry's Law Constant. The accurate determination of the Henry's Law Constant is often problematic (particularly for compounds with very low solubility or very low vapour pressure); hence, the calculation of fluxes is difficult for certain compounds. Fluxes are also influenced by turbulence factors in the air and water phases and so the prediction of evaporative fluxes is complex.

2.3 Sediment-Water Partitioning

In addition to affecting the volatility of a contaminant, solubility also influences the partitioning of a contaminant between the water column and stream sediment. Whilst polar (hydrophilic) compounds will tend to dissolve in the water, non-polar (hydrophobic) compounds will tend to partition to and accumulate in the sediment. The ratio of the concentration of a compound in the solid phase (C_s) to the concentration in the water phase (C_w) is the partition coefficient K_p :

$$K_p = C_s/C_w$$

The value of K_p is dependent on the sediment characteristics and the physico-chemical properties of a compound. For organic compounds K_p is primarily dependent on the fraction of organic carbon in the sediment (f_{oc}) and an organic-carbon water partition coefficient (K_{oc}) provides a better indication of the partitioning:

$$K_p = f_{oc} * K_{oc}$$

However, other factors may influence partitioning including the organic carbon type, sediment pH and dissolved oxygen content. In addition to partitioning to aquatic sediments, contaminants can also partition to suspended sediments which can then be transported long distances before being incorporated into bed sediments. Concentrations of contaminants in the water column can also be influenced by resuspension and redeposition processes, which increase the residence time and bioavailability of contaminants in the water column.

Studies have indicated that one of the critical factors in the assessment of organotin antifoulant compounds in water, sediment and food webs is the uncertainty in their partitioning behaviour. One possible reason for this is that organotins can exist in water as either cationic and/or a number of neutral species which may exhibit different partitioning characteristics. The nature and relevant proportions of the neutral and cationic species is dependent on the solution chemistry (i.e. pH, type and concentrations of anions present). Consequently, in order to assess the partitioning of organometallic compounds between water and sediment, their aqueous speciation and partitioning between water and sediment and the characteristics of the aquatic system need to be known.

Arnold *et al* (1997) have proposed a model for describing the partitioning of triorganotin compounds between water and octanol, the species and equilibria considered are illustrated in Figure 2-1.

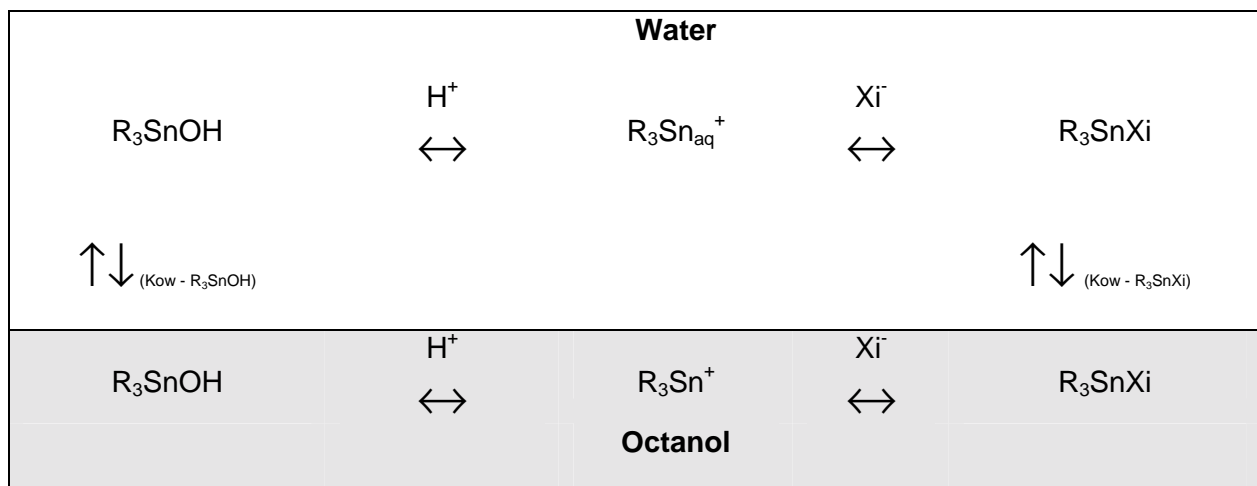


Figure 2-1 Schematic representation of the processes involved in the partitioning of triorganotin compounds in a 1-octanol-water system.

Partitioning of organotin compounds to bed sediments is further complicated by the sorption of the cationic species from aqueous solution onto mineral surfaces. Clay minerals and metal oxides bearing a net negative charge adsorb triorganotins under environmentally relevant conditions; sorption to clay minerals is thought to be due to cation exchange processes. The

type of exchangeable cations and pH are probably the most important factors controlling sorption of triorganotins in environments rich in clays and silicates.

A quantitative prediction of the sorption of organotins to natural sediments is therefore very difficult, mainly due to the heterogeneity of naturally occurring mineral surfaces and a lack of understanding of those processes controlling the interactions of organotins with organic matter. However, a very rough estimate of partitioning could be obtained by considering only adsorption of the organotin cation to mineral surfaces and the partitioning of neutral hydroxyl species into organic matter using the following equation:

$$K_d \text{ tot} = K_d \text{ min} + K_d \text{ oc} = f_{\text{min}} * K_{\text{min}} + f_{\text{oc}} * K_{\text{oc}} \quad \text{Equation 1}$$

Where:

- K_d = the sediment : water partition coefficient;
- K_{d min} = the sediment mineral : water partition coefficient;
- K_{d oc} = the sediment organic carbon : water partition coefficient;
- f_{min} = the weight fraction of minerals bearing negatively charged surface sites (e.g. clay minerals, silica, manganese oxides);
- K_{min} = adsorption coefficient of organotins at such minerals;
- f_{oc} = the fraction of organic carbon and
- K_{oc} = the partition coefficient into organic carbon.

2.4 Interactions with Dissolved Organic Matter

A number of studies have indicated that sediment-water partitioning observed in the field can not always be replicated by laboratory experiments or by predictions. One cause of these differences is the effect of dissolved organic matter (DOM). DOM has been shown to increase the effective solubility of some compounds, probably resulting in a reduction in partitioning to suspended sediments, bed sediments or air. Possible effects of DOM include the incorporation of contaminants into micelles, the lowering of water surface tension, or direct partitioning of a contaminant between the water and organic material. Binding of contaminants to DOM is related to their octanol-water partition coefficient (K_{ow}).

Natural organic matter in the aquatic environment covers the complete spectrum in water from dissolved organic macromolecules (such as humic and fulvic acids and polysaccharides) through colloidal material to microparticulates. These forms are mainly composed of carbohydrates and peptides originating from micro-organisms and plants. The presence of DOM, colloidal material, macromolecules and microparticulates can all effect the partitioning of contaminants (particularly those with low solubility).

2.5 Degradation

Following its release into the environment, a chemical may undergo various chemical reactions (abiotic degradation) or biochemical reactions (biotic degradation) or a combination of both. In order to characterise and quantify the degradation it is necessary to distinguish between the various types of reactions and processes.

2.5.1 Abiotic degradation

The most common abiotic degradation processes are photochemical degradation, redox reactions and hydrolysis.

Hydrolysis involves the attack of a compound by a water molecule or hydroxide ion. Hydrolysis is most common in organic compounds with ester, epoxide, alkyl halide, amide, carbamate or organophosphate groups.

For primary photochemical degradation to occur, the emission spectrum of the sun needs to overlap with the absorbance spectrum of the pollutant (although some compounds photodegrade even when this fit is not observed). Photodegradation is dependent on the intensity of light reaching an aquatic system and the dispersion within that system, once contaminants reach the deeper zones of aquatic systems or become associated with sediment they are probably resistant to photodegradation.

2.5.2 Biotic degradation

Biodegradation by aquatic micro-organisms can play an important role in the removal of organic pollutants from a system. In aerated water columns and in oxic surface sediment, biodegradation will proceed aerobically. However in anoxic sediments, anaerobic biodegradation is the most important process. In order to quantify the biodegradability of a chemical in an aquatic system it is necessary to determine the rates of anaerobic and aerobic degradation and to determine the distribution of the chemical between the water column, surface sediment and the bottom sediment.

2.6 Kinetics

The distribution of a compound in an aquatic system at any moment in time will also be influenced by the rates at which the physical, chemical and biological processes described above occur. This information is probably critical for assessing the distribution of a pollutant pulse caused by, for example, a spill. However, information on the rates of a number of the processes is probably not necessary for determining the fate of chemicals that are discharged continuously, such as antifouling biocides.

2.7 Prediction of Fate

In order to predict accurately the fate of antifouling biocides in the environment it is therefore necessary to consider a number of processes and chemical and environmental properties. This can be achieved using environmental fate models that are made up of a collection of mathematical equations that describe the processes.

3. ENVIRONMENTAL FATE MODELS

Environmental fate models use combinations of mathematical equations to relate environmental input concentrations to chemical fate and transport processes in order to predict environmental concentrations. If assumptions are made concerning the processes in the environment, the models can theoretically predict the behaviour of a compound using a set of parameters that describe the environment of interest and the physico-chemical properties of the contaminant.

3.1 Types of Models

Models are developed to predict the overall fate and transport of a substance in a whole environment or in more detail in a sub-component of the whole environment. A wide range of models are available which have been developed for a number of uses and environmental scenarios. These include:

- whole-environment models: predict the concentration of a chemical in every environmental compartment.
- surface water models: concentrate on surface water processes and deal with water, biota and sediment as the main environmental phases; they can include interactive processes with other environmental phases.
- run-off models: compute chemical concentrations in runoff water from land.
- soil fate models: predict the fate of a compound in soil; a number of soil compartments are usually included in the model, including organic soil matter, inorganic soil matter, soil pore water and root material.
- groundwater models: predict the fate and transport of a chemical within a groundwater flow.
- atmospheric models: predict the effect of atmospheric processes on the distribution of chemical pollutants.
- process models: predict the fate of a compound during an environmental process; the models are often used as sub-models within larger models (e.g. whole environment models or surface water models).
- biotic models: express mathematically the processes by which organisms interact with the environment. Processes that are modelled include the absorption of a compound during respiration or via ingestion and the release of compound via metabolism and egestion. Examples of biotic models include a single fish bioaccumulation model or a whole food web model. The models can be used to relate tissue concentrations to concentrations in water, sediment, soil and air.

- pharmacokinetic models: used to model the distribution of a compound within an organism. The approaches used calculate the disposition of a compound between tissues in an organism as it is transported via diffusion or blood flow. These models are used extensively in the pharmaceutical industry.
- exposure models: used to determine exposure experienced by humans and other organisms; normally multimedia in nature.

3.2 Modelling Concepts

The mass balance equation states that the change in inventory of a chemical in a particular compartment (e.g. a river or soil) will equal the sum of inputs to the compartment less the sum of the outputs. The inputs can include advective flow, diffusion from other compartments, direct discharges or formations from other chemical compounds. Outputs may include flow, degradation processes and diffusion to another compartment. In order to model the fate of a compound in the environment, it is necessary to develop expressions, equations or quantities for each of the terms in the mass balance equation.

Environmental compartments such as water or surface sediment are usually considered to be well mixed and thus fairly homogeneous in concentration. If more detailed modelling is required (e.g. to account for spatial variability in sediment characteristics), a compartment can be split up into further compartments. As the number of compartments increases, the predictions probably more closely reflect behaviour in the real environment. However, the mathematics become considerably more complex and more input data is required.

Transport and transformation processes, such as evaporation, sedimentation, biodegradation or photolysis, can be described by a series of equations. However, these equations can vary with changes in variables such as temperature, pH, (sun)light intensity or microbial activity. Whilst reliable data for inclusion in these equations can be obtained from laboratory experiments performed under controlled conditions, relating these to the real environment is often problematic.

Inputs of a contaminant into a compartment are determined by the discharges to the compartment (which may be from adjacent compartments, industrial sources, spills or leaching from groundwater). The magnitude of the discharge rate influences the chemical concentration and thus its fate.

Once the rates or rate expressions are defined for the various terms in the mass balance equation for a particular compartment, the equations can be solved to provide estimates of environmental concentrations of a contaminant. Concentrations can be determined either at equilibrium or at a moment in time. Concentrations of a chemical at equilibrium can usually be determined based on knowledge of the partition coefficients of the chemical. To calculate environmental concentrations at a moment in time, rate constants for the different processes determining fate are required.

3.3 Identification of Fate Models and Assessment

A literature review was performed using WRc in-house and external databases to identify models that are currently available for assessing the fate of chemicals in aquatic systems. In

addition, an Internet search was conducted to identify other models that are not cited in the literature. On the basis of these searches, 22 models were identified.

Information and, where possible, the software for each of the models was obtained. The models were then assessed against a number of criteria in order to determine their suitability for modelling the fate of antifouling biocides. The criteria were that the model:

1. must provide acceptably accurate predictions for all antifoulant types with different properties, namely inorganics, organometallics and organics;
2. should cover the major factors and processes that determine the fate of each antifoulant type in an appropriate manner;
3. should be simple to use and allow simple, interactive processing of results;
4. input data requirements should not be unduly complicated and should be readily available to the Health and Safety Executive;
5. approach should be appropriate, clearly defined and soundly based for all of the antifoulant types;
6. source code should be obtainable;
7. should have been validated for at least some antifoulant biocides.

A brief summary of each of the models is given in Section 3.4 and the results of the model assessment are summarised in Table 3.1 and discussed in Section 3.5.

3.4 Available Models

3.4.1 Fugacity models

These use the concept of fugacity to describe how an organic compound partitions between a number of environmental compartments. The fugacity of a chemical in a given phase can be regarded as its tendency to escape from that phase to another. Consequently, when two phases are at equilibrium, their fugacities are equal (Mackay *et al*, 1983, 1986).

There are a number of fugacity (sometimes referred to as Mackay) model levels, the complexity of the model increasing with level.

Level 1 fugacity model

This model assumes a single input of a chemical into a non-reacting system. The compartments are at steady-state equilibrium and no flow occurs.

The model calculates the amount and concentration of a contaminant in each environmental compartment on the basis of a number of input parameters, namely environmental temperature, solubility, Log Kow and vapour pressure.

Level 1 calculations provide a rough guide to the likely environmental distribution of a contaminant within an ecosystem.

Level 2 fugacity model

Level 2 calculations represent a situation where a compound is present in an equilibrium steady state flow system. The compartments are in equilibrium with each other and there is a constant inflow of the compound into the system, as well as reactive and mechanical removal processes. The model calculates specific and total reaction rates and percentage transformations. In addition to the properties required for a Level 1 calculation, the Level 2 model requires the input of data concerning emissions into the system, first order reaction rates and advection currents.

The approach provides a rough guide to environmental persistence and the effectiveness of removal processes in the various compartments. Some studies have indicated that level 2 model predictions for some contaminants are within an order of magnitude of measured values.

Level 3 fugacity model

The level 3 calculations model a non-equilibrium steady state flow system where there is transport between the various compartments as well as continuous input and removal processes. The model predicts the effects of intercompartmental transport on the partitioning and persistence of a contaminant, but chemical inputs must be specified for each compartment. Predictions of the fate of a contaminant are more realistic since a non-equilibrium situation is modelled.

Level 4 fugacity model

Level 4 involves both a non-steady state flow and a non-equilibrium system. The model can be used to assess the long term partitioning of a contaminant and ecosystem recovery after releases of contaminants have stopped.

QWASI

Quantitative Water, Air, Sediment Interaction (QWASI) fugacity models are modified versions of the Mackay models. Compartment parameters are altered to realistically simulate an environment at a specific location in order to obtain at least semi-quantitative predictions of local chemical fate.

3.4.2 EXAMS

The Exposure Analysis Modelling System (EXAMS) was developed by the United States Environmental Protection Agency (USEPA) to evaluate the behaviour of a contaminant and its transformation products in the aquatic environment. The system uses differential equations to represent loadings, transport and transformations, as well as the principle of conservation of mass in order to calculate the fate of a chemical. The model can be used in a steady state or

dynamic mode which allows the use of 3 temporal models within the model framework, namely:

- steady-state analysis - long term consequences of continued chemical releases
- initial value problems - detailed examination of immediate consequences of chemical releases
- intermediate-scale resolution of events over a period of years - including seasonal data, effects of variable loadings.

An environment can be modelled using a maximum of 25 aquatic compartments but air and biota are not included. Air is regarded as a chemical sink whilst contaminants taken up by biota are considered a part of the water column.

Four sets of data are required for an individual simulation; these are - chemical data, environmental data, information on loadings and on products. The model requires extremely detailed information in order to utilise fully its capabilities. This includes information on ion and species-specific rate constants, light absorption across a wide range of wavelengths and quantum yields for individual ions and species.

Detailed information is also required on the compartment (environmental) parameters in order to utilise fully the system. These values include - latitude, longitude, altitude, atmospheric ozone concentration and climatic conditions.

The model calculates the distribution of a contaminant, including the mass, percentage and concentration in each compartment. The program allows the results to be presented graphically including vertical and longitudinal concentration profiles and kinetic data plots.

3.4.3 WASP5/DYNHYD5

The Water Quality Analysis Simulation Programme (WASP5) is a USEPA generalised modelling framework that simulates contaminant fate in surface waters. Based on a flexible compartment modelling approach, WASP5 can be applied in 1, 2 or 3 dimensions. The programme is designed to permit easy substitution of user-written routines into the programme structure. The model has been used to study biochemical oxygen demand, dissolved oxygen dynamics, bacterial contamination and the movement of toxic chemicals. DYNHYD5 is a simple hydrodynamic model that simulates variable tidal cycles, wind and unsteady inflows. It produces output files that can be linked to WASP5 to supply flows and volumes to the water quality model.

3.4.4 SMPTOX

The USEPA regulatory programme sponsored the development of an interactive computer programme for performing waste load allocations for toxics. This programme is known as Simplified Method Program - Variable Complexity Stream Toxics Model (SMPTOX). The model provides user-friendly access to a technique for calculating water column and stream bed toxic substance concentrations from point source discharges into streams and rivers. It predicts pollutant concentrations in dissolved and particulate phases for water column and bed sediments and total suspended solids. It contains a full screen editor to facilitate the entry

and modification of inputs; separate simulation routines are provided for model calibration, waste load allocation and sensitivity analysis. High resolution graphics of the model results are given during the programme operation.

3.4.5 CHEMSEE

CHEMSEE is a flexible “model construction kit” for the modelling of chemical processes in lakes. Underlying the programme is the mathematical description of the behaviour of a substance in terms of a one-dimensional vertical model. Such a model, in which horizontal concentration differences are neglected, is suitable for the description of reactive substances in deep lakes. Any number of variables can be defined by the user to represent concentrations of substances in the water column and sediment. Transport and transformation processes (e.g. loading, adsorption, sedimentation, air-water and sediment-water exchange and chemical reactions) can be defined interactively. The programme can be applied in the following ways:

- set up of dynamic models using information on a system of interest
- discrimination between different hypotheses that explain measured concentrations of substances of interest
- identification of relevant transport and transformation processes

3.4.6 CemoS

CemoS is a programme for estimating exposure concentrations of hazardous chemicals. It is based on the fugacity approach but uses partition coefficients instead of fugacities. The model calculates steady state concentrations in water, air, soil, sediment, suspended solids and fish and assumes that equilibrium is reached immediately. All compartments are regarded as homogeneously intermixed.

3.4.7 E4CHEM

The Exposure Estimation for Potentially Ecotoxic Environmental Chemicals Programme describes the fate and behaviour of compounds in the environment. A number of environmental compartments are modelled.

3.4.8 CE-QUAL-W2

CE-QUAL-W2 is a 2 dimensional (longitudinal/vertical) hydrodynamic and water quality model. It has been successfully applied to over 100 systems, including rivers, lakes, reservoirs and estuaries. The current version includes only eutrophication related water quality state variables. However, the inclusion of the variables required for modelling the fate of antifoulants is probably relatively straightforward.

3.4.9 ICM/TOXI

ICM/TOXI can be used for 1, 2 and 3 dimensional applications. Unlike CE-QUAL-W2, ICM/TOXI does not include hydrodynamics. Instead, the model takes flows and diffusivities generated by a chosen hydrodynamic model and uses these to drive the transport algorithm. Both the water column and bed sediments are modelled and various chemical species and phases are accounted for through equilibrium partitioning. The model has the option to either compute a dynamic solids balance (for three classes of solids) within the water column and bed or to read in suspended solids information and the associated water column bed fluxes from the external sediment transport model CH3D-SED. It includes the kinetic algorithms in the USEPA's TOXIWASP for contaminants but is more state of the art, in terms of the transport algorithms than WASP. The programme is also more flexible. The software, however, is not available at present since it is currently under test and the associated documentation is being prepared.

3.4.10 RECOVERY

RECOVERY is a screening level model for contaminants; it is much simpler than ICM/TOXI and easier to use. It assumes a zero dimensional, fully mixed water column, so no hydrodynamic information is required. It is a simple point model and requires information on residence time in the water column. It uses a steady state solids balance for sediments and water column and the bed is modelled as a single column with 1.0 cm layer. RECOVERY is a PC-based model with a graphical user interface.

3.4.11 TOXFATE

From the limited amount of data available on this model, it appears to be similar to WASP4 i.e. it calculates in some detail the aquatic fate of organic pollutants. However, unlike WASP4, TOXFATE uses a less complex chemical transformation procedure (e.g. only neutral organic compounds are considered) and biological uptake is calculated directly by the model. Fish, plankton and plant bioconcentration processes are considered separately and are calculated using terms such as faecal deposition of plankton, fish predation rate on plankton, and respiration rates. TOXFATE models the main processes that affect chemical fate.

3.4.12 MICHIV

MICHIV is a simple, interactive, steady-state model for simulating the fate of organic chemicals and metals in rivers. The model considers transport and transformation by first order kinetics of dissolved and sorbed chemical species. Both the water column and benthic sediments are included in the model. Benthic exchange includes deposition and scour, as well as pore water diffusion. Sorption is modelled by equilibrium partition coefficients.

3.4.13 GEOTOX

GEOTOX is a comprehensive multimedia compartmental fate and exposure model that calculates chemical partitioning, degradation reactions and non-diffusive inter-phase transport. GEOTOX models air, aerosols, biomass, upper and lower soil, ground water, surface water and sediments in an area the size of a US region. These media are made up of

sub-phases of gas, liquid and solid. Chemical partitioning between compartments, interphase transport, reactive and advective loss rates are described by first-order rate constants. The model can be applied to defined regions to constant or time-varying chemical sources.

3.4.14 SMCM

The Spatial Multimedia Compartment Model (SMCM) describes the fate of chemicals in a conventional air-water-soil-sediment system under steady-state or unsteady-state conditions. It has the unusual feature that it allows for concentration variation with depth in the soil and sediment i.e. these compartments are not treated as well-mixed 'boxes'. Whilst the approach is relatively complex, the results are probably more relevant to the 'natural environment'. The model is 'user friendly' with the capability of presenting data in tabular or graphical form.

3.4.15 ENPART

ENPART (Environmental Partitioning Model) is a first-level screening tool for new and existing organic chemicals. It is a fugacity-based approach that estimates steady-state equilibrium or dynamic partitioning among environmental compartments. It identifies dominant pathways, data gaps and estimates the chemical's persistence and bioconcentration potential.

3.4.16 TOXSCREEN

TOXSCREEN is a time-dependent, multimedia model designed to assess the potential for environmental transport and accumulation of chemicals released to air, surface water or soil. The approach is modular and incorporates intermedia transfer processes.

3.4.17 MINTEQA1

MINTEQA1 is an equilibrium metal speciation model applicable to metallic contaminants in surface and groundwaters. It calculates the equilibrium aqueous speciation, adsorption, gas-phase partitioning, solid-phase saturation states and precipitation-dissolution of 11 metals (As, Cd, Cr, Cu, Pb, Hg, Ni, Se, Ag, Tl and Zn).

3.4.18 AQUATOX

AQUATOX is a risk model that represents the combined environmental fate and effects of conventional pollutants. It can be used to model pollutants such as nutrients, sediment and toxic chemicals in aquatic ecosystems.

AQUATOX has been implemented for streams, ponds, lakes and reservoirs and models the partitioning amongst organisms, detritus, inorganic sediments and water. It considers several trophic levels, including algae, aquatic vegetation, invertebrates and fish.

The fate portion of the programme is particularly applicable to organic toxicants where volatilisation, hydrolysis, photolysis, ionisation and microbial biodegradation are all considered.

The current version runs in Microsoft Windows and provides flexibility by allowing additional compartments to be added to the model.

3.5 Overview of Models

The assessment process demonstrated that none of the models identified met all of the required criteria listed in Section 3.3. Whilst some of the models would be suitable for modelling the fate of antifouling biocides, the information required and their complexity make them unsuitable for routine use. For many of the models, it is not known whether the source code is available and if it were, there may be copyright issues that prevent its free use by a third party. This is an important issue because there is a requirement for the antifoulants model to be freely available to any user.

It was therefore decided to develop a new model that draws upon processes and features that were identified to be important and useful during the survey of models.

During the course of this project, a model was developed by Delft Hydraulics for CEPE (European Council of Paints, Printing Inks and Artists Colours Industry) to predict the environmental concentrations of marine antifoulants (CEPE 1999). This model was called MAM-PEC (Marine Antifoulant Model to Predict Environmental Concentrations). This model uses five defined marine environments (although others can be added) and models the environmental fate of antifouling biocides. The model operates using a graphical interface within the Windows operating system and has been validated using existing monitoring data for antifoulants.

Table 3.1 Assessment of available environmental models

Model	Covers all classes	Factors/ processes modelled	Simple to use	Input data available	Appropriate modelling approach	Source code availability	Validation
Fugacity Level 1	-	-	+	+	-	+	+
Fugacity Level 2	-	-	+	+	-	+	+
Fugacity Level 3	+/-	+	+	+	+	+	+
Fugacity Level 4	+/-	+	+	+	+	+	+
QWASI	+/-	+	+	+	+	+	+
EXAMS	+	+	-	-	+	+	+
WASP5/DYNHYD5	+	+	-	-	+	+	+
SMPTOX	+/-	+/-	+	+	+/-	+	+
CHEMSEE	+	+	?	?	?	?	+
CemoS	-	-	+	+	-	?	?
E4CHEM	+/-	+	?	?	+	?	?
CE-QUAL-W2	-	-	+	-	-	?	?
ICM/TOXI	+	+	?	?	+	?	?
RECOVERY	+	+/-	+	+	+/-	?	+
TOXFATE	+	+	?	?	+	?	?
MICHRIV	+/-	+	?	?	+	?	?
GEOTOX	+/-	+	?	?	+/-	?	?
SMCM	+/-	+	+/-	+	+	?	?
ENPART	-	-	+	+	-	?	?
TOXSCREEN	?	?	+	+	?	?	?
MINTEQA1	-	+ *	-	+/-	+ *	+	+
AQUATOX	+	+	-	?	+/-	?	?
MAM-PEC	+	+	+	+	?	?	-/+

+ probably satisfactory +/- possibly satisfactory - unsatisfactory ? not known * for metals

4. FIELD SURVEYS

4.1 Introduction

As part of the model validation study (Chapter 6), field samples were collected from two of the modelled estuaries with a high degree of boating activity (Orwell; Figure 4-1 and Hamble; Figure 4-2).

Samples of water and sediment were taken from various points in the estuary and connected marinas. The samples collected were analysed for diuron, Irgarol 1051, copper and zinc.

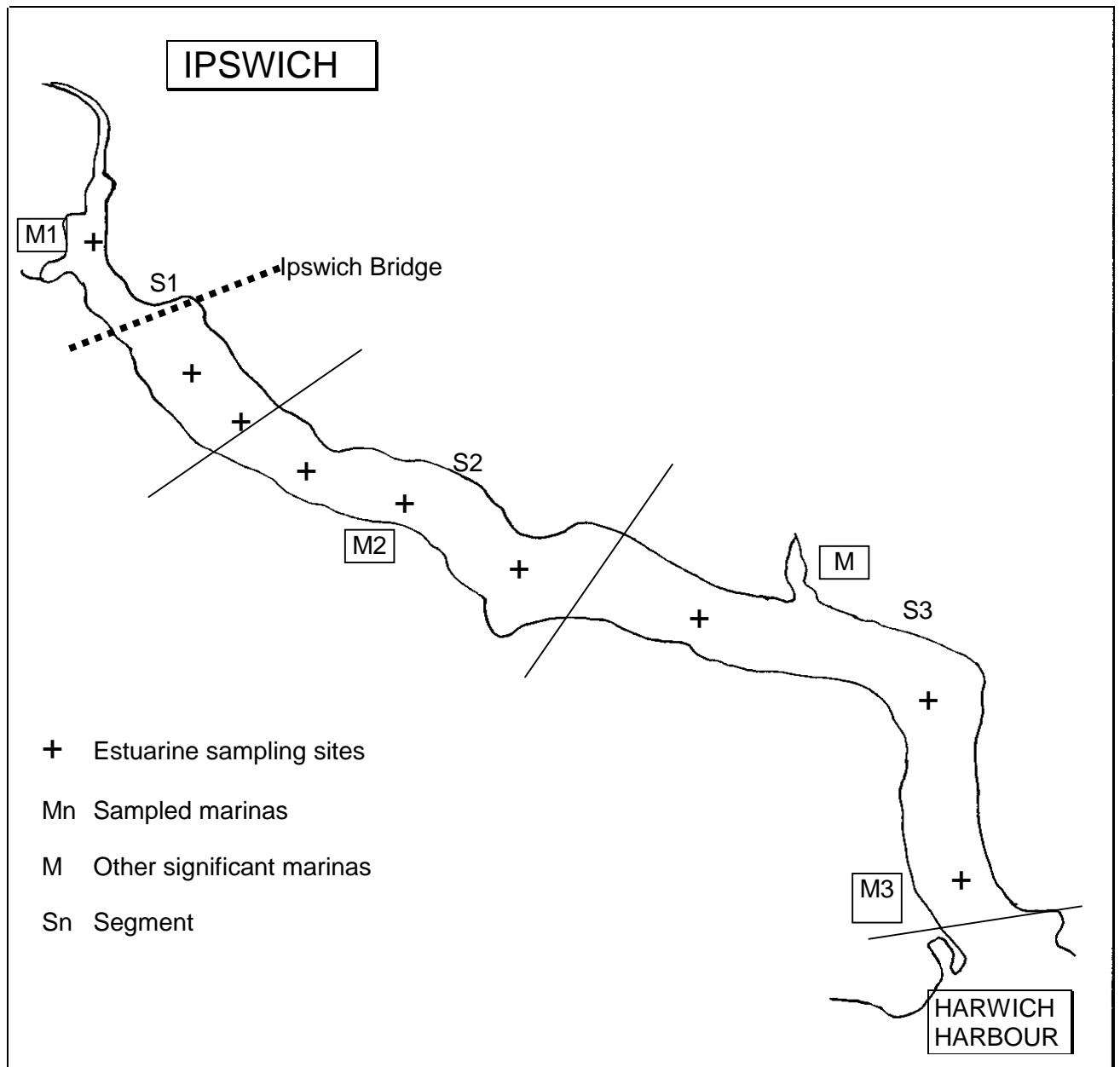
4.2 Sampling

In order to obtain extreme values for the purpose of model validation, sampling was carried out when boating activity was at its maximum (August 1998) and minimum (February 1999).

Samples were collected from sites located in the estuary, as well as from within marinas. These sites were selected to best represent the segments defined in the model, this required each estuary to be divided into upper (S1), middle (S2) and lower (S3) sections each of which had an associated marina.

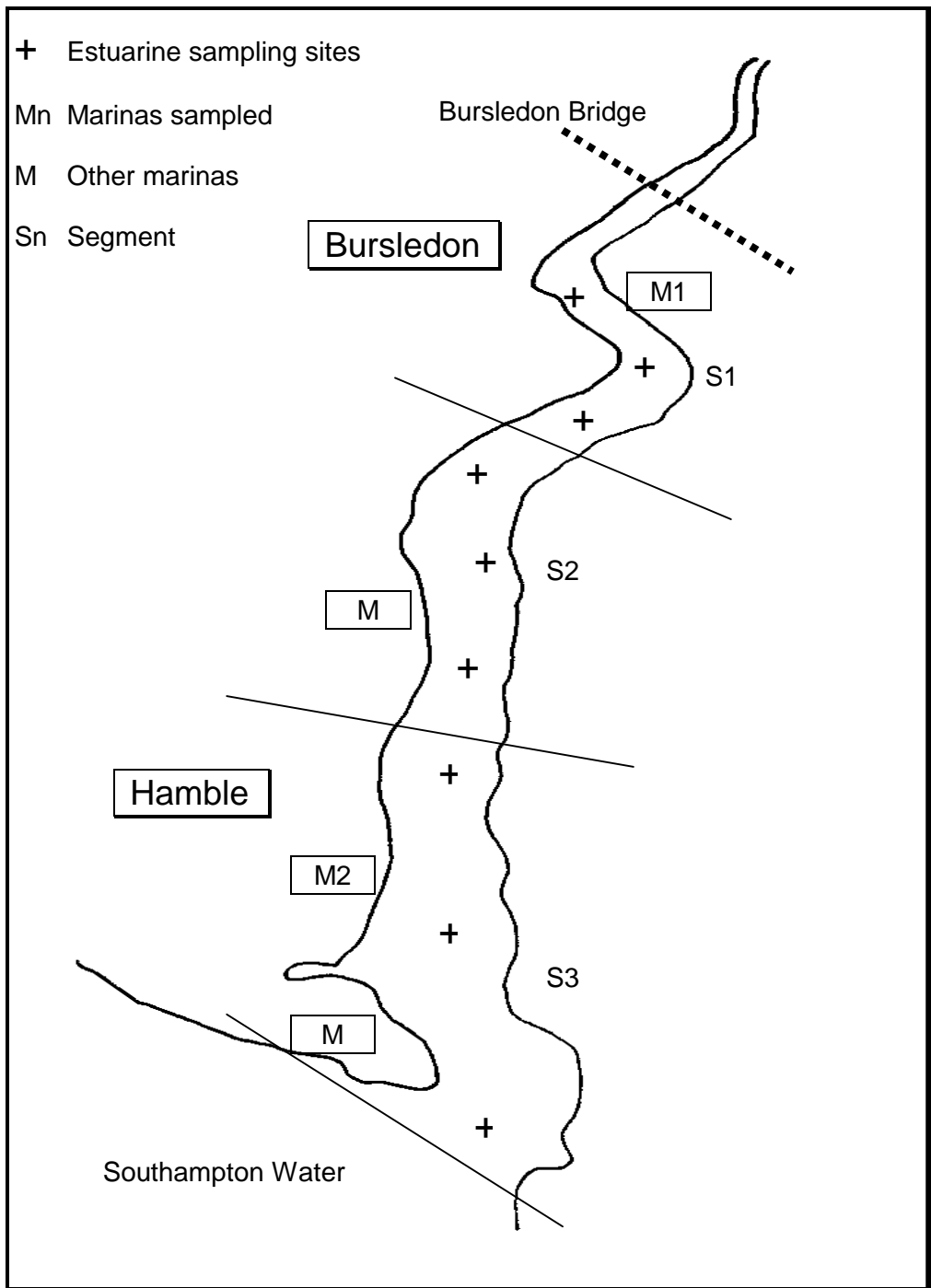
4.2.1 Orwell

Sampling points on the Orwell estuary are shown in Figure 4-1. Three marinas were sampled in the Orwell estuary; a locked marina (Shotley Point), one built within a natural inlet (Fox's) and one situated within the estuary using pontoons (Woolverstone). For the purposes of the model, each marina was located in one of the three defined sectors. Three samples were collected from different parts of each marina on the two sampling occasions. The areas sampled included slipways where antifoulant paint may have been power-washed off boats and into the marina, as well as more remote parts of the marina. Three estuarine samples were collected from each of the three sectors extending from Felixstowe docks at the mouth of the estuary, to Ipswich docks not far from the freshwater interface (a total distance of approximately 15 km). For the summer survey, samples were taken at low and high water to identify potential diurnal variations in dissolved concentrations.



Segment	Segment Code (Sn)	Associated Marina	Marina Code (Mn)
Upper segment	S1	Fox's	M1
Middle segment	S2	Woolverstone	M2
Lower segment	S3	Shotley Point	M3

Figure 4-1 Map of sampling points on Orwell Estuary



Segment	Segment Code (Sn)	Associated Marina	Marina Code (Mn)
Upper segment	S1	Swanwick	M1
Middle segment	S2	n/a	n/a
Lower segment	S3	Hamble Point	M3

Figure 4-2 Map of sampling sites on Hamble Estuary

4.2.2 Hamble

Sampling points on the Hamble estuary are shown in Figure 4-2. Boat density within the Hamble estuary (maximum 3000 boats), was so high that there was little difference between the marinas sited on pontoons within the estuary (e.g. Mercury, Hamble Point, etc) and the open water. Three samples were taken from different pontoons within Hamble Point Marina at the mouth of the estuary and Mercury Marina near the freshwater interface at Bursledon. Mid-estuarine samples were collected at 9 sites, roughly equi-distant from Hamble Buoy (within Southampton Water) up to Bursledon Bridge near the freshwater interface, (approximately 6 km upstream). Given the relatively small riverine input to the estuary, samples were only collected during one state of the tide (around high water).

4.2.3 Sampling procedure

Water samples for analysis for Irgarol 1051 and diuron were collected using 1 litre Pyrex glass bottles with PTFE lined screw caps (Duran Ltd). Sediment samples (250 g) were obtained using a sediment grab and placed in 250 ml glass bottles. All glassware was rinsed with methanol and deionised water prior to use. Samples were stored at 4°C prior to analysis. Water samples (approximately 250 ml) for trace metal determination were filtered onsite through acid washed 0.45 µm Gelman PVDF disposable filters (BDH-Merck) into acid washed LDPE bottles (Nalgene). Samples were preserved with high purity concentrated nitric acid (AristaR, BDH Merck), at a concentration of 2 ml of acid per litre of sample.

4.3 Analysis

4.3.1 Water

Organics

Water samples for Irgarol 1051 and diuron determination were filtered within 24 hours of collection, to 0.45 µm under vacuum, prior to extraction. Irgarol 1051 and diuron were extracted from the filtered water samples using an Envirolut Herbicide solid phase extraction column (6 ml containing 500 mg sorbent; Varian, CA). The columns were eluted with 5 x 1 ml of HPLC grade methanol (Rathburn) and the eluates were combined and evaporated to 1 ml in a VisiPrep vial using a stream of high purity nitrogen.

Irgarol 1051 and diuron were determined in extracts of water using a Varian 9010 liquid chromatograph attached to a Spectroflow 757 UV detector (Kratos Analytical). Samples (20 µl) were chromatographed on a 25 cm ODS column using an eluent of 40%:60% Methanol (containing 10 mmol cetyl trimethylammonium bromide modifier): distilled deionised water mix at a flow rate of 1 ml/min. Absorbance was measured at 247 nm. Quantification was by peak area and concentrations were calculated using calibration curves obtained for standards of known concentration (limit of detection typically 10 ng/l for Irgarol 1051, 4 ng/l for Diuron).

Metals

Copper was determined by complexation-solvent extraction followed by graphite furnace atomic absorption spectrometry (AAS) (Apte and Gunn 1987) using a Perkin Elmer PE4000 instrument (limit of detection 0.5 µg/l, typical relative standard deviation <5%).

Zinc was determined either directly by flame AAS (limit of detection 5 µg/l) or by complexation-solvent extraction using ammonium pyrrolidine dithiocarbamate (APDC) and methyl *iso*-butyl ketone (MIBK) (limit of detection 0.5 µg/l, typical relative standard deviation <5%; Comber and Gardner 1999).

4.3.2 Sediment analysis

Organics

For Irgarol 1051 and diuron, dried sediment samples were extracted in accordance with USEPA Method 3545 (pressurised fluid extraction). The sample was ground to 150 - 75 µm and extracted with 15 ml of a mixture of dichloromethane (DCM) and acetone (1:1 v/v) in a Dionex ASE 200 Accelerated Solvent Extractor. The final extracts were concentrated in a Turbo-Vap apparatus to approximately 100 µl and transferred into vials for analysis.

Concentrations of Irgarol 1051 in sediment extracts were then determined using GC-MS. The GC-MS system consisted of a Hewlett-Packard 5890 gas chromatograph equipped with a cool on-column injector (2 µl injection volume). This was directly coupled to a VG Trio-1 mass spectrometer operated in the electron impact mode and linked to a VG MassLab data system. A 60 m x 0.32 mm DB-5MS column with a film thickness of 0.25 µm was used under the following conditions: isothermal at 40°C for two minutes, heating to 200°C at 20°C per minute and then at 4°C per minute to a final temperature of 300 °C. The mass spectrometer was operated in the selective ion monitoring (SIM) mode using positive ion electron impact ionisation (+EI). A solution of Irgarol 1051 in methanol and DCM was analysed in order to confirm its identity, retention time and mass-spectrometric characteristics (limit of detection ca 20 µg/kg dry weight).

For the determination of diuron, an aliquot of the extract (500 µl) was placed into a Gilson autosampler vial and blown to dryness under a stream of nitrogen. The analyte was then redissolved in 100 µl of the mobile phase (63% methanol:37% 0.1M ammonium acetate) containing the internal standard benzanilide. The contents of the vial were mixed by ultrasonication and the samples analysed using LC-MS. A Hichrom Spherisorb S50DS1 column (25cm) was used on a Hewlett Packard 1090 liquid chromatograph (1 ml/min flow rate), which was linked to a Trio-3 Mass Spectrometer utilising plasmaspray ionisation and monitoring in SIM (masses 198 - benzanilide; 213 - carbanilide the extracted internal standard and 233 - diuron) (limit of detection typically 20 µg/kg dry weight).

Metals

Copper and zinc in sediment were determined by digesting approximately 2g of wet sediment in 20ml boiling aqua-regia for 4 hours followed by centrifugation. The supernatant was poured into LDPE bottles (Nalgene Corp) and made up to 150ml

with deionised water. Samples were analysed using either Flame Atomic Absorption Spectrophotometry (FAAS) or Inductively Coupled Plasma Mass Spectrometry (ICPMS). Concentrations were calculated on a dry weight basis.

4.4 Results

As a check on the quality of data obtained for dissolved concentrations of the booster biocides, a brief comparability experiment was performed on Hamble samples collected during the summer survey. Four samples were collected in duplicate from four sites within the estuary. One set was determined at WRc and the other by CEFAS for diuron and Irgarol 1051. Trace organic analyses performed on substances present at the part per trillion (ng/l) level can show quite large variability particularly when different methods are used and the analyses are carried out in different laboratories. Errors as high as +/- 50% are not unusual for a single result. The results presented in Table 4.1 therefore show reasonable comparability between laboratories which are using different analytical techniques (WRc - HPLC-UV analysis; CEFAS/PML - GC/LC-MS).

Table 4.1 Comparison of WRc and CEFAS/PML analytical data for four Hamble Samples (dissolved fraction).

Sample No.	WRc Values (ng/l)		CEFAS/PML (ng/l)	
	Diuron	Irgarol 1051	Diuron	Irgarol 1051
H3	151	16	124	35
H5a	277	109	214	44
H9	281	36	175	48
H11a	387	48	226	57

A summary of the field data is provided in Figure 4-3 to Figure 4-6, with a full set of analytical data presented in Appendix B. The data presented in the bar graphs is based on mean concentrations. The figures quoted below are the maximum and minimum values to show the spread of concentrations measured in the samples.

4.4.1 Dissolved Concentrations

Estuaries

Estuarine concentrations of the dissolved organic booster biocides (Irgarol 1051 and diuron) were broadly in agreement with previously reported data (Gough *et al.* 1994; Lord *et al.* 1997; Thomas *et al.* 1999). Winter concentrations were found to be significantly lower than summer values for both the Hamble and Orwell.

The variation in summer and winter values for organic biocides in the estuaries is probably due to decreased boat density in the winter (reducing input rates) and higher river flows (diluting and transporting the biocide).

Dissolved estuarine levels of the trace metals (zinc and copper) showed a different pattern to the organic biocides since there are other significant inputs to the estuaries besides that from antifoulant paints.

For the Orwell estuary, dissolved concentrations of copper range from around 1 µg/l in the summer to 2 µg/l in the winter and zinc from 1-3 µg/l in the summer to 4-10 µg/l in the winter.

Higher levels in the winter result from increased volume of river water being present in the estuary, carrying with it a greater load of trace metals (including copper and aluminium) from runoff, sewage and industrial discharges upstream in Ipswich (Bird *et al.* 1996).

For the model validation exercise, the model was set up to calculate the likely input to water from copper used in antifoulant paints and zinc used in sacrificial anodes. The latter was used since the probable input of zinc from its use in the antifoulant zinc pyrithione would be orders of magnitude lower than the amounts input from anodes.

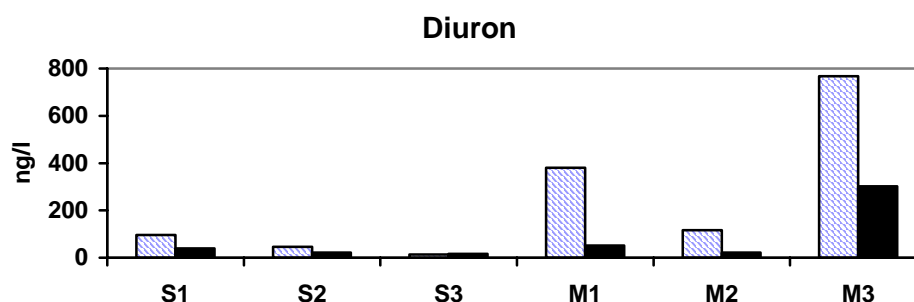
For the Hamble estuary winter concentrations of all four determinands were significantly lower, caused mainly by a reduction in boat density. Freshwater inputs are unlikely to significantly influence dissolved levels due to the small volume of uncontaminated riverine inputs.

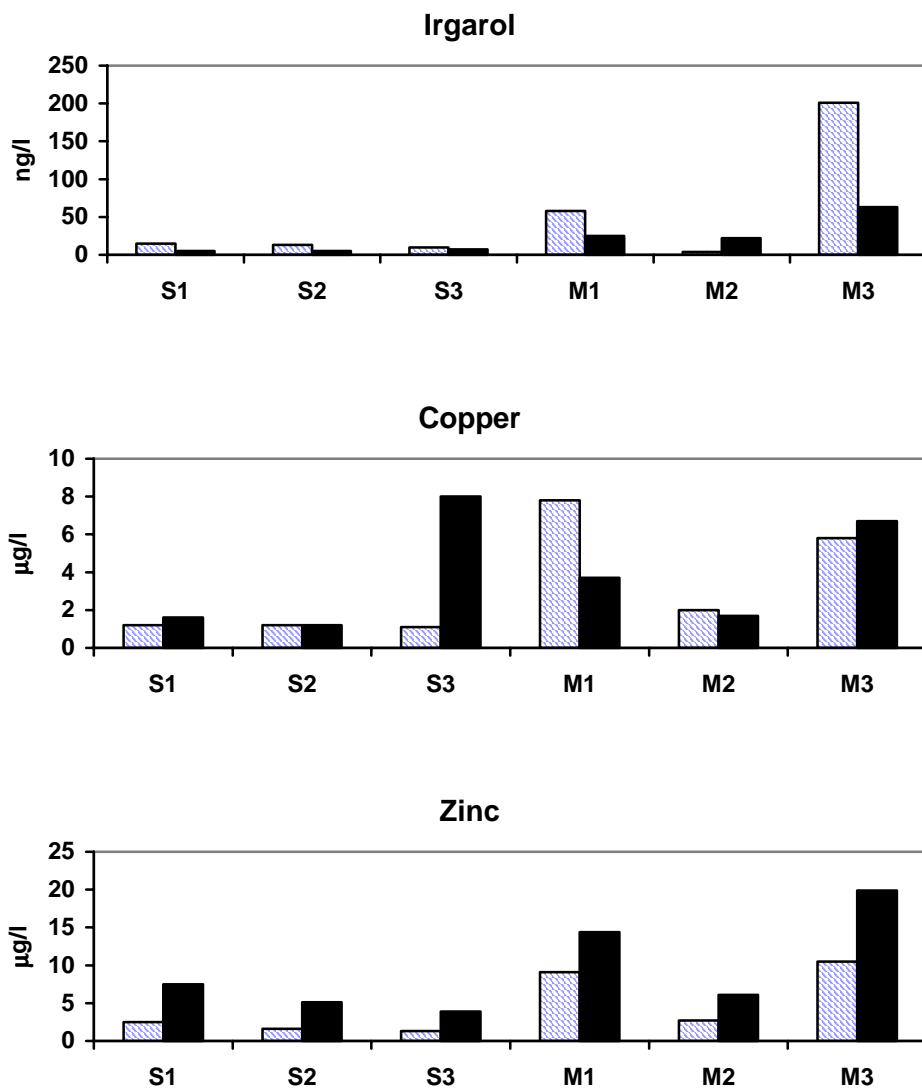
Marinas

In the Orwell, Irgarol 1051, diuron and trace metal concentrations were of a similar magnitude for both summer and winter samples. Variations could be accounted for through a decrease in boat numbers where levels were lower in winter (e.g. Cu in Fox's), and through increased river inputs (e.g. Zn at Woolverstone and Fox's), or reduced water exchange (e.g. Zn and Cu at Shotley), where levels were higher.

For the Hamble, similar temporal variations in biocide concentrations to those seen in the estuarine values were observed in the marinas. Variations between the estuarine and marina levels, however, are much lower than observed in the Orwell because:

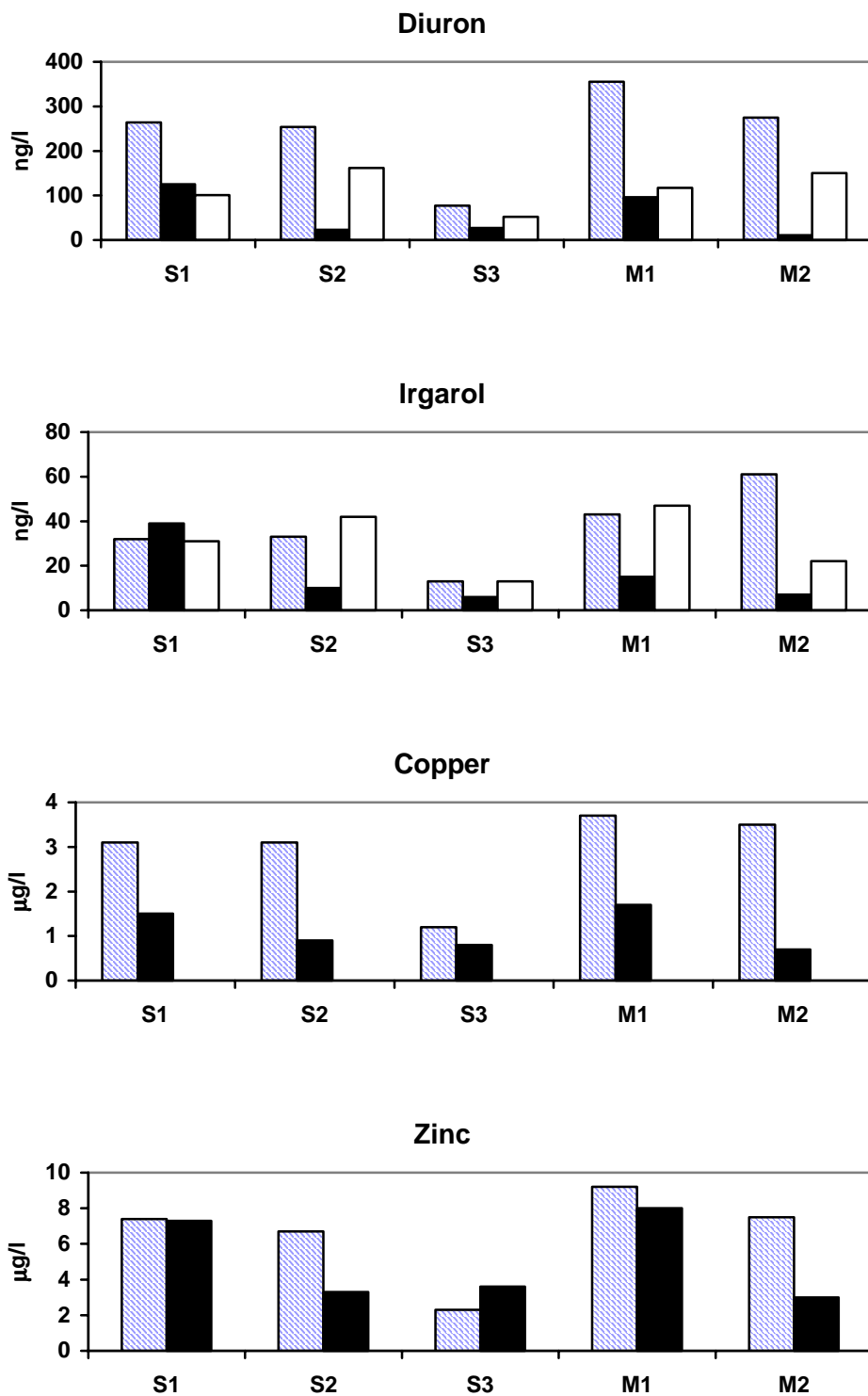
1. the marinas sited in the Hamble are all located within the estuary on pontoons;
2. the boat density in the Hamble is so high, there is little difference between the marinas and the open estuary.





Key: Summer 1998 (mean of high and low water values) (hatched bars)
 Winter 1999 (black bars)

Figure 4-3 Summary of dissolved concentrations in Orwell Estuary



Key: Summer 1998 (hatched bars)
 Winter 1999 (black bars)
 CEFAS (mean concentrations April-October 1998). (white bars).

Figure 4-4 Summary of dissolved concentrations in Hamble Estuary

4.4.2 Sediment Concentrations

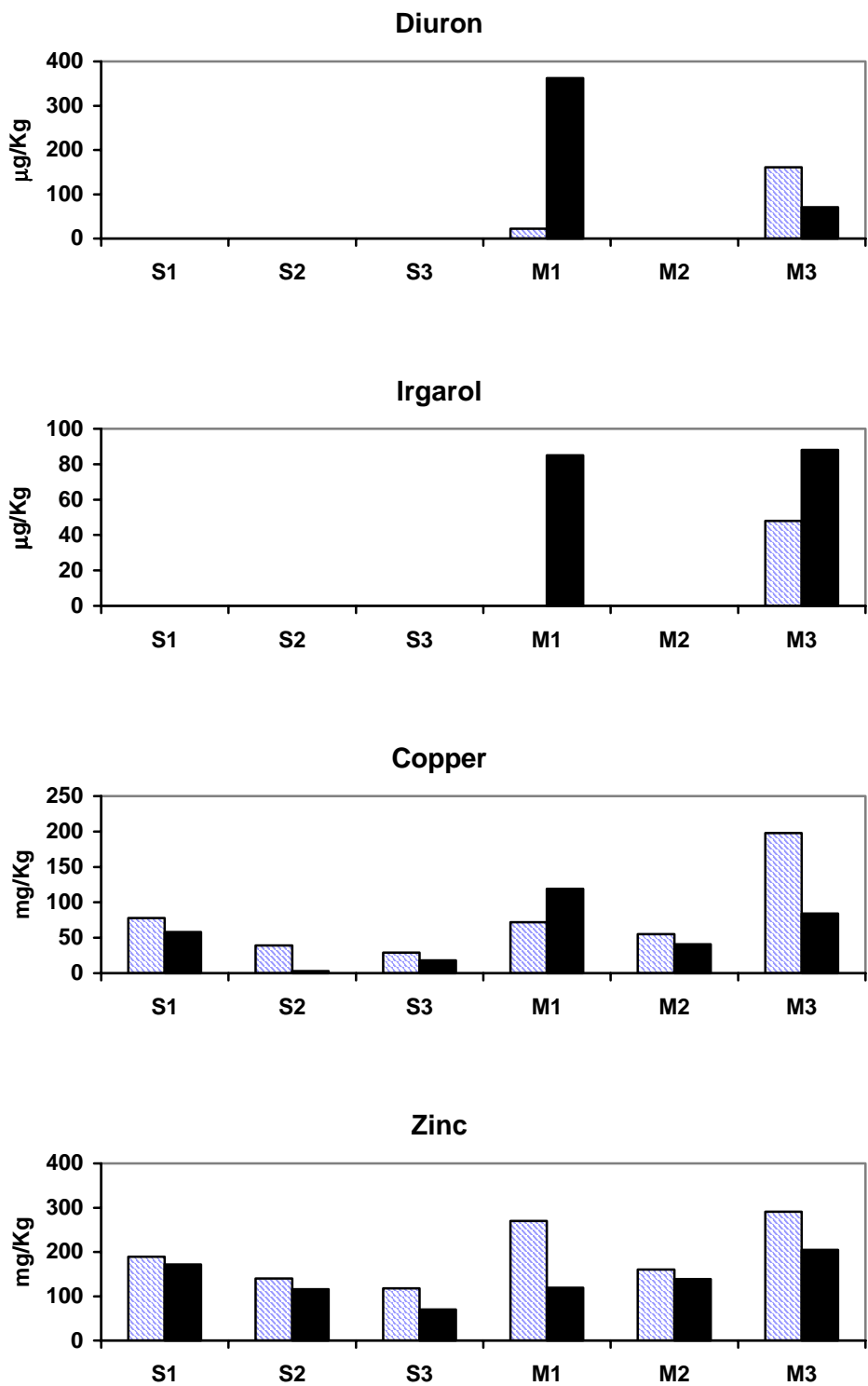
Sediment concentrations for the summer and winter surveys were very similar in concentration for copper, zinc, Irgarol 1051 and diuron, as would be expected due to the reduced mobility of bottom sediment. Variations are most likely to occur due to the heterogeneous nature of the bottom sediment. There were, however, significant variations between estuarine and marina concentrations, as would be expected due to the differences in boat density.

Orwell

Marina concentrations of copper and zinc ranged from 50 - 1000 mg/kg and 150 - 614 mg/kg respectively compared with significantly lower levels in the estuary (Cu 5 - 87 mg/kg; Zn 27 - 230 mg/kg). Diuron levels were only detectable in the marina sediment of Fox's (<12 - 16 µg/kg) and Shotley marinas (24 - 1000 µg/kg), and Irgarol 1051 was only present above the limit of detection at Shotley marina (24 - 2980 µg/kg). The low concentrations in the sediment reflected the lack of affinity (and hence low log K_{oc}) that Irgarol 1051 and diuron have for particulate material. The highest concentrations measured at Shotley for all of the determinands were at the bottom of the slipway, near to where the majority of antifoulant paint removal and application occurs. The sediment is therefore likely to contain chips of paint enriched in these substances.

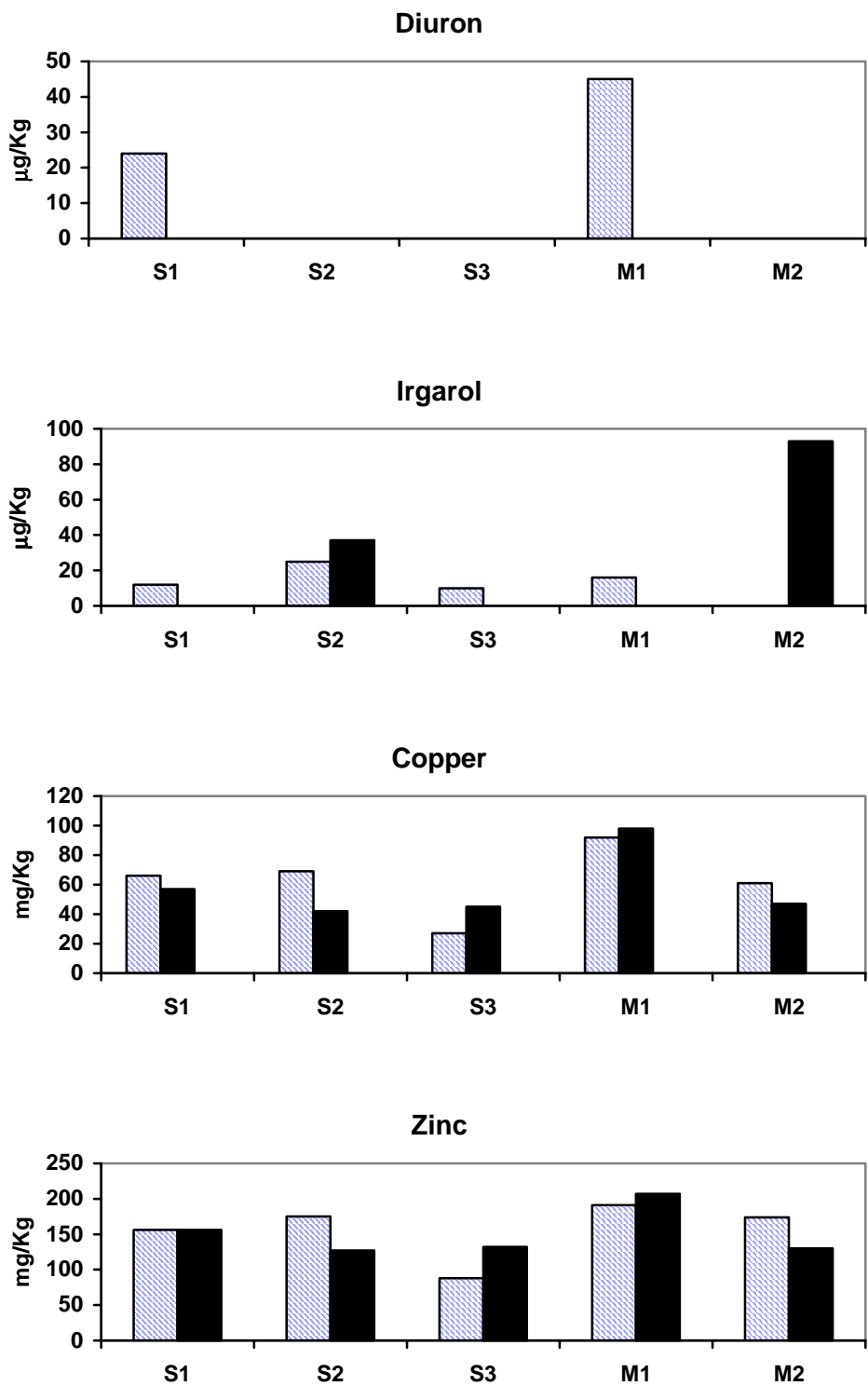
Hamble

Differences between the estuary and the marinas were less variable due to the large number of vessels moored in the estuary and the fact that the marinas are sited on pontoons within the estuary itself (e.g. Cu in marina ca. 100 mg/kg, in estuary 50 mg/kg; Zn in marina ca. 200 mg/kg, in estuary 100 mg/kg). Similar to the Orwell, Irgarol 1051 and diuron concentrations were very low and only above the limit of detection at a few sporadic sites (Irgarol 1051 <10 - 31 µg/kg; diuron <12 - 26 µg/kg). The fact that Irgarol 1051 was detected in more samples than diuron even though dissolved concentrations of diuron were significantly higher, may reflect the more persistent nature of Irgarol 1051.



Key: Summer 1998 (hatched bars)
 Winter 1999 (black bars).
 Blanks are below limits of detection (all less than $20 \mu\text{g/Kg}$).

Figure 4-5 Sediment concentrations in Orwell



Key: Summer 1998 (hatched bars)
 Winter 1999 (black bars).
 Blanks are below limits of detection (all <20 ug/kg).

Figure 4-6 Sediment concentrations in Hamble Estuary

5. PARTITIONING EXPERIMENTS

The degree to which the constituents of antifoulant paints partition between the dissolved and particulate phases is critical to understanding their eventual fate and behaviour in the aquatic environment.

For metals the partition coefficient (K_p) is defined as:

$$K_p \text{ (l/kg)} = \frac{\text{mass of substance in particulate phase (mg/kg)}}{\text{mass of substance in dissolved phase (mg/l)}}$$

For organic compounds partitioning is generally dominated by adsorption to particulate organic carbon present in the sediment. As a result the partition coefficient is normalised to the organic carbon fraction:

$$K_{oc} = \frac{K_p}{f_{oc}}$$

where:

K_{oc} = the organic carbon : water partition coefficient
 K_p = the partition coefficient
 f_{oc} = fraction of organic carbon present in the sediment

For example, substances with low partition coefficients will predominantly exist in the dissolved phase which means that although they will be rapidly dispersed and diluted within the aquatic environment, they may be more bioavailable, and contamination is potentially spread over a wider area. On the other hand, substances with a high partition coefficient will predominate in the particulate phase. Their relative lack of mobility will potentially result in high localised concentrations which may have implications when dredging etc. The situation is made even more complex by the fact that the partitioning is largely controlled by the physico-chemical properties of the particulate material. In general the partitioning of organic compounds and trace metals is dominated by adsorption to particulate organic carbon and the <63 μ m fraction present in sediment, respectively.

Another important controlling parameter in the partitioning of contaminants between the dissolved and particulate phases is the kinetics of adsorption. The rate at which adsorption/desorption occurs is of particular importance under non-equilibrium conditions encountered in tidal estuaries. Here, major physical processes are occurring over a 12 hour cycle that can have a significant influence on the partitioning of substances. For example, the kinetics of antifoulants released from vessels will be influenced by a number of estuarine physico-chemical processes such as:

- the turbidity maxima in an estuary,
- the arrival of 'fresh' seawater and particulates with each tide,
- exposure of sediment at low tide,
- changes in river water volumes within an estuary.

In order to gain a better understanding of the fate and behaviour of the antifoulants in the marina and estuarine environment, as well as provide default values for the model, a series of partitioning experiments were performed using 6 sediments of varying physico-chemical characteristics. The initial characteristics of the sediments used in the experiments are shown in Table 5.1.

Table 5.1 Characteristics of sediments used for the partitioning experiments*

Sediment	Description	TOC (%)	<63 µm (%)	Cu (µg/g)	Zn (µg/g)
Arun Estuary	Small muddy relatively clean estuary (W. Sussex)	1.25	69.8	23.5	77.7
Bracklesham Bay	Clean sandy beach (W. Sussex)	0.07	3.1	0.54	11.7
Bosham Harbour	Organic rich mud within Chichester Harbour (W. Sussex)	3.57	91.5	35.6	133.0
Chichester Harbour	Muddy sediment from main part of harbour - a few boats moored (W. Sussex)	1.07	73.1	59.2	80
Dell Quay	Sandy/shale/mud sediment from creek within Chichester Harbour (W. Sussex)	0.70	35.2	20.0	34.7
Pagham Harbour	Mud/sand from 'clean' muddy inlet/harbour (W. Sussex)	0.99	69.4	9.8	50.0

* Irgarol 1051 and diuron concentrations all less than 10 ng/g.

5.1 Irgarol 1051 and Diuron Partitioning Experiments

5.1.1 Method

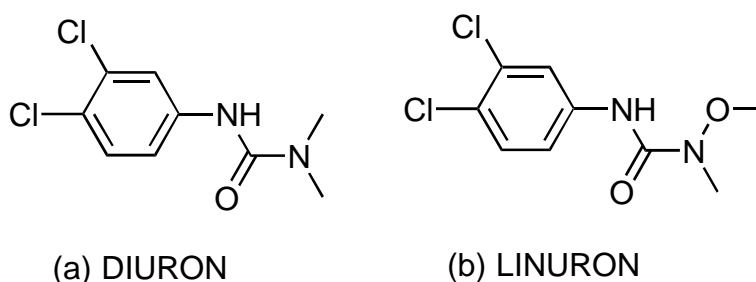
Batch partitioning experiments were carried out in duplicate in methanol and deionised water rinsed 1l Pyrex bottles (Duran Ltd). Sufficient wet weight of sediment was added to each litre of filtered seawater to provide suspended solid concentrations equivalent to 1, 20 and 200 g sediment dry weight / litre. To each vessel a fixed concentration of Irgarol 1051 and diuron was added (250 ng/l for 20 g/l suspended solids and 500 ng/l for 1 g/l and 200 g/l solids) by dilution of a stock standard. These concentrations offered a good compromise between measuring the partitioning at an environmentally realistic concentration, whilst allowing sufficiently accurate and precise analytical determinations.

Samples were equilibrated for 24 hours. This has been shown to be sufficient time to achieve equilibration (Comber *et al.* 1992), without allowing the samples with high levels of solids to become anoxic and therefore solubilise iron (this will precipitate upon filtering causing interferences with the extraction and analysis procedures). For the duration of equilibration the samples were shaken constantly at a temperature of 15 °C (+/- 1°C) in the dark.

Filtration and analysis was carried as described in the Section 4.

The ready availability of a rapid method for the determination of copper and zinc meant that the kinetics of adsorption of the trace metals to the particulates from the dissolved phase could easily be investigated (see next section). The analysis of Irgarol 1051 and diuron at environmentally realistic concentrations (ppb), however, involves filtering a litre of sample followed by extraction, elution, blow-down and analysis which is lengthy (and costly) and therefore not suitable for studying the kinetics of reaction. As has already been described however, the kinetics of adsorption is a very important parameter when considering the environmental fate and behaviour of a substance under non-equilibrium environments, such as those encountered in tidal areas. As a consequence a brief kinetic experiment was undertaken using ^{14}C -labelled linuron that was available at our laboratory.

Diuron (see structure (a) below) is very similar chemically to linuron (see structure (b) below) with one of the methyl groups on the terminal nitrogen replaced with a methoxy group.



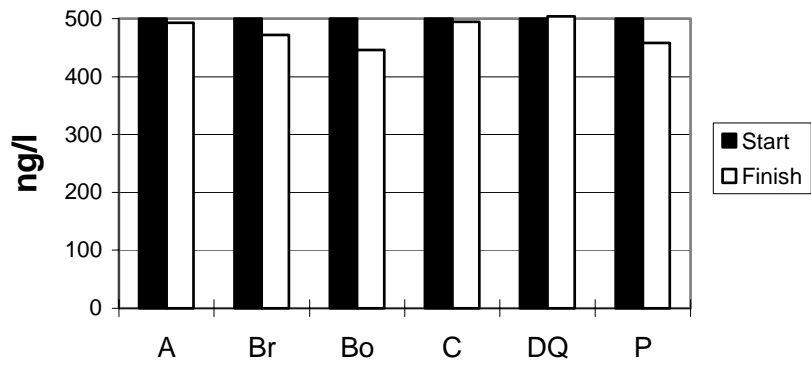
Literature values for K_{oc} of linuron (experimental data: mean 2.78, SD 0.29, n 137. SRC estimate: 2.54) at equilibrium are close to those of diuron (experimental: mean 2.47, SD 0.3, n 156. SRC estimate: 2.13). This suggests that its partitioning behaviour would also be very similar. Radiochemical measurement offers the advantages of being a very rapid, simple and sensitive procedure with the potential for kinetic experiments. A ^{14}C -linuron standard (26.8 mCi/mg, 1.5 mBq/ml, in methanol) was spiked at a level of 1000 Bq/ml into 500 ml clean glass bottles (Duran Ltd) containing duplicate sets of the 6 sediments at 20g/l solids (dry weight). The bottles were shaken in the dark for 12 days. Samples were withdrawn at appropriate time intervals (5 and 30 minutes, 1.5, 4, 7 hours and 1, 2, 5, 9, 12 days). At each time interval approximately 8 ml of sample was poured into clean glass vials and centrifuged for 15 minutes at 4000 rpm to separate the particulates from the aqueous phase. An aliquot (0.5 ml) of the aqueous phase was then pipetted into 10 ml of scintillant (Instagel plus, Canberra Packard), counted in a Beckman liquid scintillation counter (LS6000SE) for 2 x 5 minutes and the mean count calculated. In order to check for degradation at day 1, 5, 9 and 12, an aliquot (50 μl) of the dissolved phase was taken and injected onto a HPLC column (Waters ODS1, 25 cm 4.6 mm id) and eluted using 65:35 acetonitrile:water (retention time 4.7 minutes). Detection was achieved using a Packard liquid scintillation flow detector. Peaks for the samples were compared with those obtained for a standard.

5.1.2 Results and Discussion

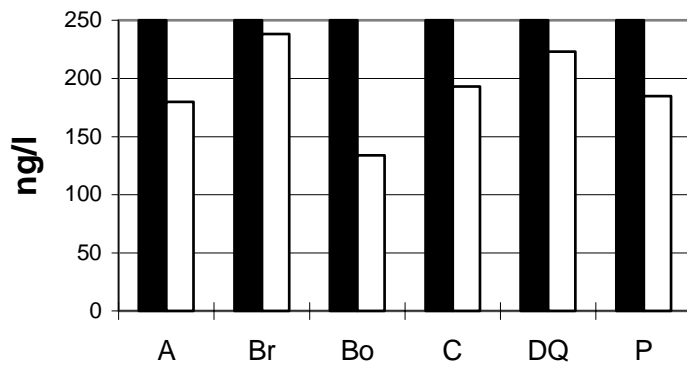
Figure 5-1 and Figure 5-2 illustrate the degree of adsorption of the antifoulants Irgarol 1051 and Diuron occurring at the three different suspended solids concentrations (1 g/l, 20 g/l and 200 g/l), with Figure 5-3 exhibiting the log K_{oc} values for each sediment.

From Figure 5-1 and Figure 5-2 it can be seen that only at high suspended solids concentrations is there significant adsorption of Irgarol 1051 or diuron to the particulate phase. This behaviour is consistent with the known partitioning behaviour of these two compounds. In addition the degree of adsorption measured is proportional to the amount of organic carbon present in the sediment, as is generally observed for organic substances in sediment (Karickhoff *et al.* 1979). As a consequence, the calculated partition coefficients normalised to organic carbon content ($\log K_{oc}$) for the six sediments at the three suspended solids concentrations are similar.

Dissolved irgarol at 1 g/l suspended solids



Dissolved irgarol at 20 g/l suspended solids



Key:
 A=Arun
 B=Bracklesham
 Bo=Bosham
 C=Chichester
 DQ=Dell Quay
 P=Pagham

Dissolved irgarol at 200 g/l suspended solids

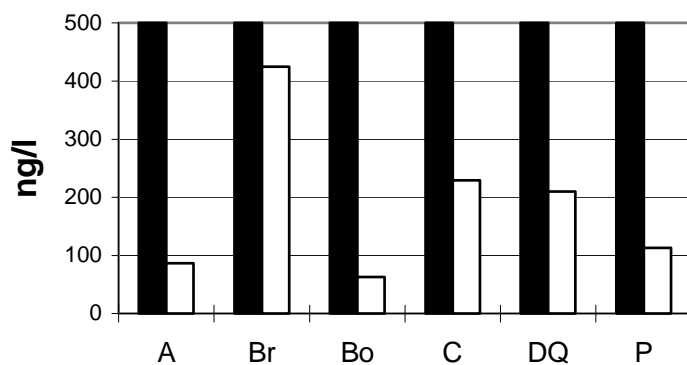
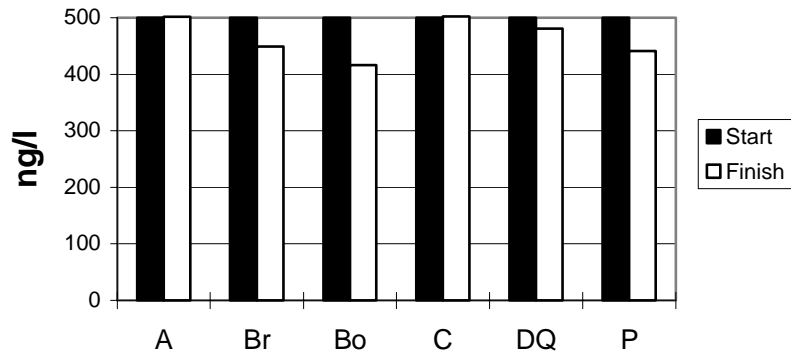
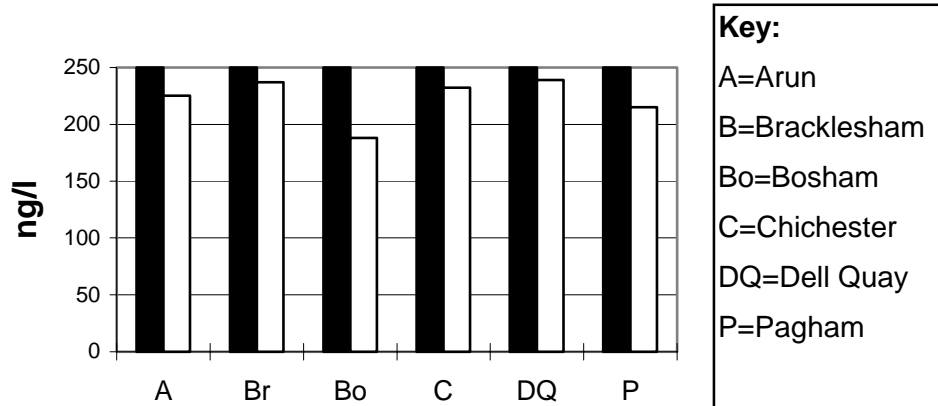


Figure 5-1 Dissolved concentrations of Irgarol 1051 in sediment tests

Dissolved diuron at 1 g/l suspended solids



Dissolved diuron at 20 g/l suspended solids



Dissolved diuron at 200 g/l suspended solids

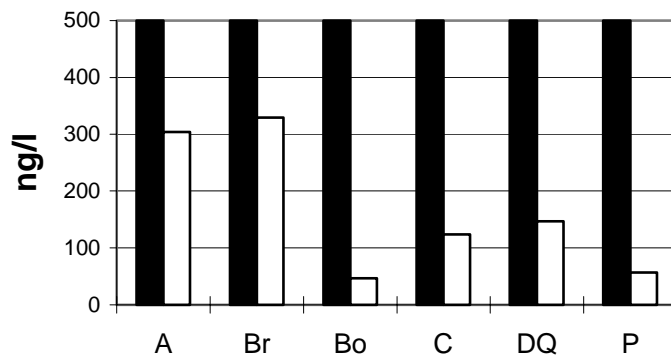


Figure 5-2 Dissolved concentrations of Diuron in sediment tests

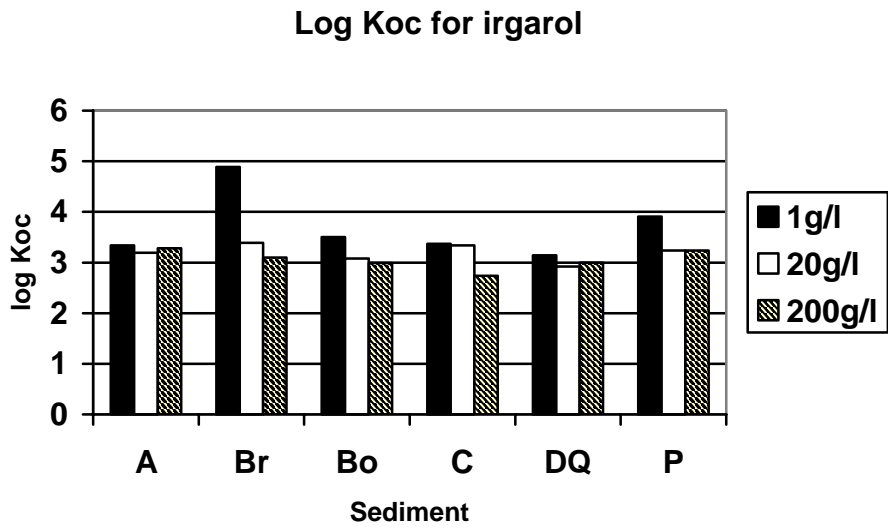
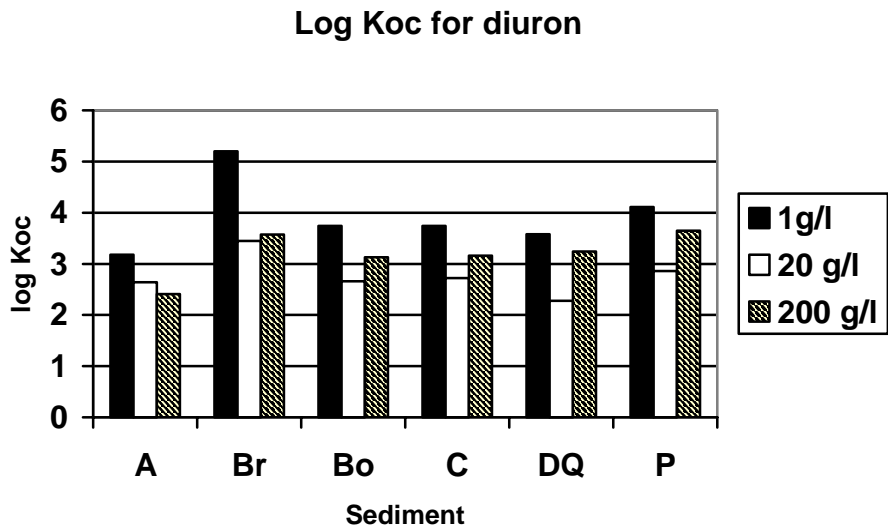


Figure 5-3 Log Koc calculated for diuron and Irgarol 1051 for the six experimental sediments at the three different suspended solids levels

There is substantial literature data currently available for diuron Koc, most of which is for soils. Much less data has been published regarding Irgarol 1051 Koc. Results obtained from this work show reasonable agreement with those that are available at higher suspended solids concentrations.

Measured log Koc's for diuron and Irgarol 1051 at 1 g/l suspended solids levels were generally higher than literature values (Table 5.2).

Table 5.2 Literature log Koc values for diuron and Irgarol 1051

Compound	Log Koc	No. of samples (s.d.)	Reference
Diuron	2.6	-	Lewis and Gardiner (1996)
Diuron	2.82	8 (0.17)	J. of Env. Qual, (1980), 9, 1, 101-106
Diuron	2.47,	156 (0.3)	Gerstl (1990)
Irgarol 1051	2.38	predicted	Rogers <i>et al.</i> (1996)
Irgarol 1051	>3.56		Ciba (1998)

The kinetic experiment performed with ¹⁴C-labelled linuron shows how the adsorption of organic compounds can vary dramatically between sediments (Figure 5-4). For all sediments equilibrium is not fully achieved until after approximately 100 hours, which is longer than has often been reported elsewhere. Normalising the partitioning to the fraction of organic carbon present in the sediment, however (Table 5.3), provides log Koc values that are very similar. This reflects how the particulate organic carbon controls the adsorption of organic compounds. The values obtained are only a little higher than previously reported values (mean 2.78, SD 0.29, n 137 - experimental; Gerstl 1990) for Koc of linuron in soils.

Table 5.3 Equilibrium log Koc values for linuron adsorption to the six experimental sediments

Sediment	foc	log Koc
Arun	0.0125	3.03
Bracklesham Bay	0.0007	3.69
Bosham	0.0357	3.07
Chichester	0.0107	3.13
Dell Quay	0.007	2.70
Pagham	0.0099	3.20

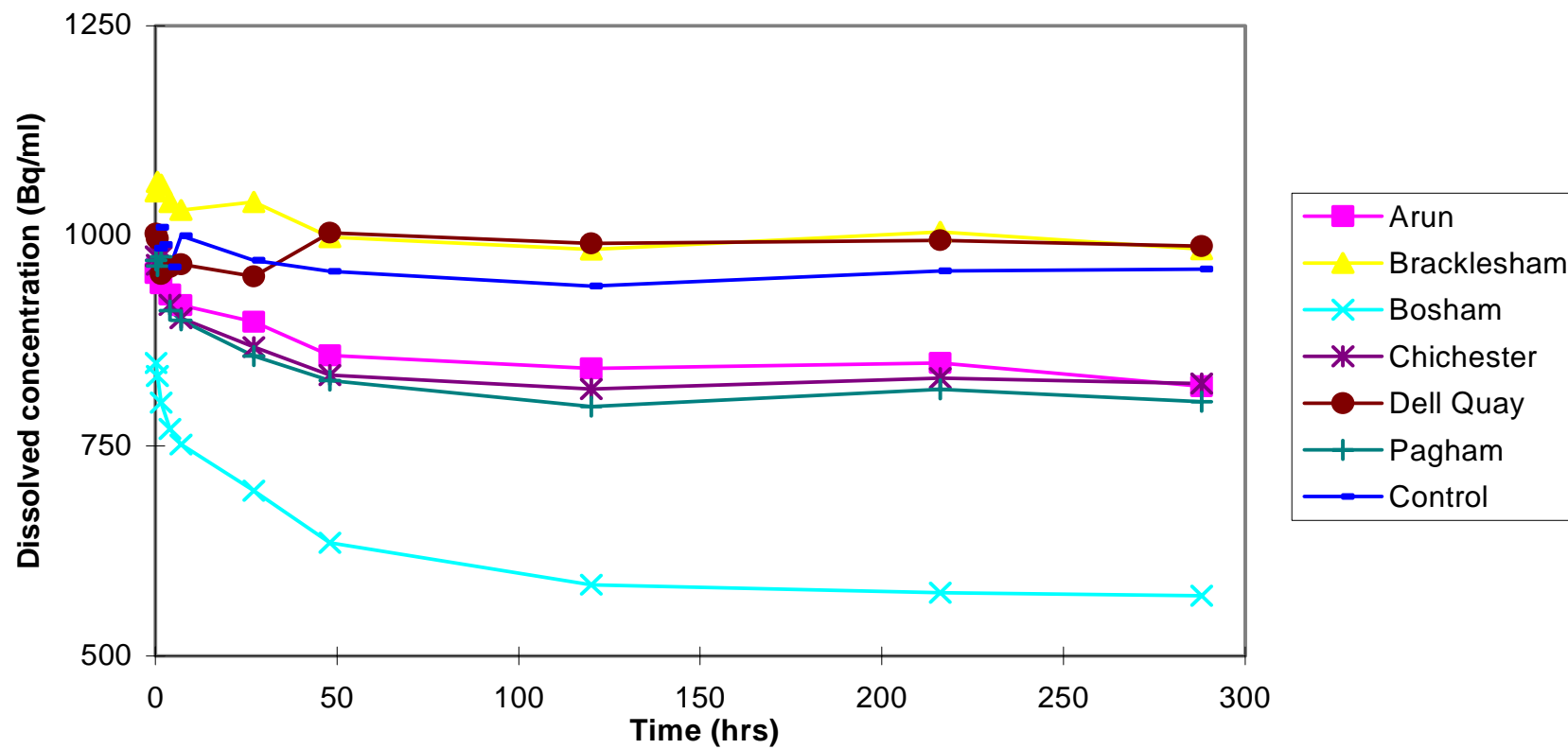


Figure 5-4 Dissolved concentration of ¹⁴C-labelled linuron with time for six different sediments

The results presented in the above tables show that at low suspended solids concentrations, very little of the added diuron and Irgarol 1051 adsorbs to the particulate phase; as would be predicted from the relatively low log K_{oc} and low organic carbon content of the sediment. At 1 g/l suspended solids, an average of only 4.4% (22 ng/l) of the added booster biocide was adsorbed, which made discrimination between the initial and final dissolved concentrations very difficult during the analytical stage. This was likely to be the cause of the slightly higher values for K_{oc} obtained compared with the literature values. As the suspended solids content of the water increases, so a relatively higher proportion of the biocides adsorb to the particulate phase; log K_{oc} values obtained for the 20 and 200 g/l suspended solids levels reflected those obtained by other workers.

This partitioning data demonstrates that in the aquatic environment both diuron and Irgarol 1051 will be predominantly detected in the dissolved phase unless there are very high suspended solids concentrations. This has also been shown to be the case with the field monitoring data where the majority of sediment samples contained concentrations of less than 10 ng/kg Irgarol 1051 and diuron, compared with dissolved concentrations which were in the range 10 to 100 ng/l for Irgarol 1051 and 10 to 1000 ng/l for diuron. The kinetic experiment conducted with radio-labelled linuron, which would be expected to behave in an almost identical manner to diuron, showed that complete equilibrium between the dissolved and particulate phases was not achieved until after approximately 4 days for all of the experimental sediments.

In summary, the experimental and field data suggest that in a marina environment, where high boat density ensures high levels of antifoulants in the water and suspended solid concentrations are generally low (<20 mg/l), the booster biocides examined here will be transported out of the marinas in the dissolved phase rather than adsorb to, and settle out on, the particulates. Accumulation in the sediment, producing a 'pool' of contaminants, is therefore unlikely to happen although it does suggest that the biocides will be transported further afield and will potentially be more bioavailable. Environmental levels measured during the field surveys as part of the work and previous studies (Thomas *et al.* 1999), however, show that even in locked marinas diuron concentrations are almost always less than the Environmental Quality Standard (guideline EQS) of 2 µg/l. There is currently no equivalent EQS for Irgarol 1051 but measured concentrations were even lower than for diuron.

5.2 Copper and zinc partitioning experiments

5.2.1 Methods

Experiments were performed to investigate the partitioning behaviour of zinc and copper between water and sediment for 6 estuarine and coastal surface sediments collected from relatively uncontaminated sites along the south coast of England. These tests were initially performed at a concentration of 1 g dry sediment/l of water and included a series of experiments to determine the kinetics of partitioning as well as the ultimate equilibrium partition coefficient.

Further investigations were performed at sediment concentrations of 0.1 g/l (to mimic a "typical" marina/harbour suspended solid concentration) and 200 g/l (1:5 sediment:water). The highest concentration represents conditions experienced at the water column/sediment interface of harbours and estuaries and also corresponds to the sediment concentration used in the OECD soil/sediment adsorption/desorption test. It was assumed that the kinetics of sorption for the 0.1 and 200 g/l experiments would be similar to those observed for the

original 1 g/l tests, consequently; equilibrium partition coefficients were measured after 18 days only.

All experiments were carried out in triplicate in 250 ml acid-washed Nalgene low density polyethylene bottles, using a total sample volume of 200ml. In order to achieve a suspended sediment concentration of 0.1 and 200 g/l, an equivalent of 20 mg and 40 g dry weight of sediment respectively was used. Uncontaminated sea water collected from the south coast was used for all experiments; 100 µg/l of copper and zinc (20 µl of 1000 mg/l Spectrosol standards) was spiked into each bottle. For consistency the spiked concentration was kept constant at 100 µg/l for all experiments. This meant that aqueous concentrations at equilibrium were not atypical of levels measured in estuaries (typically 1 - 8 µg/l for Cu and 1 - 15 µg/l for Zn), marinas or harbours (e.g. greater than 20 µg-Zn/l in locked marinas; Bird *et al.* 1996). Copper concentrations in marinas and harbours are unknown but are likely to be significantly greater than 10 µg/l.

Samples were kept in the dark and continuously agitated for the duration of the experiment. For each test a control (sea water spiked with 100 µg/l copper and zinc) was included to test for adsorption to vessel walls. In addition deionised water and seawater blanks were included to identify potential contamination during sample handling and filtration. After 18 days equilibration, samples were filtered and analysed as described previously.

Additional characterisation of the sediment was undertaken by measuring the total organic carbon (TOC) and the particle size distribution. TOC data is essential for the determination of the organic carbon:water partition coefficient (K_{oc}) used in the model for organic compounds and has a strong influence on the partitioning of copper in particular. Particle size is also an important parameter controlling the behaviour of metals and organics in the aquatic environment. In general, metals and organics are concentrated in the fine material (<63 µm), due to the increased surface area associated with this fraction (Taylor 1986).

5.2.2 Results and Discussion

Results from these experiments are tabulated in Table 5.4 and presented in the form of barcharts in Figure 5-5 and Figure 5-6.

Table 5.4 Partition coefficients for copper and zinc in estuarine sediments

	Cu K _p (l/kg) x 10 ³			Zn K _p (l/kg) x 10 ³		
	0.1	1	200	0.1	1	200
Susp. Solid conc (g/l)	0.1	1	200	0.1	1	200
Arun (A)	5.1	14	5.6	1.0	1.6	11
Bracklesham Bay (Br)	0.29	0.27	0.25	0.41	0.31	1.4
Bosham (Bo)	19	28	13	2.1	1.9	93
Chichester (C)	4.7	18	120	0.94	0.92	30
Dell Quay (DQ)	6.1	7.2	69	0.88	0.52	67
Pagham (P)	8.8	19	13	1.3	1.3	3.1

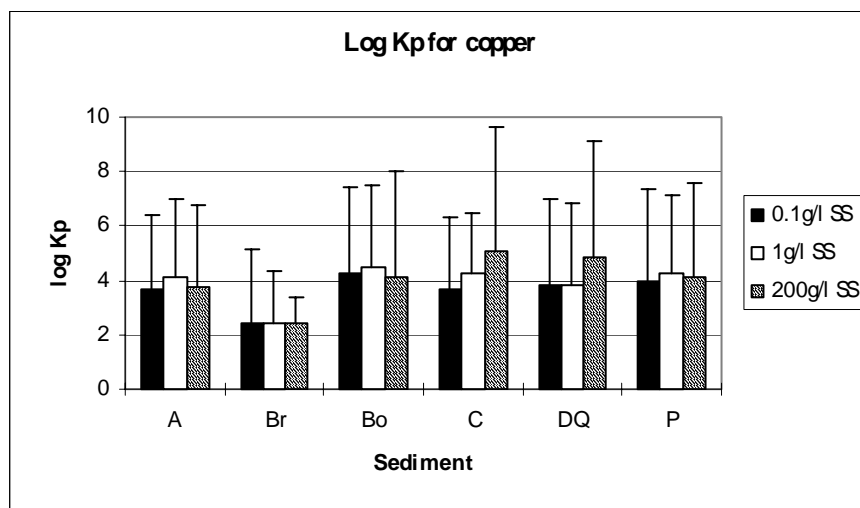


Figure 5-5 Kps for copper for six coastal sediments at three suspended sediment levels (with standard deviations)

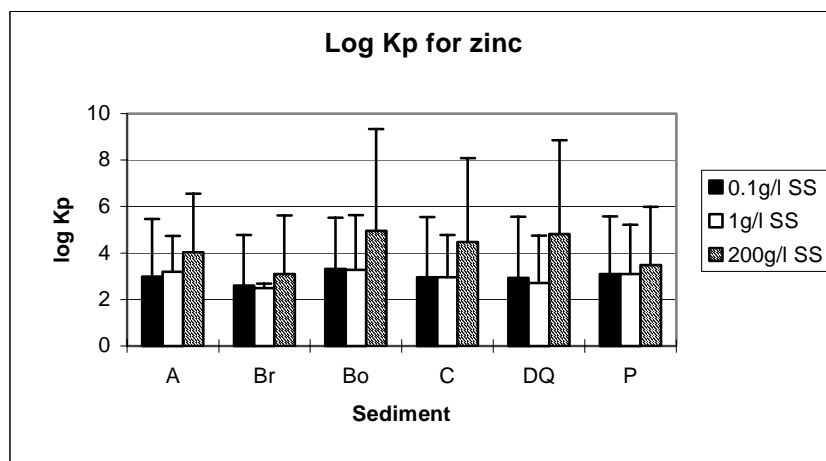


Figure 5-6 Kps for zinc for six coastal sediments at three suspended sediment levels (with standard deviations)

The above data show similar trends in equilibrium K_p for both copper and zinc. The sandy Bracklesham Bay sediment showed little affinity for the metals at all suspended solid concentrations, and had a correspondingly low partition coefficient. The low percentage of fine particulate matter (and correspondingly high proportion of inert sand) in the sample was the reason for the low adsorption capacity (Figure 5-7). For the other samples, there was a general trend of copper K_p s being 5 to 10 times greater; this behaviour is typical in other studies of UK sediments, and has been attributed to copper's greater affinity for particulate organic carbon (Comber *et al* 1995). The fact that the highest K_p s for copper (which are also 10 times greater than zinc K_p s) are associated with sediments containing the highest organic carbon content (Figure 5-8), offers further support to this theory.

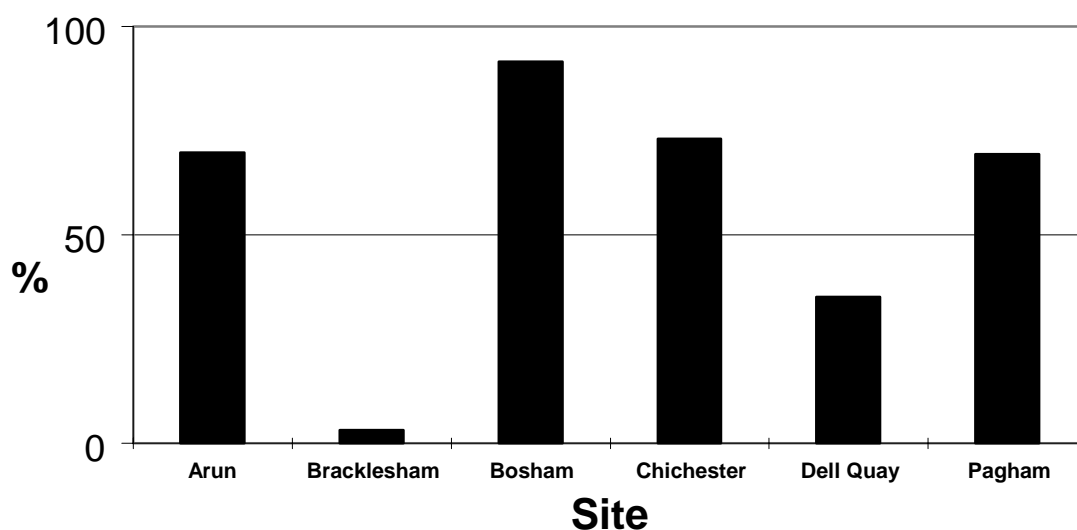


Figure 5-7 Percentage of particulates <63 μm in the six coastal sediment samples

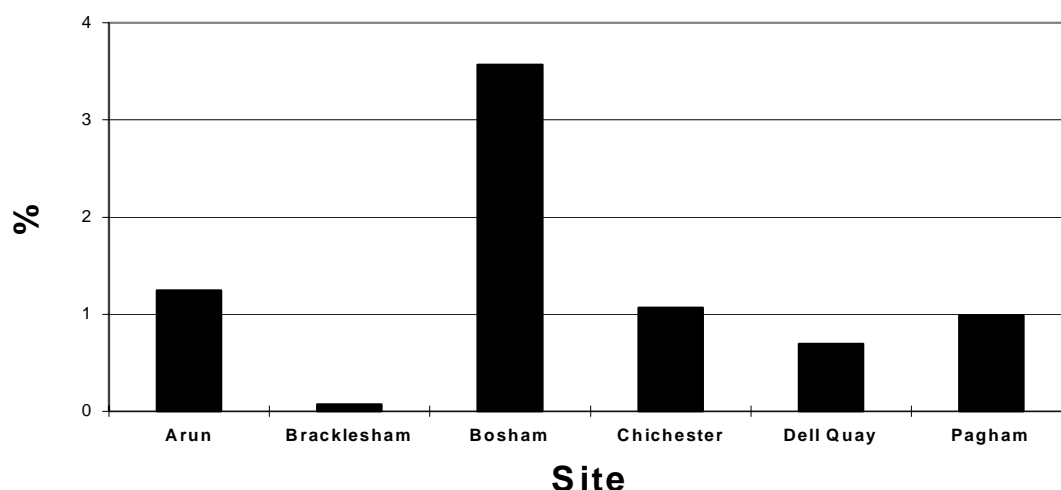


Figure 5-8 Percentage of organic carbon in the six coastal sediment samples

There was little difference between the equilibrium K_p s for suspended solids concentrations of 0.1 and 1 g/l, zinc values were almost identical, with copper values being marginally higher for the greater suspended sediment concentration. Previous studies have indicated that K_p is likely to decrease with increasing suspended solids loadings; the reasons for this include particle induced desorption and higher concentrations of dissolved organic carbon stabilising greater amounts of trace metal in the aqueous phase. However, most previous studies were carried out using oxic suspended sediment collected from the water column (Balls 1989, Turner *et al.* 1992; Turner 1996), with the intention of deriving fluxes and budgets for trace metals passing through estuaries and into coastal waters. Attention was therefore focused on

the interaction between metals in the dissolved phase (typically derived from industrial inputs) and suspended solids within the water column.

For this work however, interactions within marinas, harbours and estuaries are the focus of attention. Within these environments resuspended bottom sediment, and its influence on the partitioning of substances in overlying water, is of much greater importance; hence the use of bottom sediments in the above experiments. The main difference between experiments using resuspended bottom sediment compared with suspended sediment collected from the water column is that bottom sediments are generally anoxic and contain greater concentrations of sulphides. Metal sulphides are insoluble and hence partitioning experiments using resuspended bottom sediments will result in the sulphides showing a very strong affinity for the trace metals, thus increasing the K_p . As the suspended sediment concentration increases, so will the sulphide levels and hence the proportion of metal being associated with the sulphide phase. This is particularly evident for the 200 g/l suspended solid experiments, where K_p for both zinc and copper increased very significantly for certain sediments (at least 1 order of magnitude for Bosham and Chichester sediment for both Zn and Cu and Dell Quay for Cu). The reason why K_p increases dramatically for some sediments and not others at 200 g/l suspended solids is not entirely clear. It is possibly due to differences in sulphide levels in sediments and/or the degree to which the sediments become anoxic during the equilibration period (the more anoxic suspended sediments become, the greater the sulphide production and hence the greater the adsorption of metals). This behaviour observed in the laboratory experiments would be expected to reflect the partitioning that occurs in a marina or harbour environment.

5.3 Laboratory experiments used in a predictive capacity

The experiments carried out as part of this work have demonstrated how important the partitioning process is in controlling the fate and behaviour of antifoulants in the aquatic environment. Experimental data showed that in a low suspended sediment environment diuron and Irgarol 1051 would be found primarily in the dissolved phase. This was confirmed by the measurements obtained from samples from the Hamble and Orwell estuaries. The experiments also demonstrated that the use of normalisation of the partition coefficient (K_p) to the fraction of organic carbon present in the sediment to provide a K_{oc} value, effectively removed any variations in the partitioning behaviour of diuron and Irgarol 1051 for all of the sediments even though they had wide range of organic carbon and $<63\mu\text{m}$ particles present. The new REMA model contains input values for fraction of organic carbon and K_{oc} which should allow most environmental scenarios to be adequately accounted for.

Copper and zinc demonstrated a stronger affinity for the solid phase than that of the organic biocides. Their partition coefficients varied by several orders of magnitude depending on three key parameters – the particle size distribution, the fraction of organic carbon and the suspended solids concentration. There is, however, currently no widely accepted normalisation method to describe the partitioning of trace metals between the dissolved and solid phases although in general, the degree of adsorption is proportional to the percentage of fine material present in the sediment.

For the purpose of generating partitioning data for the antifoulant model, mean partitioning values were used to describe ‘typical’ sediment expected to be encountered in the estuaries of interest. However, the user may wish to use the model to predict environmental concentrations under ‘non-typical’ conditions, such as those in an organic carbon-rich environment, or in a marina where the predominant fraction of sediment was fine clay

minerals. Provided fractions of organic carbon are known, then obtaining accurate predictions for the concentrations of organic biocides in the water and sediment should not prove problematic. For copper and zinc, however, in order to accurately predict antifoulant levels, the partition coefficients should be changed to reflect the 'non-typical' environment. Figures 5-9 to 5-14 show correlations between copper and zinc and the two physico-chemical parameters most likely to control the partitioning behaviour of trace metals, fraction of organic carbon and percentage of sediment <63µm.

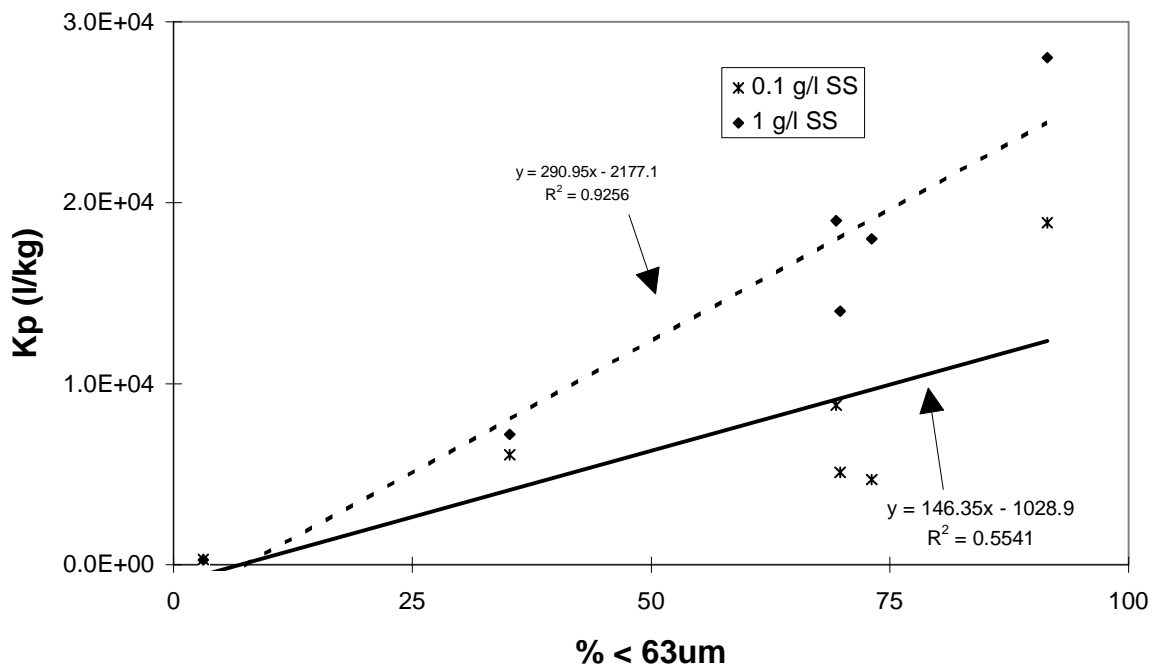


Figure 5-9 Kp for Cu vs percentage of sediment < 63 µm for six coastal sediments

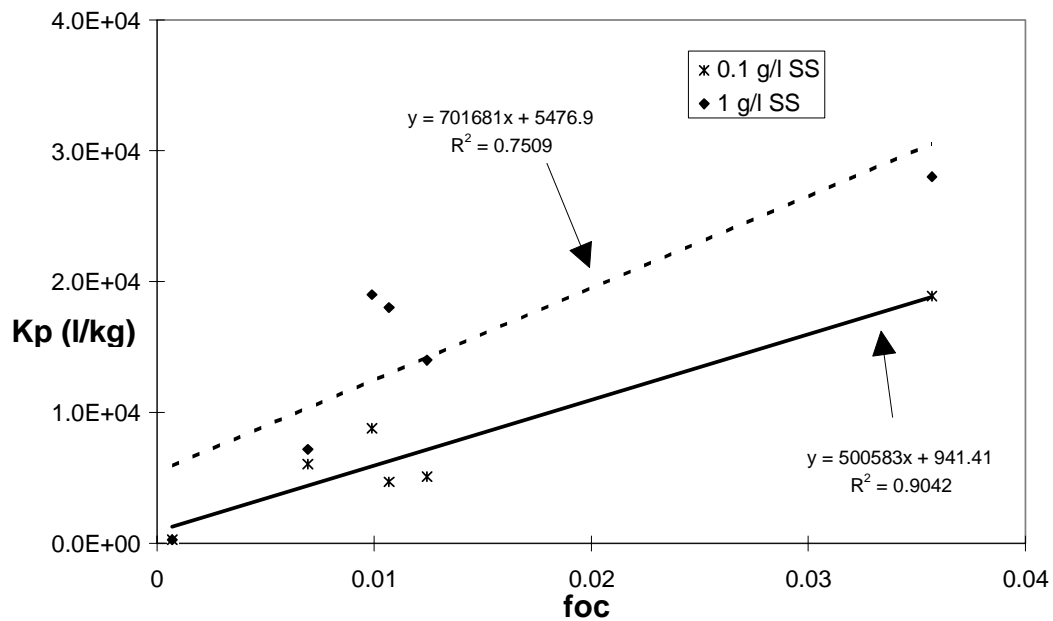


Figure 5-10 Kp for Cu vs fraction of organic carbon (foc) in six coastal sediments

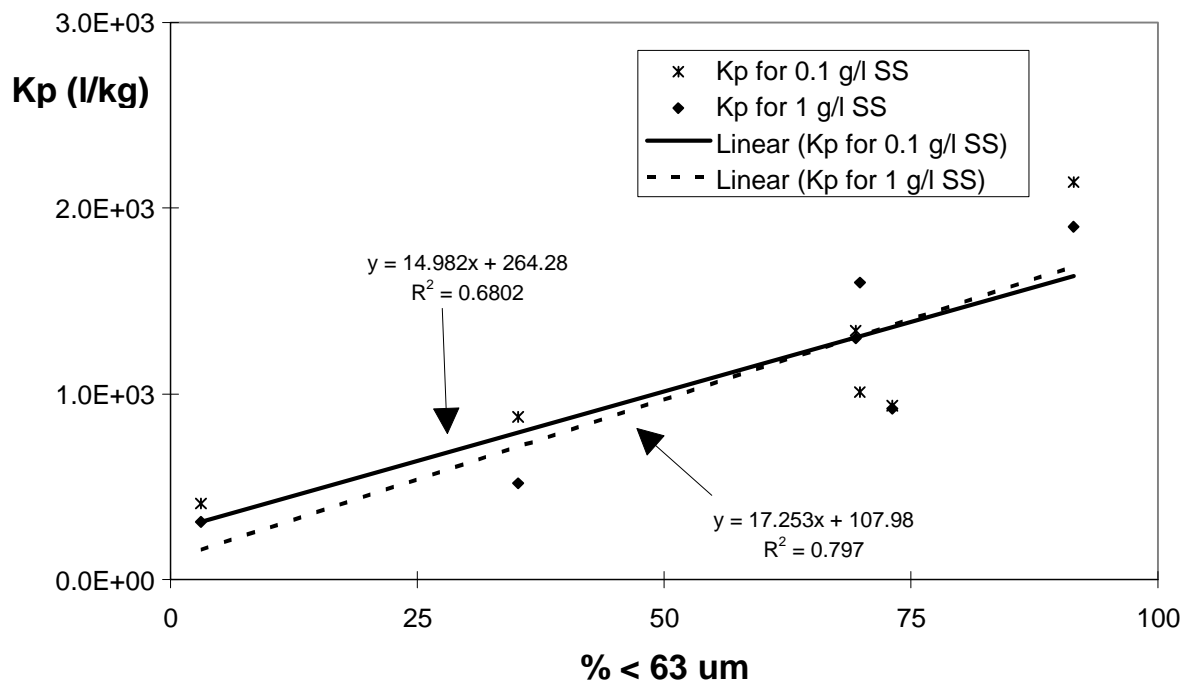


Figure 5-11 Kp for Zn vs percentage of sediment < 63 μm for six coastal sediments

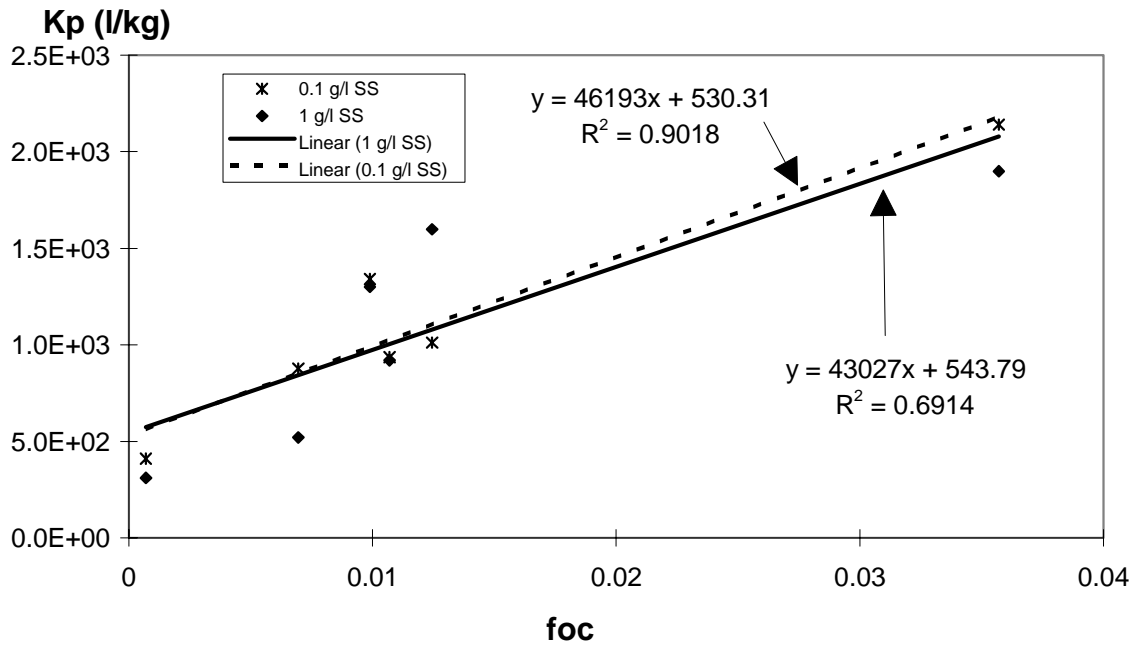


Figure 5-12 K_p (200 g/l SS) for Zn and Cu vs percentage of particles < 63 μm in six coastal sediments

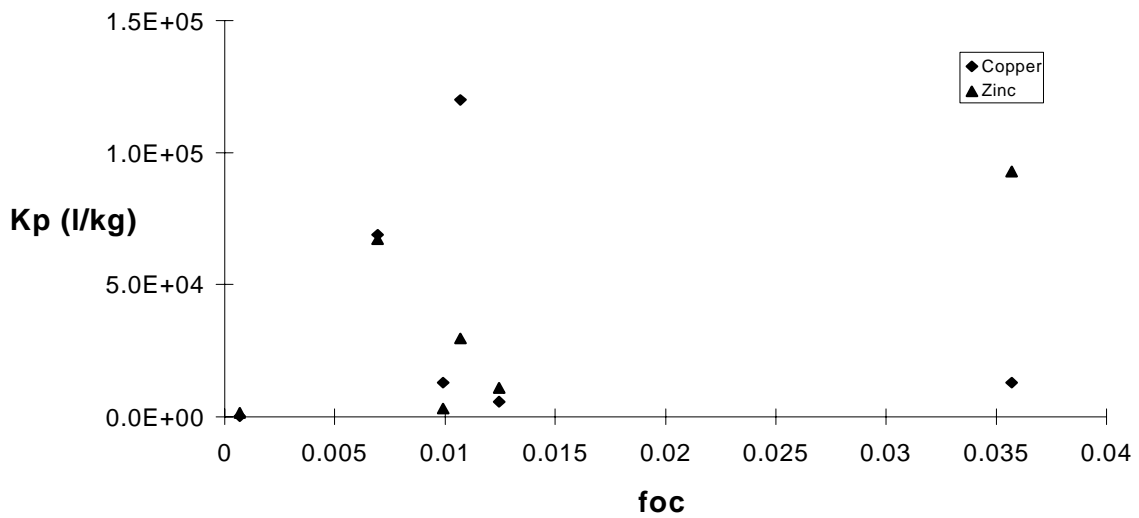


Figure 5-13 K_p (200 g/l SS) for Zn and Cu vs fraction of organic carbon (foc) in six coastal sediments

From the above figures it can be seen that there are no significant correlations between K_p and the sediments' physico-chemical parameters for suspended solids concentrations of 200 g/l, for either copper or zinc. This probably reflects the sulphide chemistry occurring under these conditions and already discussed above.

All of the other figures show a roughly linear directly proportional relationship between K_p for Cu and Zn and either foc or percentage of particles < 63 μm . Indeed several of the plots show an excellent correlation ($R^2 > 0.9$), with the others having correlation coefficients (R^2) of 0.55 or more (Table 5.5). This shows that the data derived from this study is in agreement with earlier work showing the affinity of organic carbon for the fine fraction of sediment and that the K_p for the metals increases with increasing organic carbon content and/or increasing amount of fine (<63 μm) material present in the sediment. Therefore it may be possible to use these relationships to predict the likely K_p for copper and zinc under extreme conditions of suspended sediment concentration possibly found in the marine environment.

Table 5.5 Correlation coefficients between sediment physico-chemical parameters and K_p for copper and zinc

Trace metal	Suspended Solids	
	0.1 g/l	1 g/l
Cu		
% <63 μm	0.55	0.93
% TOC	0.90	0.75
Zn		
% <63 μm	0.68	0.80
% TOC	0.90	0.69

6. MODEL DEVELOPMENT

None of the available computer models described in Section 3 were found to be fully suitable for modelling the fate of antifouling biocides for PRS.

A new model REMA (Regulatory Environmental Modelling of Antifoulants) was designed, written and validated to aid the PRS in its decision making processes.

A number of criteria for the development of a new model were identified. It was decided that, the model should include a number of environmental compartments and processes and require a number of inputs (Table 6.1).

Table 6.1 Environmental compartments and processes required in the Model

Model components	Processes / inputs included
Inputs	
Environment	size of marina/harbour/estuary, number of boats, size and types of boat
Antifoulant	leaching rates, partition coefficients (air/water, water/suspended sediment, water/bed sediment, water/biota), kinetic information, quantity used
Model compartments	air, water, suspended sediment, biota, bed sediments
Processes	
Biological	aerobic biodegradation, anaerobic biodegradation, bioaccumulation
Chemical	partitioning, aqueous hydrolysis, photolysis
Hydrological	water and sediment output rate, water and sediment input rates

A three-segment model was specified, with each segment containing a marina as shown in Figure 6-1. The model is based on the quantitative water-air-sediment interaction (QWASI) model developed by Mackay *et al.*, (1983). These types of QWASI based models have been successfully applied to various aquatic systems (e.g. Mackay *et al.* 1986) including rivers.

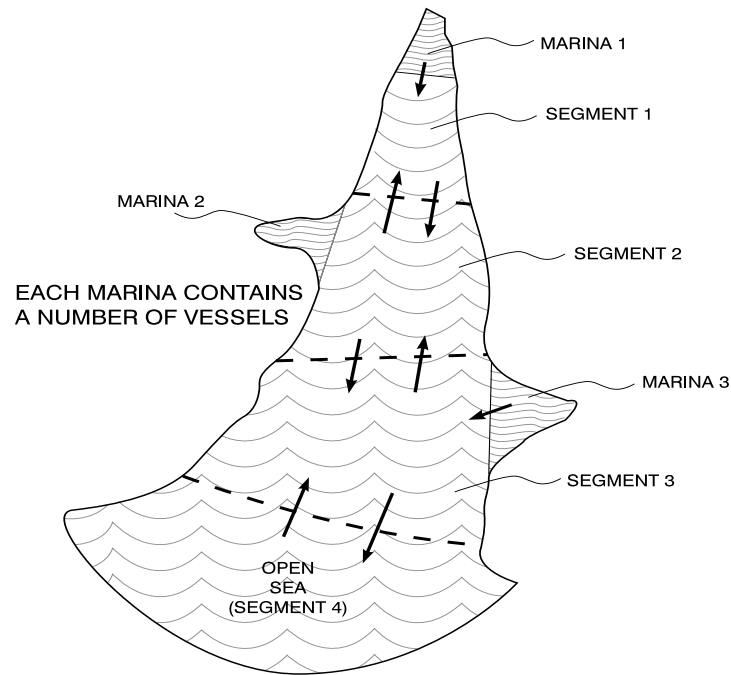


Figure 6-1 Schematic diagram of the proposed model

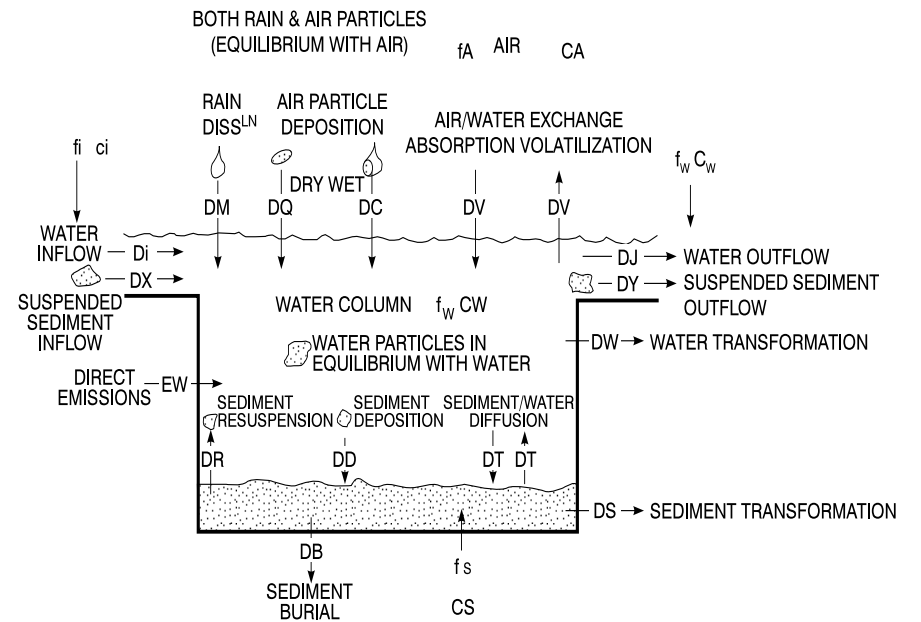
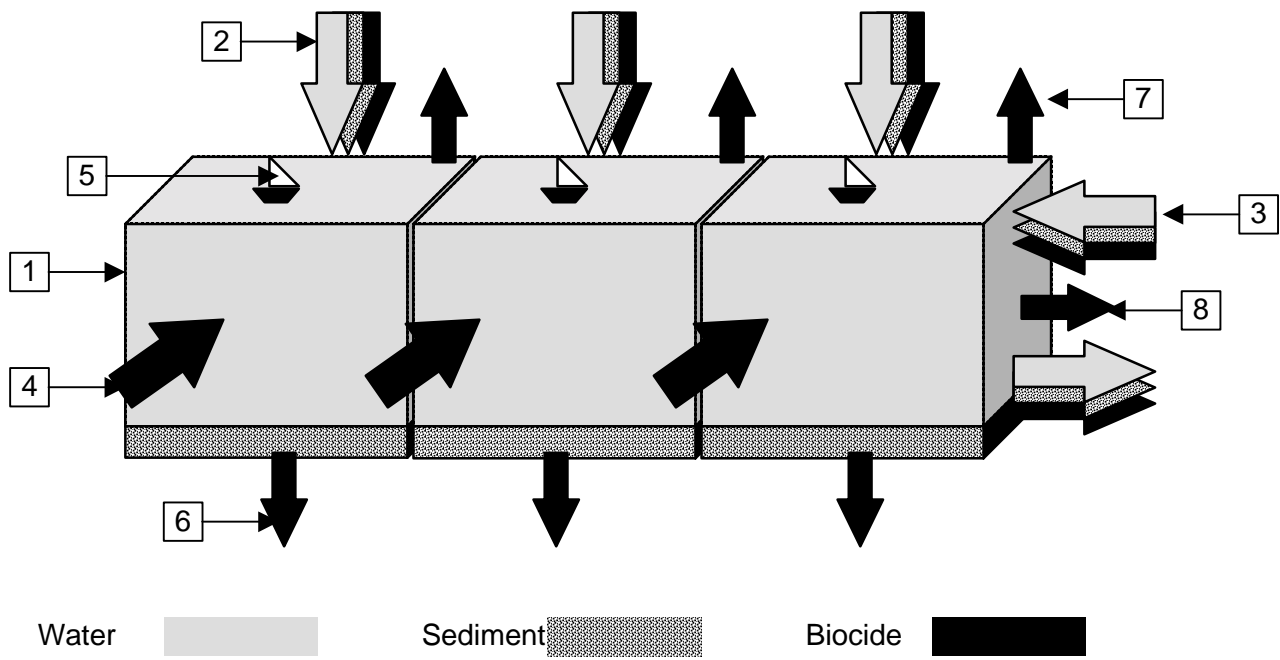


Figure 6-2 Structure of the quantitative water-air-sediment interface model which makes up each segment



- | | |
|--|--|
| <p>1 Three estuary segments, each made up of water, sediment and biocide which flows between them.</p> <p>2 Inputs to the estuary segments from rivers containing water, sediment and biocide.</p> <p>3 Sea water carrying sediment and biocide, enters and leaves the bottom estuary segment with the tides.</p> <p>4 Biocide enters the estuary segments from the marinas.</p> | <p>5 Biocide enters the estuary segments from boats moored in the estuary.</p> <p>6 Biocide is lost due to burial.</p> <p>7 Biocide is lost due to evaporation.</p> <p>8 Biocide is lost in flows to the open sea.</p> |
|--|--|

Figure 6-3 Interactions between estuary segments

The basic unit of the QWASI model is illustrated in Figure 6-2 and consists of a well mixed sediment compartment underlying a well mixed water column that is exposed to the atmosphere. The air compartment consists of an air/aerosol mixture, the water compartment contains water and suspended solids and the sediment compartment is comprised of solids and pore water. The overall model therefore consists of 3 such sediment-water compartments each with an associated marina, and the interactions between these segments are illustrated by Figure 6-3. The model can however be run using fewer segments. The model has been written in BASIC but after extensive testing and refinement it was programmed in Visual Basic to provide a user friendly system that can be used in the risk assessment process. The parameters and qualifiers used in the model are shown in Table 6.2. In order to use the model a number of inputs are required relating to the antifoulant biocide, the number and types of boat in each segment, the properties of each marina and segment and the transport of water and solids between segments. The inputs required for the biocide and the use made of them in the model are shown in Table 6.3.

The BASIC programme, which forms the 'engine' of the new model software, was tested using a hypothetical situation and shown to give a correct mass balance.

Table 6.2 Symbols used for Model Parameters and Qualifiers

Parameters		Qualifiers	
A	area (m ²)	A	air
B	transport/transformation per unit area (mol/h.Pa.m ²)	B	burial and biota
C	concentration (mol/m ³)	D	sediment burial
D	transport/transformation (mol/h.Pa)	I	water inflow
E	emission (mol/h)	J	water outflow
f	fugacity (Pa)	L	liquid phase
F	volume fraction of suspended sediment	M	rain
G	flow rate (m ³ /h)	N	sediment pore water
h	depth (m)	P	suspended sediment particles
H	Henry's Law Constant (Pa.m ³ /mol)	Q	air particle
I	group of D or B variables	R	resuspension
J	flow rate per unit area (m ³ /m ² .h)	S	sediment
k	rate constant (h ⁻¹)	T	sediment-water transfer
k ₁	overall time rate constant (h ⁻¹)	V	volatilisation
k ₂	overall distance rate constant (m ⁻¹)	W	water
K	mass transfer coefficient	X	water particles inflow
L	length (m)	Y	water particles outflow
P	pressure (Pa)		
R	gas constant (8.314 Pa..m ³ /mol K)		
T	temperature (K)		
U	velocity (m/h)		
V	volume (m ³)		
W	width (m)		
Z	fugacity capacity (mol/m ³ .Pa)		

See also Figure 6-2

6.1 Model Setup

It is apparent that compiling the model requires a large number of input variables describing discharges, physicochemical properties (including transformation half-lives) and environmental parameters. Therefore, in its initial form, the model was probably unsuitable for routine use or for use by inexperienced operators. WRc therefore set up the model for a number of UK marinas, harbours and estuaries. These cover a number of scenarios, with estuaries of varying sizes and dynamics and marinas of different types (e.g. locked, open, pontooned etc). Using this approach, the only information a user needs to input would be the properties of the antifoulant and the number of vessels in each marina.

Ideally the programme would predict the fate of an antifouling biocide in a range of different estuary types e.g.:

1. a small estuary that dries out (e.g. Hamble River)
2. a well mixed estuary (e.g. River Orwell)
3. a large, complex estuary (e.g. Southampton Water)

Input values on the properties of each model system were obtained using data from existing hydrological models and data on boat density and antifoulant usage from a survey which was performed by WRc for the Environment Agency (Boxall et al., 1998). Partitioning data used in the model is presented in Appendix D. Input values for the biocide concentrations have been obtained from a combination of survey data (Appendix C) and literature values.

Further description of the QWASI model and the outputs produced is provided in Appendix D.

Table 6.3 Input data required for the REMA Antifouling Fate Model

Input	Parameters required	Use for Parameter in Model
Properties of antifouling biocide	molecular mass melting point solubility vapour pressure Henry's Law Constant octanol-water partition coefficient water reaction half life sediment reaction half life leaching rate from paint	calculation of molar concentrations calculation of fugacity for substances that are liquids at ambient temperature calculation of partitioning coefficients calculation of partitioning coefficients partitioning calculations partitioning calculations degradation calculations degradation calculations input calculations
Discharges to marinas and segments	number of boats in marina size distribution of boats in marina type of boat in marina	} antifoulant input calculations
Segment properties	fraction of organic carbon in suspended solids fraction of organic carbon in the sediment density of particles in water density of surficial sediment particles volume fraction of water particles concentration of water column particles volume fraction of solids in sediment water area sediment area water volume sediment volume mean water depth mean active sediment depth water inflow and outflow rate	} partitioning calculations

Input	Parameters required	Use for Parameter in Model
Marina properties	fraction of organic carbon in suspended solids fraction of organic carbon in the sediment density of particles in water density of surficial sediment particles volume fraction of water particles concentration of water column particles volume fraction of solids in sediment water area sediment area water volume sediment volume mean water depth mean active sediment depth water inflow and outflow rate	transport and fate calculations
Sediment-water exchange processes	sediment deposition sediment resuspension sediment burial	partitioning calculations

6.2 Model validation

Model validation, probably better described as 'reconciliation', is ostensibly a simple process that involves comparison of the predicted concentrations produced by the model with measured concentrations produced from a field sampling and laboratory analysis programme. However, there are uncertainties associated with many of the key input and environmental data required to run the model and with the measured data. Consequently, model validation tends to be an iterative process whereby the predictions made by the model (using the input and environmental data that is considered to be the most appropriate) are compared with the available measured data. If there are substantial discrepancies (typically more than 1-2 orders of magnitude) between the predicted and measured concentrations, then both the measured data and the model data are scrutinised to determine likely potential sources of these discrepancies. Where this shows there is a valid, technically justifiable modification required to the input and/or environmental data, this will be made and the model will be run again to produce estimated concentrations for comparison with the measured data. This iterative process stops when there are no further valid, technically justifiable modifications that can be made, irrespective of the final correlation between the predicted and measured data.

In the case of the REMA model, a dataset was compiled for 4 estuaries; the Orwell, Hamble, Crouch and Southampton Water. Concentrations of four selected biocides (diuron, Irgarol 1051, copper and zinc) in the river water and receiving water were mainly derived from the field monitoring exercises (see Chapter 4) carried out for the Hamble and Orwell; but also include best estimates for the Crouch and Southampton Water from available monitoring data produced by CEFAS for DETR (Thomas et al., 1999).

For the REMA model, only two main validation exercises were necessary, since the input and environmental data had been carefully considered during the early stages of the project.

6.2.1 UK Usage Data

Usage data were obtained from the Environment Agency antifoulant survey (Boxall et al., 1998). These were based on the average minimum leaching rates which were considered to be representative of the majority of the time that a vessel's hull would be exposed to water. The higher leaching rates presented in that report are more suitable for predicting concentrations from boats entering the water immediately after painting, when the rate of release of the biocide would be at its greatest.

A survey of boat owners, boatyards, chandlers, marina operators, harbour masters and manufacturers was performed in two stages. In the first stage, a pilot study involving in-depth interviews was performed on a small number of interviewees. The aims were to:

- 1) identify the type and quality of information that was likely to be available on the usage of antifouling paints; and
- 2) obtain information to assist in the preparation of survey questionnaires.

In the second stage of the project, questionnaires were produced and used in order to obtain information on antifouling usage around the UK. A number of

questionnaires were produced for surveying chandlers, boatyards, harbour and marina operators and boat owners. Each survey group was surveyed either by telephone or post between April and July, 1998. A summary of the survey strategy that was used is shown in Table 6.4.

Table 6.4 Outline of approach used for antifouling usage survey.

Survey Group	Number of samples	Survey Medium
Biocide Manufacturers	3 (2)	T
Paint Manufacturers	4 (2)	T,I
Chandlers	50 (50)	T, P, I
Harbours/Marinas	50 (50)	T,P,I
Boatyards	50 (50)	T,P,I
Shipyards	1 (1)	T
Boatowners	500 (390)	P
Royal Yachting Association	1	T
British Marine Industries Federation	1	T

T = Telephone Interview; P = Postal Survey; I = Face to Face Interview

Figures in parentheses refer to the number of respondents to the survey

The estimated numbers of leisure craft afloat in UK waters ranged from approximately 73,000 to 150,000. The mean boat length was 9.2 m and 47% were motor boats and 53 % were sailing yachts. The average number of vessels kept in a UK marina was 213 (ranging from 30 – 500). The estimated surface area below the water line for an average vessel was 30.7 m². Due to their larger surface area, motorboats required a greater volume of antifouling paint than sailing yachts. The majority of vessels (85%) were antifouled annually with 7.5 % being antifouled every 2 years and 6.5 % being antifouled every 3 years. Generally, vessels were prepared for antifouling using pressure hosing and new paint was then applied on top of existing paint. The majority of boat owners did however remove all of the excess paint every 5 years.

The majority of vessels were antifouled ashore although a significant proportion (10.7%) were antifouled either on scrubbing piles or on the beach. Most boatyards (65%) disposed of scrapings and washings in waste bins, skips or controlled areas. A significant proportion (19.2%) of boatyards washed away the scrapings to the river or sea.

In addition to the above survey groups a number of biocide manufacturers were contacted to obtain information on the concentrations of biocides in antifouling products; and on the environmental fate, behaviour and effects of the antifouling biocides that they produce. In addition, information was obtained from Environmental Quality Standards where available (e.g. Lewis and Gardiner, 1996).

Five paint manufacturers and twenty nine antifouling paint products were identified containing either diuron, dichlofluanid, Irgarol 1051, zinc pyrithione, copper(I) oxide or copper thiocyanate. Reported concentrations in each product covered a wide range (Table 6.5) and for certain paints the biocides used changed with paint colour.

The rank order in terms of number of vessels treated with a particular biocide was copper(I) oxide > diuron > copper thiocyanate > Irgarol 1051 and zinc pyrithione > dichlofluanid. The other biocides that are approved for use by amateur owners (i.e. zineb, 2-thiocyanomethyl-benzothiazole, 2,3,5,6-tetrachloro-4-sulfuroxypyridine, and chlorthalonil) were not incorporated into any of the products identified.

Information on volumes of each product sold and concentrations of biocides in each of the products demonstrated that the rank total amounts of biocide used by boatowners and boatyards or sold by chandlers was copper(I) oxide > diuron > copper thiocyanate \approx Irgarol 1051 \approx zinc pyrithione > dichlofluanid (). Quantities of antifouling biocide distributed in the UK in a 1 year period ranged from 59 kg (minimum estimate for Irgarol 1051) to 331769 kg (maximum estimate for copper) (Table 6.5)

Table 6.5 Biocide in antifouling paints : concentration, use and distribution in the UK

	Concentration range (% w/w)	No. of products containing biocide	Proportion of boats treated (%)	Amount distributed in UK (kg/yr)
Copper oxide	2.5 -100	25	99 - 100	75173 - 331769
Copper thiocyanate				282 - 4216
Dichlofluanid	1.35 - 1.53	1	2.1 - 3.2	3288 - 25738
Diuron	1 - 5	5	45 - 52	59 - 10186
Irgarol 1051	0.1 - 5.0	17	27 - 32	1369 - 8246
Zinc pyrithione	2 - 25	3	0.6 - 3.8	153 - 388

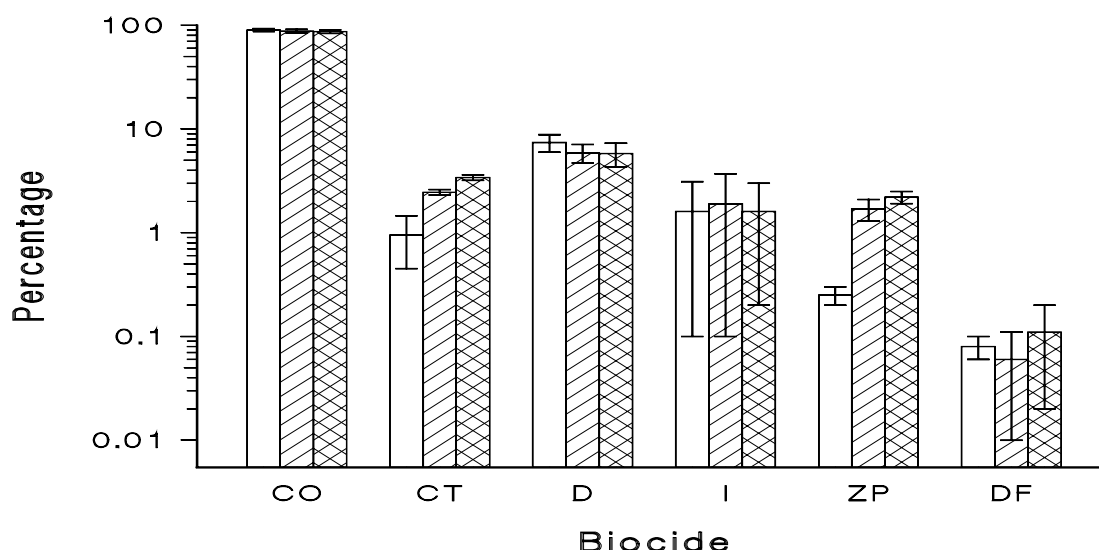


Figure 6-4 Biocide use

Percentage of each biocide used by boatowners (open bars), boatyards (hatched bars) or sold by chandlers (cross-hatched bars). CO = cuprous oxide; CT = copper thiocyanate; D = diuron; I = Irgarol 1051; ZP = zinc pyrithione; DF = dichlofluanid.

Estimations of the quantities of biocide used by leisure craft in UK waters were obtained based on estimates of the numbers of leisure craft afloat in UK coastal waters and on sales from UK chandlers and boatyards using the following equations.

$$B_{\text{boatyards}} = \left(\sum_{i=1}^n B_{\text{painti}} * f \right) * N_v * V_b$$

$$B_{\text{chandlers}} = \left(\sum_{i=1}^n B_{\text{painti}} * f \right) * N_c * V_c$$

$$B_{\text{total}} = B_{\text{boatyards}} + B_{\text{chandlers}}$$

Where:

$B_{\text{boatyards}}$, $B_{\text{chandlers}}$ and B_{total} are the amounts of biocide used by UK boatyards, sold by UK chandlers and used in the UK respectively;

B_{painti} is the amount of the paint that is biocide;

N_v is the number of vessels treated by boatyards;

N_c is the number of chandlers in the UK;

f is the fraction of vessels treated with the biocide;

V_b is the annual average volume of paint used by boatyards/vessel;

V_c is the annual average volume of paint sold by chandlers.

The inputs of each biocide to the aquatic environment will be dependent on the method and location of paint application, the leaching behaviour of the biocide and the method by which residual antifouling paint is removed from the hull of a vessel. A number of approaches were used to assess the inputs of biocides from each of these sources.

6.2.2 Inputs from leaching

Product information on the volumes of each antifouling paint product used to paint leisure craft and on the concentrations of individual biocides in the products was used to obtain an average 'worst case' leaching rate for each biocide. It was assumed that the lifetime of the paint was 9 months and that all of the biocide leached from the paint during this nine month period.

$$\text{Leaching Rate (ug/cm}^2\text{/day)} = \sum_{i=1}^n \frac{C_i * N}{275 * A}$$

Where:

C is the concentration of biocide in the product;

N is the number of coats of paint applied;

A is the area covered by 1 l of paint ($\text{cm}^2\text{/l}$).

The number of coats of paint was assumed to be 2; and the area covered by 1 l of paint was assumed to be 94000 cm² (International, 1998).

Estimates of total inputs to the aquatic environment from leaching were obtained based on the assumption that an average leisure craft has a surface area below the waterline of 30.7 m² and that there are between 72,766 and 150,000 leisure craft that are antifouled in UK coastal waters.

Calculated mean leaching rates for the biocides ranged from 0.12 (Irgarol 1051) to 25.3 (copper) (Table 6.6). The rank order for the leaching rates was copper(I) oxide > copper thiocyanate > zinc pyrithione > diuron > Irgarol 1051 and dichlofluanid. Tonnages of biocide leaching into the environment (based on estimated boat number in UK waters) ranged from 0.98 tonnes (Irgarol 1051) to 425.7 tonnes (copper oxide).

Contributions from antifoulant paints for zinc would be negligible compared with inputs from sacrificial anodes attached to the hulls and props of vessels as an anti-corrosion measure due to the limited usage of zinc pyrithione. Typically, 2kg of zinc are used per boat of which 60% dissolves per season (Environment Agency antifoulant survey data). Assuming that each boat spends 9 months of the year in the water then a leaching rate (µg/cm²/day) can be calculated for the leaching rate of zinc anodes into the water. It is this figure that has been used in the model for validation purposes.

Table 6.6 Calculated leaching rates for booster biocides present in antifouling paints applied to small vessels.

Data represent means; maximum and minimum rates are shown in parentheses

Biocide	Minimum leaching rate (µg/cm²/day)	Maximum leaching rate (µg/cm²/day)	Minimum inputs (Tonnes)	Maximum inputs (Tonnes)
Copper oxide	16.12 (1.74 - 34.82)	25.33 (6.96 – 69.63)	131.4	425.7
Copper thiocyanate	5.13 (4.1 - 6.15)	9.23 (8.20 - 10.25)	41.8	155.1
Diuron	1.39 (0.77 - 1.93)	4.64 (1.93 - 7.74)	11.3	78.0
Irgarol 1051	0.12 (0.078 - 0.39)	3.40 (1.55 - 3.87)	0.98	57.1
Zinc pyrithione	4.64 (1.55 - 7.74)	13.54 (7.74 – 19.34)	37.8	227.6
Dichlofluanid	1.04 (-)	1.04 (-)	8.48	17.5

6.2.3 Inputs from pressure hosing

Data was only available on the releases of copper during pressure hosing of vessels in the Netherlands. This showed that amounts of copper removed during pressure hosing ranged from 90 – 2800 mg/vessel (CUWVO,1991). The total amount of copper entering the environment through water blasting was therefore estimated using this information along with information on boat numbers in UK waters.. Assuming that the number of leisure craft in UK waters is somewhere between 72,766 and 150,000, the amount of copper released during pressure hosing was calculated to be between 6.5 and 420 kg, this is approximately 0.1 % of the amount released from leaching.

6.2.4 Initial validation exercise

Some example data for the initial validation exercise are shown below in Figures 6.6 and 6.7.

The predicted concentrations for the River Orwell showed reasonable agreement with the measured values for marina and estuary waters (and for the sediments which are not shown here) for all of the biocides. However for the Hamble, there was much poorer agreement between predicted and measured concentrations, the predicted values tending to be significantly higher than the measured values particularly for segment one. Further examination of the available input data relating to amounts of the biocides used in antifouling paints and the amounts of the paints used at each of the locations showed some areas for modification of input values. Similarly for examination of the data on the numbers of boats and ships in the marinas and estuary segments. However, the uncertainty in these values would not of itself, account for the over-estimate produced by the model. Close scrutiny of the model calculations showed that the values used for the flows between the segments were probably too low since the residence times for the water were far too high. This was partly due to the fact that the flow into an estuarine segment from its associated marina was not balanced by an equivalent flow back to the marina or out of the segment into the adjacent downstream segment. This flow discrepancy was rectified for all of the marinas as shown in Figure 6.5 below. Revised input values were also estimated for the proportion of boats treated and the numbers of boats in each marina.

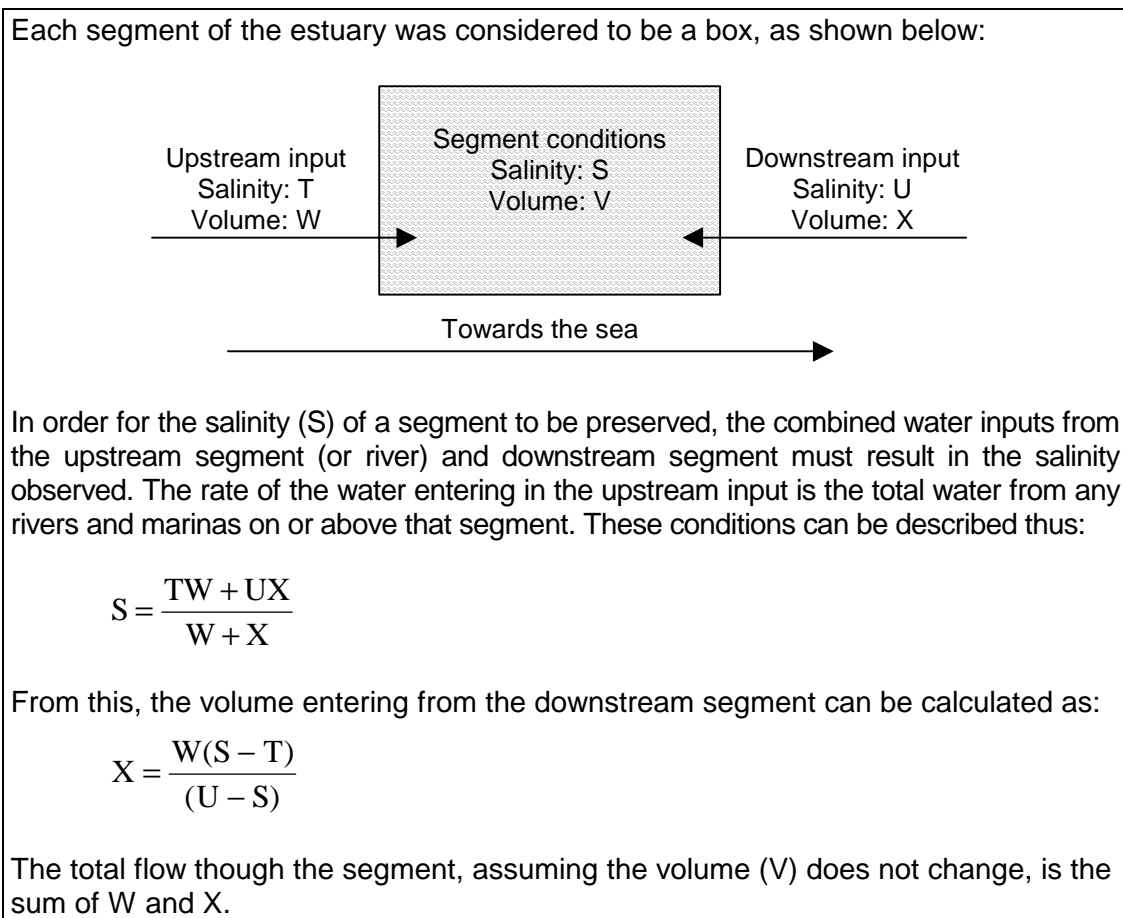
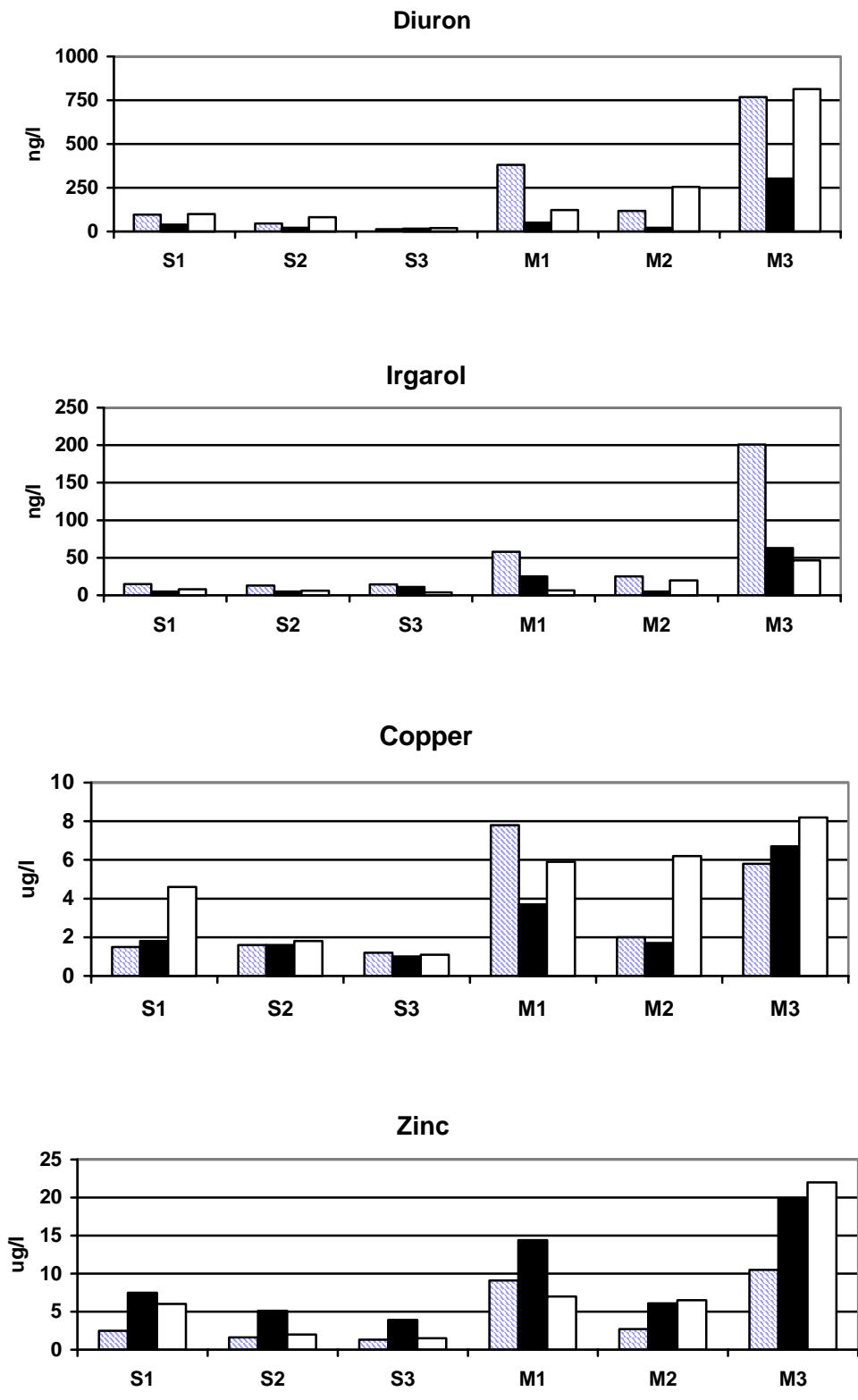
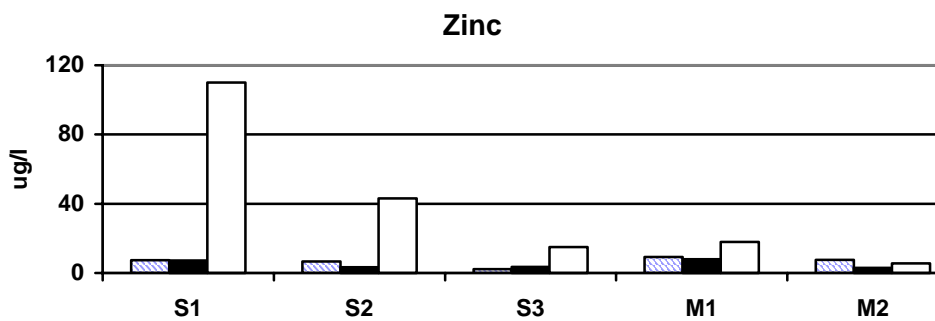
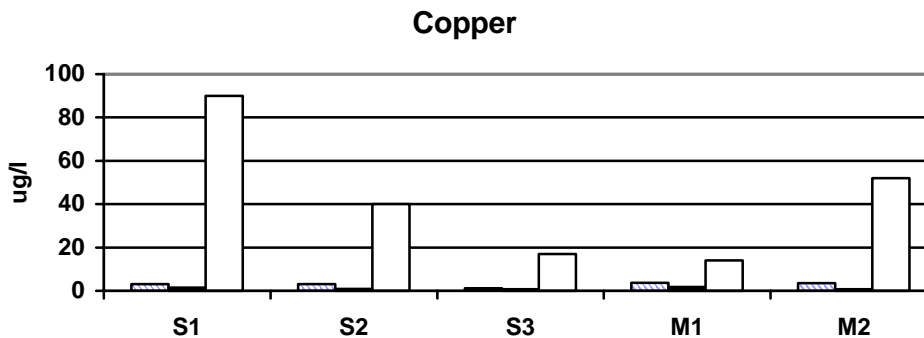
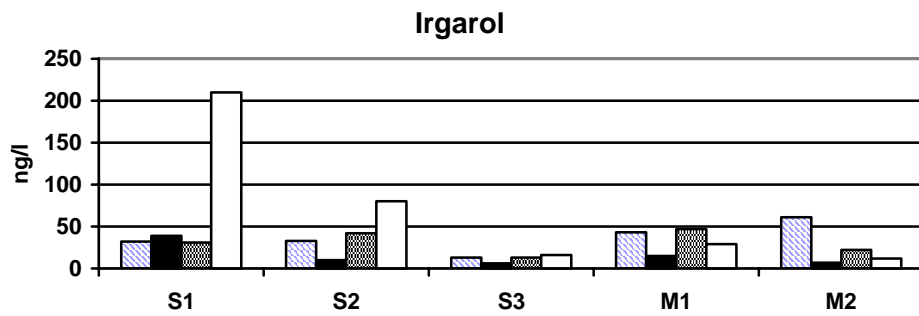
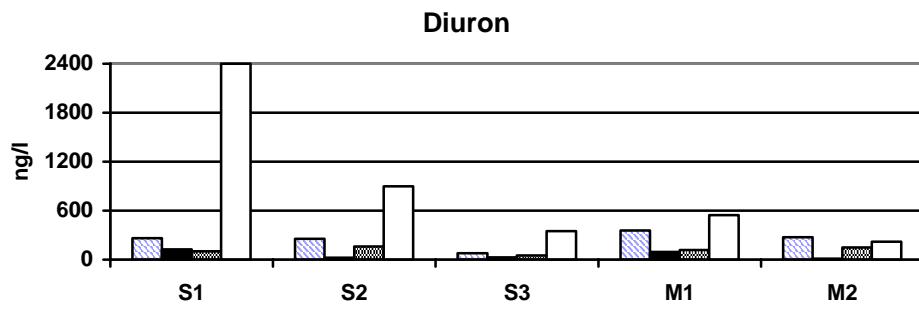


Figure 6-5 Calculation of the flows through model segments



Key: Predicted (white bars);
 Measured, summer 1998 (hatched bars)
 Measured, winter 1998 (black bars)

Figure 6-6 Dissolved concentrations in Orwell estuary from initial validation exercise



Key: Predicted (white bars): Measured CEFAS Apr-Oct 1998 (chequered bars)
 Measured summer 1998 (hatched bars): Measured winter 1998 (black bars)

Figure 6-7 Dissolved concentrations in Hamble Estuary from initial validation exercise

6.2.5 Second validation exercise

The data used for this validation exercise are shown in the following Tables.

Table 6.7 Concentration data used for model

Input Parameter	Biocide			
	Zinc	Copper	Diuron	Irgarol 1051
Input of biocide from river ($\mu\text{g/l}$)				
Orwell	3	1	0	0
Hamble	5	2	0	0
Crouch	5	2	0	0
Soton Water	3	1	0	0
Receiving waters (all estuaries) ($\mu\text{g/l}$)	1	0.5	0.001	0.001
Leaching rates ($\mu\text{g cm}^{-2} \text{day}^{-1}$)	as default	16.12	1.39	0.12
Temp ($^{\circ}\text{C}$)	15	15	15	15

Table 6.8 Marina data used for model

Estuary	No. of Boats	Name of Marina	Water half time (hrs)	Comments
Crouch				
M2	300	Burnham marina	12	Nos. based on CEFAS data Concrete basin marina
Soton Water				
M1	300	Ocean village	12	Nos. based on CEFAS data
M2	500	Hythe marina	48	Nos. based on CEFAS data Locked marina
Orwell				
M1	as default	Fox	12	Marina situated in inlet
M2	as default	Woolverstone	12	Pontooned marina
M3	as default	Shotley	48	Locked marina
Hamble				
M1	as default	Swanwick	12	Pontooned marina
M3	as default	Hamble Point	12	Pontooned marina

Outputs from the model were compared with estuarine and marina sediment and dissolved values obtained from the winter and summer monitoring surveys of the Orwell and Hamble estuaries. The measured values for dissolved diuron and Irgarol 1051 in the Crouch and Southampton Water were the mean of 6 monthly values (Apr-Oct 1998) reported by CEFAS.

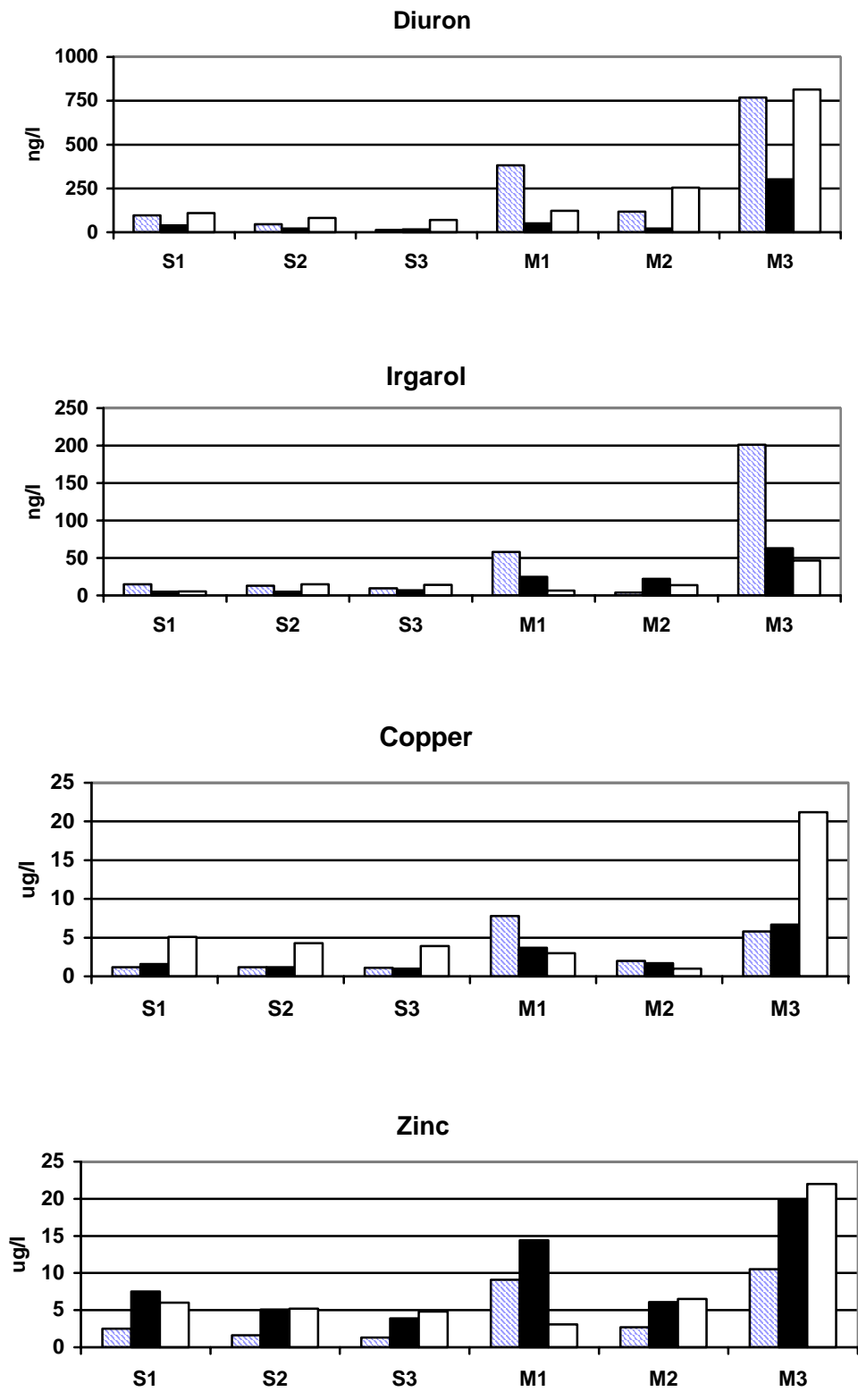
Selected results from the second validation exercise are shown for Orwell and Hamble waters in Figures 6-8 and 6-9. Model predictions for the two estuaries where a full set of 'actual' dissolved and particulate biocide concentrations were available, show good agreement, particularly for the Orwell estuary. The overestimation for the Hamble is no longer so great, less than a factor of four in the worst case.

Predictions for the organic biocides (diuron and Irgarol 1051), where antifoulant paints are the predominant source, match the measured data well with concentrations in the marinas significantly higher than in the estuarine water. The low affinity of diuron and Irgarol 1051 for the sediment (particulate) phase is also reflected in the model outputs, where concentrations were predicted to be less than the analytical limits of detection (as confirmed during the surveys).

For copper and zinc the model data is lower than measured values, particularly for the sediment, which reflects the fact that antifoulant paints are not the only source of these elements. Industrial inputs, sewage effluent, runoff and atmospheric fallout all contribute to the inputs of trace metals to estuaries. Under these conditions the model is useful in allowing an estimate of the likely contribution of antifoulants/sacrificial anodes to the metal burden within an estuary.

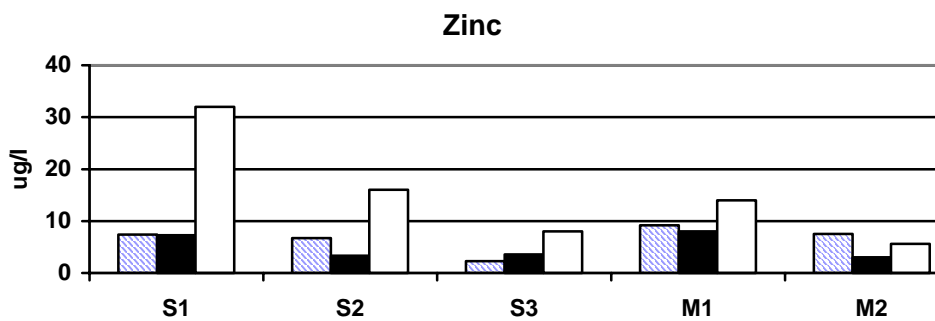
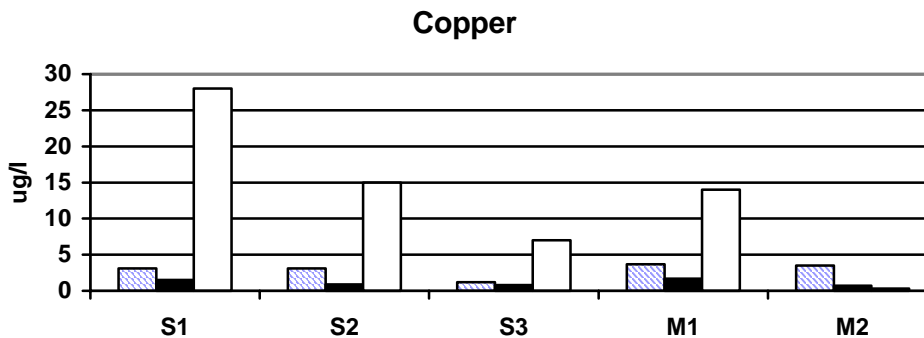
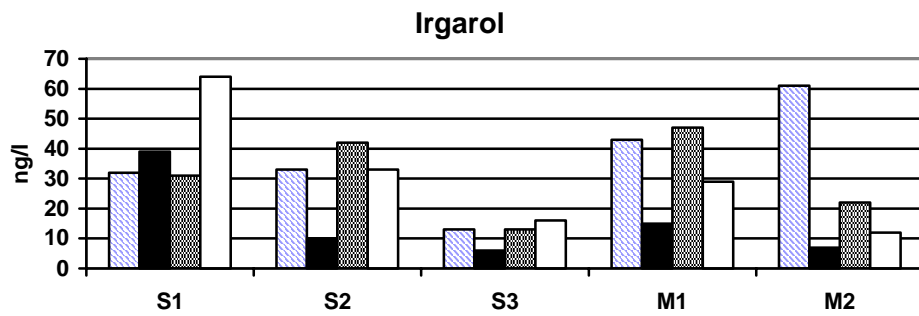
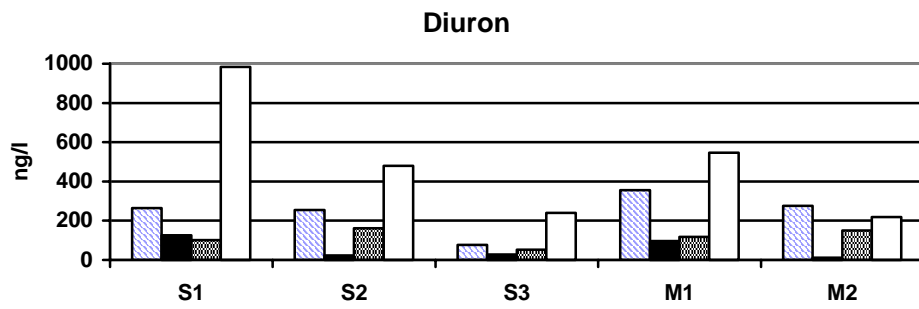
Good agreement between measured (where available) and predicted values for the Crouch and Southampton Water provide a degree of confidence that the model will accurately predict biocide concentrations in estuaries where data is limited, provided realistic input values can be obtained (e.g. biocide partition coefficients and leaching rates, estuarine flow data etc).

The full validation dataset is shown in Appendix E.



Key: Predicted (white bars)
 Measured Summer 1998 (hatched bars)
 Measured Winter 1998 (black bars).

Figure 6-8 Dissolved concentrations in Orwell Estuary



Key: Predicted (white bars)
 Measured Summer 1998 (hatched bars)
 Measured Winter 1998 (black bars).

Figure 6-9 Dissolved concentrations in Hamble Estuary

7. CONCLUSIONS

Biocides used in antifoulant paint formulations on boats and ships are input to the aquatic environment from a multitude of point sources. In marinas, harbours and estuaries, the majority of that input probably occurs when the vessels are moored.

The review of existing environmental fate models showed that none of these was ideally suited for the prediction of environmental concentrations of antifoulant biocides in waters and sediments of marinas, harbours and estuaries.

REMA (Regulatory Environmental Modelling of Antifoulants), a new environmental model has been developed based on the Mackay fugacity concept and a quantitative water, air and sediment interaction model and was set up for four UK estuaries.

A field sampling and laboratory analysis exercise was carried out during the summer and winter periods and provided measured concentration data for four antifoulant biocides in waters and sediments from two of the four selected estuaries.

An extensive study of laboratory partitioning of the four biocides produced a good understanding of the factors controlling their behaviour and good quality data for use in the model.

Initial validation of the model, by comparison of the predicted concentrations with measured concentrations, showed that for some of the biocides for some parts of the estuaries, the model significantly overestimated the concentrations actually present.

Further examination and modification of some of the input and environmental values and re-validation of the model produced predictions, for the two estuaries where a full set of data were available, which showed good agreement with measured data. The predictions were particularly good for the Orwell estuary and the previous overestimation for the Hamble estuary was reduced significantly.

8. RECOMMENDATIONS

When using the REMA model for biocides or estuaries other than those for which the model has been validated, particular attention should be paid to critical input parameters such as leaching rate, partition coefficients and estuarine flows. These parameters have the most significant effects on the PEC's (Predicted Environmental Concentrations) produced and need to be as accurate as possible to ensure the accuracy of the predictions.

The model has been validated using a limited monitoring dataset from two estuaries. If the model is applied to other estuaries with distinctly different environmental characteristics, then validation involving comparison of PEC's with measured concentrations of biocides should be carried out.

Installation and use of the REMA model software has been tested on a number of PCs using MS Windows 95[®] and MS Windows NT[®] operating systems. If the software is installed for use on another operating system it should be tested to ensure that it functions correctly. User guidance (Appendix F) and GWBASIC programme (Appendix G) have been provided. However, additional use of the REMA programme for purposes other than that for which it has been developed will require expert knowledge, additional data and validation.

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APPENDIX A LUTTIK MODEL DETAILS

An Evaluation System for Pesticides (ESPE), which included a marina model that could be used for predicting the environmental concentrations of pesticides, was published by Luttkik et al (1992). This model was incorporated into the environmental risk assessment software, USES (Uniform System for the Evaluation of Substances) developed by the National Institute of Public Health and Environmental Protection (RIVM). It has been used in the assessment of a number of antifoulants and an overview of the model is given below.

Emissions of antifoulings to the environment during the consumer phase

For calculating the risk of antifoulings in the aquatic environment a middle size yacht-basin is modelled. For this calculation it is necessary to have results of a lixivation study (average flux over a certain period).

Hazard evaluation for water organisms and indirect exposure will be handled analogous to agricultural pesticides.

Input/output of emissions of antifoulings

variable [unit]	symbol	S/D/E/O
input		
Number of yachts in yacht-basin	N_{ship}	D
Mean ship deck area [m ²]	$\text{DECKAREA}_{\text{avg}}$	D
Water/ship ratio in yacht-basin	$R_{\text{w/s}}$	D
Fraction of ships in water in the summer	F_{ship}	D
Volume of paint per yacht [m ³]	L_{anti}	S/D
Cover of antifouling paint [m ² .m ⁻³]	R_{anti}	S/D
Depth of yacht-basin [m]	$\text{DEPTH}_{\text{y-b}}$	D
Fraction ships in yacht-basin	$F_{\text{s/ns}}$	D
Mean flux of compound [kg m ⁻² .s ⁻¹]	$\text{FLUX}_{\text{anti}}$	S/D
DT50 for advection in the yacht-basin [s]	$\text{DT50}_{\text{advec, y-b}}$	D

variable [unit]	symbol	S/D/E/O
Suspended solids-water partition coefficient [m'.kg ⁻¹]	Kp _{susp}	SIE
Concentration suspended matter in water [kg.m ⁻³]	SUSPCONC _{surf}	D
First order degradation rate for biodegradation in water [s ⁻¹]	kdeg _{water}	E
output		
Equilibrium diss. conc. in yacht-basin water in summer [kg.m ⁻³] (this concentration is used for the periods of 0, 4, 21, 28, Tbird _{toxtest} Tmammal _{toxtest} , days and one year)	Cwaterpest, equi	

Model calculations

Necessary harbour area per yacht

$$AREA_{w/s} = (1 + R_{w/s}) \cdot DECKAREA_{avg}$$

Total water volume [m3]

$$VOLUME_{water,y-b} = N_{ship} \cdot AREA_{w/s} \cdot DEPTH_{y-b}$$

Antifouling surface area in the yacht-basin (m2)

$$AREA_{anti} = R_{anti} \cdot L_{anti} \cdot N_{ship} - F_{ship} F_{s/ns}$$

Average emission per unit of volume of yacht-basin water [kg s⁻¹ m⁻³]

$$E_{avg,y-b} = \frac{AREA_{anti} \cdot FLUX_{anti}}{VOLUME_{water,y-b}}$$

First order rate constant for advection in the yacht-basin [s^{-1}]

$$k_{\text{advec,y-b}} = \frac{\ln 2}{DT50_{\text{advec,y-b}}}$$

Fraction of the chemical dissolved

$$F_{\text{diss,y-b}} = \frac{1}{1 + K_{\text{p,susp}} \cdot \text{SUSPCONC}_{\text{surf}}}$$

Total first order rate constant [s^{-1}]

$$k_{\text{y-b}} = k_{\text{deg}_{\text{water}}} \cdot F_{\text{diss,y-b}} + k_{\text{advec,y-b}}$$

Equilibrium dissolved concentration in the yacht-basin in the summer [$\text{kg}_{\text{chem}}\text{m}^{-3}$]

$$C_{\text{water}_{\text{pest,eqi}}} = \frac{E_{\text{avg,y-b}} \cdot F_{\text{diss,y-b}}}{k_{\text{y-b}}}$$

APPENDIX B SURVEY DATA

Table B-1 Data for summer survey of Orwell Estuary - Low water samples

Site	Date	Sampling time	Distance from freshwater interface (km)	Temp (°C)	Salinity (‰)	Suspended solids (mg/l)	Diuron (ng/l)	Irgarol 1051 (ng/l)	Cu (µg/l)	Zn (µg/l)
9L	27/08/98	10:25	2.0	16.6	34.6	18.2	76.7	<10.0	1.12	3.09
FOX 1L	26/08/98	19:05	2.0	16.0	26	10.9	257.4	35.7	10.15	10.2
FOX 2L	26/08/98	19:05	2.0	16.0	20.5	12.6	264.0	59.4	8.96	9.8
FOX 3L	26/08/98	19:05	2.0	16.2	29	13.1	342.2	56.3	6.14	9.4
8L	27/08/98	10:11	3.3	16.6	34.5	20.3	67.7	10.7	1.21	2.45
7L	27/08/98	10:00	5.0	16.4	34.7	22.5	50.8	<10.7	1.31	2.45
6L	27/08/98	09:53	6.7	16.0	34.5	22.4	93.9	<11.8	1.34	2.16
WOOL 1L	26/08/98	19:30	6.7	16.0	34.4	32.0	136.0	26.8	2.79	2.88
WOOL 2L	26/08/98	19:30	6.7	16.0	34.1	28.1	77.7	11.4	2.34	2.76
WOOL 3L	26/08/98	19:30	6.7	16.0	34.3	31.3	169.7	21.4	1.85	2.25
5L	27/08/98	09:45	8	16.0	34.8	23.3	82.7	23.7	1.32	1.97
4L	27/08/98	09:35	9.3	16.0	34.8	23.9	57.1	<11.3	1.17	1.67
3L	27/08/98	09:25	11	15.8	35.1	21.6	42.9	<14.0	1.18	1.51
2L	27/08/98	09:13	12.7	15.4	35.8	26.5	23.7	<10.0	1.15	1.27
1L	27/08/98	09:00	15.3	15.8	36.2	29.9	<4.0	<10.0	1.29	1.12

¹ Fox's Marina;

² Woolverstone Marina;

³ Shotley Marina

Table B-2 Data for summer survey of Orwell Estuary - High water samples

Site	Date	Sampling time	Distance from Freshwater interface (km)	Temp (°C)	Salinity (‰)	Suspended Solids (mg/l)	Dissolved Concentrations				Sediment Concentrations				
							Diuron (ng/l)	Irgarol 1051 (ng/l)	Cu (µg/l)	Zn (µg/l)	Cu (mg/kg)	Zn (mg/kg)	Diuron (µg/kg)	Irgarol 1051 (µg/kg)	% <63µm
9H	27/08/98	15:05	2	20.6	34.5	20.8	102.6	30.8	1.15	3.14	87.4	213.7	<17	<14	72.9
Fox 1H ¹	26/08/98	14:00	2	18	26.2	12.4	625.9	78.6	8.5	9.28	229.1	299.1	21	<15	74.7
Fox 2H	26/08/98	14:00	2	17.2	32	14.3	431.4	53.6	6.8	8.88	156.4	258.8	22	<14	69.0
Fox 3H	26/08/98	14:00	2	17.4	30.9	16	362.7	64.3	6.32	6.84	130.1	250.9	<17	<14	63.0
8H	27/08/98	15:13	3.3	17	35.5	21.6	91.4	21.3	1.22	2.5	82.6	190.8	<19	<16	84.3
7H	27/08/98	15:20	5	17.6	35.2	20.2	54.1	21.3	1.22	1.51	52.8	162.8	<18	<15	92.0
6H	27/08/98	15:30	6.7	17.3	36	21.5	37.2	13	1.22	1.12	33.9	123.9	<23	<19	78.1
Wool 1H ²	26/08/98	15:30	6.7	16.8	35.2	21.6	141.5	16.1	3.3	2.96	47.2	152.3	<19	<16	76.9
Wool 2H	26/08/98	15:30	6.7	17	35	22	104.6	<14.7	2.31	2.7	69.8	165.9	<18	<15	78.5
Wool 3H	26/08/98	15:30	6.7	17	35.1	26.1	73.1	62.5	1.55	2.6	48.3	163.0	<18	<15	81.3
5H	27/08/98	15:40	8	16.8	36.6	31.4	<5.6	15.8	1.11	1.89	45.8	166.4	<16	<14	91.7
4H	27/08/98	15:50	9.3	16.8	36.4	25.5	<3.4	14.2	1.13	0.86	35.9	129.3	<23	<19	76.7
3H	27/08/98	16:00	11	16.6	36.6	19.2	<5.6	<15	1.16	1.86	33.5	138.6	<18	<15	88.0
2H	27/08/98	16:10	12.7	16.8	36.6	34.4	<5.6	26.5	1.17	0.99	23.2	94.4	<25	<21	80.5
1H	27/08/98	16:30	15.3	16.8	36.6	37.8	<4.2	11.4	0.94	0.98	30.0	119.8	<22	<18	78.0
Shot 1H ³	26/08/98	16:30	15.3	16.8	36.4	20	880	234.5	6.19	10.39	964.9	614.0	1680	5006	83.4
Shot 2H	26/08/98	16:30	15.3	16.8	36.2	26	576	160	5.63	10.1	164.4	266.2	150	43	85.3
Shot 3H	26/08/98	16:30	15.3	16.8	36.3	23.5	847	209.7	5.48	10.99	230.8	314.7	171	50	86.3

¹ Fox's Marina;

² Woolverstone Marina;

³ Shotley Marina

Table B-3 Data for winter survey of Orwell Estuary (high tide)

Site	Date	Time	Distance Downstream (km)	Temp (°C)	Salinity (‰)	Suspended Solids (mg/l)	Dissolved Concentrations				Sediment Concentrations				
							Diuron (ng/l)	Irgarol 1051 (ng/l)	Cu (µg/l)	Zn (ug/l)	Cu (mg/kg)	Zn (mg/kg)	Diuron (ug/kg)	Irgarol 1051 (ug/kg)	%<63um
9	25/02/99	13:00	2	4.9	29.9	11	66.6	5.1	1.93	9.24	74.3	172.3	<36	<30	72.9
Fox 1 ¹	24/02/99	12:10	2	8.1	3.5	13	31.3	13.8	3.95	22.51	155.5	235.7	1049	226	74.7
Fox 2	24/02/99	12:20	2	6.4	6.5	6.6	70.7	23.1	3.38	10.14	99.7	174.2	<36	<30	69.0
Fox 3	24/02/99	12:30	2	5.8	8	7.4	50.3	37	3.67	10.40	102.5	185.6	<38	<31	63.0
8	25/02/99	12:50	3.3	5	29	13.1	22.2	4.8	1.39	7.36	26.5	108.4	ND	<24	75.3
7	25/02/99	12:35	5	4.8	31	15.2	28.8	4.3	1.39	6.01	74.6	233.9	ND	<29	92.0
6	25/02/99	12:25	6.7	4.7	31	11.8	31.9	5.3	1.31	5.83	41.1	146.6	<26	<22	78.1
Wool 1 ²	24/02/99	14:50	6.7	6.4	32.3	15.2	32.5	3.5	1.96	6.55	42.0	141.5	<33	<28	76.9
Wool 2	24/02/99	14:59	6.7	5.8	32	19.5	23	10.2	1.8	6.28	37.1	134.3	<36	<30	78.5
Wool 3	24/02/99	15:05	6.7	5.4	32.4	24.6	10.1	3	1.31	5.47	45.0	139.9	<33	<28	81.3
5	25/02/99	12:15	8	4.4	31.5	14.9	16.9	7.9	1.28	4.94	25.7	90.3	ND	<20	91.7
4	25/02/99	12:00	9.3	4.4	32.4	13.5	12.6	3	1.15	4.39	33.6	110.1	ND	<22	76.7
3	25/02/99	11:50	11	4.6	33	14.2	14.4	5.9	1	4.22	21.2	86.4	<22	<18	88.0
2	25/02/99	11:40	12.7	4.4	33.7	22.9	17.3	6.9	0.74	4.13	5.7	27.5	ND	<12	80.5
1	25/02/99	11:20	15.3	5.2	34.4	26.6	17.3	7.4	0.76	3.41	26.8	96.2	<33	<27	78.0
Shot 1 ³	24/02/99	15:45	15.3	5	35.2	13.2	251.1	52.3	6.65	21.12	1016.3	498.4	874	4369	83.4
Shot 2	24/02/99	16:00	15.3	4.6	35	11	259.2	57.6	7.01	18.91	137.8	237.7	30	99	85.3
Shot 3	24/02/99	16:05	15.3	5	34.9	16.2	396.0	78.0	6.54	19.61	28.6	171.4	112	77	86.3

¹ Fox's Marina;

² Woolverstone Marina;

³ Shotley Marina

Table B-4 Data for summer survey of Hamble Estuary (high tide)

Site	Date	Time	Distance from Bursledon bridge (km)	T (°C)	Salinity (‰)	Suspended Solids (mg/l)	Dissolved Concentration				Sediment Concentration				
							Cu (µg/l)	Zn (µg/l)	Diuron (ng/l)	Irgarol 1051 (ng/l)	Zn (mg/kg)	Cu (mg/kg)	Irgarol 1051 (µg/kg)	Diuron (µg/kg)	% <63µm
10	25/9/98	12:25	0.5	17.6	33.5	20.3	3.55	9.59	308.4	35.9	136.7	61.8	<18	46	21.7
11a¹	25/9/98	12:30	0.5	17.6	33.6	19.3	3.55	8.98	387	47.7	179.8	91.3	<27	48	81.5
11b	25/9/98	12:35	0.5	17.6	33.6	20.2	3.41	7.55	339.8	44.1	212.9	92.2	<28	42	78.1
11c	25/9/98	12:45	0.5	17.6	33.6	19.4	4.02	11.02	338.1	38.2	180.9	93.2	57	ND	79.7
9	25/9/98	12:20	0.7	17.6	33.8	19.9	2.99	6.73	280.9	35.5	158.2	61.8	55	<26	46.6
6	25/9/98	12:00	1.3	18	34	24.7	2.65	5.92	202.7	24.2	171.9	74.4	<23	<27	82.2
8	25/9/98	12:10	2	17.6	34.5	19.4	2.85	6.33	232.2	28.7	197.0	79.3	73	<28	66.0
7	25/9/98	12:05	2.6	17	35.2	21.5	3.21	6.73	256.8	34.1	156.1	60.2	<22	<26	74.1
4	25/9/98	11:35	3.2	18	34.5	24.5	3.18	7.14	274.1	35.9	172.6	66.4	<21	<25	54.5
5a²	25/9/98	11:40	3.2	18	34.8	24.5	3.49	8.37	277.2	109.1	180.3	65.4	<31	<37	77.1
5b	25/9/98	11:45	3.2	18	34.5	18	3.10	6.33	268.6	42.7	180.7	58.2	<28	ND	78.1
5c	25/9/98	11:50	3.2	18	34	23.1	4.05	7.86	280.6	31.6	161.4	60.7	<28	<33	76.9
3	25/9/98	11:30	3.9	18.2	35	26	1.31	3.47	150.8	16.1	143.5	49.6	<20	<24	79.8
2	25/9/98	11:15	4.4	17.8	35.7	39.3	1.09	1.84	45.3	<12	58.2	16.2	28.1	<18	25.0
1	25/9/98	11:00	5.9	19	35.7	24.4	1.06	1.63	34.3	17.9	61.2	16.4	<18	<22	80.3

¹ Swanwick Marina

² Hamble Point Marina

Table B-5 Data for winter survey of Hamble Estuary (high tide 10:45 and 13:00)

Site	Date	Time	Distance from Bursledon bridge (km)	T (°C)	S (‰)	Suspended Solids (mg/l)	Dissolved concentrations				Sediment Concentrations				
							Cu (µg/l)	Zn (µg/l)	Diuron (ng/l)	Irgarol 1051 (ng/l)	Zn (ug/g)	Cu (ug/g)	Irgarol 1051 (µg/kg)	Diuron (µg/kg)	% <63µm
10	16/2/99	11:35	0.5	7	22.5	20.3	1.78	8.46	71	20.3	139.4	41.2	<17	ND	40.8
11a¹	16/2/99	11:45	0.5	7	31.4	19.3	2.11	10.41	83.5	8.3	198.8	100.9	<25	<30	74.6
11b	16/2/99	11:45	0.5	7	31.2	20.2	1.69	7.31	110.6	10.3	176.8	85.4	<24	<30	47.9
11c	16/2/99	11:45	0.5	7	31	19.4	1.35	6.24	94.6	26.6	245.0	106.4	<34	<41	58.5
9	16/2/99	11:30	0.7	7	28	19.9	1.49	6.69	121.7	29.5	166.3	58.6	<22	ND	50.6
6	16/2/99	11:25	1.3	7	28	24.7	1.29	6.77	182.6	67.5	161.9	71.9	<21	<25	48.7
8	16/2/99	11:15	2	7	28	19.4	1.04	3.68	50.8	13.3	110.0	28.6	<16	ND	26.0
7	16/2/99	11:10	2.6	7	30.8	21.5	0.78	2.97	11.3	11.8	134.9	47.8	<21	ND	60.6
4	16/2/99	11:00	3.2	7	32.4	24.5	0.73	3.32	5.4	4.5	135.1	50.3	93	<25	54.6
5²	16/2/99	11:05	3.2	7	33.2	24.5	0.74	2.97	10.5	7.3	130.1	47.1	93	ND	68.9
3	16/2/99	10:50	3.9	7	33.6	26	0.82	2.79	17	5	203.4	79.6	<37	<44	57.3
2	16/2/99	10:45	4.4	7	34.8	39.3	0.63	3.41	29	5	112.8	35.2	<17	ND	64.2
1	16/2/99	10:35	5.9	7	34.4	24.4	0.92	4.56	36.3	12.9	79.3	19.9	<17	<20	48.5
Hythe³	16/2/99	09:30					5.45	26.96	2003	368.6	381.0	331.9	ND	ND	61.0

¹ Swanwick Marina

² Hamble Point Marina

³Hythe Marina, Southampton Water

ND : Not determined

APPENDIX C PARTITIONING DATA

Table C-1 Summary data for diuron partitioning experiments

Sediment	1 g/l SS				20 g/l SS				200 g/l SS			
	Initial Conc (ng/l)	Mean Final conc (ng/l)	Range (ng/l)	Log Koc	Initial Conc (ng/l)	Final conc (ng/l)	Range (ng/l)	Log Koc	Initial Conc (ng/l)	Final conc (ng/l)	Range (ng/l)	Log Koc
Arun	500	501	486-522	3.18	250	225	220-230	2.64	500	304	300-307	2.41
Bracklesham	500	449	437-460	5.20	250	237	228-246	3.45	500	329	311-346	3.57
Bosham	500	416	391-442	3.74	250	188	176-200	2.66	500	47	40-55	3.13
Chichester	500	502	469-563	3.74	250	232	225-240	2.72	500	124	96-152	3.16
Dell Quay	500	481	460-496	3.58	250	239	230-248	2.28	500	147	125-169	3.24
Pagham	500	441	416-460	4.11	250	215	206-228	2.86	500	57	31-82	3.65

Table C-2 Summary data for Irgarol 1051 partitioning experiments

Sediment	1 g/l SS				20 g/l SS				200 g/l SS			
	Initial Conc (ng/l)	Mean Final conc (ng/l)	Range (ng/l)	Log Koc	Initial Conc (ng/l)	Final conc (ng/l)	Range (ng/l)	Log Koc	Initial Conc (ng/l)	Final conc (ng/l)	Range (ng/l)	Log Koc
Arun	500	493	478-510	3.34	250	180	170-190	3.19	500	87	78-96	3.28
Bracklesham	500	472	457-482	4.89	250	238	228-247	3.39	500	425	414-435	3.10
Bosham	500	446	435-469	3.50	250	134	122-146	3.08	500	63	53-73	2.99
Chichester	500	495	485-510	3.37	250	193	170-216	3.34	500	229	188-270	2.74
Dell Quay	500	504	489-526	3.14	250	223	213-232	2.92	500	210	209-211	3.00
Pagham	500	458	435-482	3.91	250	185	170-200	3.24	500	113	94-132	3.24

APPENDIX D

DESCRIPTION OF QWASI MODEL

Process		Rates (mol/h)		D	B	B or D Group
Sediment Burial	$G_B C_S$	$G_B Z_S f_S$	$D_B f_S$	$D_B = G_B Z_S$	$B_B = J_B Z_S$	1
Sediment Transformation	$V_S C_S k_S$	$V_S Z_S k_S f_S$	$D_S f_S$	$D_S = V_S Z_S k_S$	$B_S = h_S Z_S k_S$	1
Sediment Resuspension	$G_R C_S$	$G_R Z_S f_S$	$D_R f_S$	$D_R = G_R Z_R$	$B_R = J_R Z_R$	2
Sediment-to Water Diffusion	$K_T A_S C_N$	$K_T A_S Z_W f_S$	$D_T f_S$	$D_T = K_T A_S Z_W$	$B_T = K_T Z_W$	2
Water-to-Sediment Diffusion	$K_T A_S C_W$	$K_T A_S Z_W f_W$	$D_T f_W$	$D_T = K_T A_S Z_W$	$B_T = K_T Z_W$	3
Sediment Deposition	$G_D C_P$	$G_D Z_P f_W$	$D_D f_W$	$D_D = G_D Z_P$	$B_D = J_D Z_P$	3
Water Transformation	$V_W C_W k_W$	$V_W Z_W k_W f_W$	$D_W f_W$	$D_W = V_W Z_W k_W$	$B_W = h_W Z_W k_W$	4
Water -to-Air Volatilisation	$K_V A_W C_W$	$K_V A_W Z_W f_W$	$D_V f_W$	$D_V = K_V A_W Z_W$	$B_V = K_V Z_V$	4
Water Outflow	$G_J C_W$	$G_J Z_W f_W$	$D_J f_W$	$D_J = G_J Z_W$		5
Suspended Sediment Outflow	$G_Y C_P$	$G_Y Z_P f_W$	$D_Y f_W$	$D_Y = G_Y Z_P$		5
Air-to-Water Absorption	$K_V A_W P_A/H$	$K_V A_W Z_W f_A$	$D_V f_A$	$D_V = K_V A_W Z_W$	$B_V = K_V Z_W$	6
Air Particle Deposition	$G_Q C_Q$	$G_Q Z_Q f_A$	$D_Q f_A$	$D_Q = G_Q Z_Q$	$B_Q = J_Q Z_Q$	6
Air Rain-Out	$G_M C_M$	$G_M Z_W f_A$	$D_M f_A$	$D_M = G_M Z_M$	$B_M = J_M Z_M$	6
Water Inflow	$G_I C_I$	$G_I Z_W f_I$	$D_I f_I$	$D_I = G_I Z_W$		7
Suspended Sediment Inflow	$G_X C_X$	$G_X Z_P f_I$	$D_X f_I$	$D_X = G_X Z_P$		7

$$G_B = J_B A_S, \quad G_R = J_A A_S, \quad G_D = J_D A_S, \quad G_Q = J_Q A_W, \quad G_M = J_M A_W$$

APPENDIX E MODEL VALIDATION DATA

Second Validation Exercise

Table D-1 Measured and predicted data for Southampton Water

Sediment

Site	Diuron		Irgarol 1051		Copper		Zinc	
	Measured	Predicted	Measured	Predicted	Measured	Predicted	Measured	Predicted
S1		1.3		0.4		8		3.9
S2		0.9		0.3		6.2		3.3
S3		0.6		0.3		6.8		4
M1		35		2.5		63		18
M2		44		3.3		103		35

Water

Site	Diuron		Irgarol 1051		Copper		Zinc	
	Measured	Predicted	Measured	Predicted	Measured	Predicted	Measured	Predicted
S1	1.7	37	4.7	10		1.7		3
S2	1.6	25	4.7	8		1.3		2.1
S3	1.2	15	6	6		1		1.7
M1	47	546	61	29		13.4		14
M2	101	911	1421	50		22.4		24

NB Units for diuron and Irgarol 1051 are ng/l for water and µg/kg for sediments
 Units for copper and zinc are µg/l for water and mg/kg for sediments

Table D-2 Measured and predicted data for River Crouch

Sediment

	Diuron		Irgarol 1051		Copper		Zinc	
Site	Measured	Predicted	Measured	Predicted	Measured	Predicted	Measured	Predicted
S1		2.8		0.4		20		8.1
S2		1		0.2		11	77	5
S3		0.3		0.1		7.5		4.2
M2		26		2		62	118	21

Water

	Diuron		Irgarol 1051		Copper		Zinc	
Site	Measured	Predicted	Measured	Predicted	Measured	Predicted	Measured	Predicted
S1	2.1	84	9.1	9.3		4.4		6.2
S2	3.4	31	8.5	4.9		2.4	3	3.3
S3	0.6	7.2	1	2.4		1.1		1.8
M2	117	546	15	29		1.4	7	1.4

NB Units for diuron and Irgarol 1051 are ng/l for water and µg/kg for sediments
 Units for copper and zinc are µg/l for water and mg/kg for sediments

Table D-3 Measured and predicted data for River Orwell

Sediment

	Diuron			Irgarol 1051			Copper			Zinc		
Site	Summer	Winter	Predicted	Summer	Winter	Predicted	Summer	Winter	Predicted	Summer	Winter	Predicted
S1	0	0	3.7	0	0	0.6	78	58	23	189	172	7.8
S2	0	0	2.8	0	0	0.6	39	33	20	140	116	7.9
S3	0	0	2.6	0	0	0.6	29	18	25	118	70	1.1
M1	22	362	7.8	0	85	0.6	172	119	14	270	119	4.1
M2	0	0	12.3	0	0	0.9	55	41	29	160	139	9.9
M3	161	71	9	48	88	0.9	198	84	131	291	205	48

Water

	Diuron			Irgarol 1051			Copper			Zinc		
Site	Summer	Winter	Predicted	Summer	Winter	Predicted	Summer	Winter	Predicted	Summer	Winter	Predicted
S1	96	39	110	15	5	15.2	1.2	1.6	5.1	2.5	7.5	6
S2	46	21	81	13	5	14.8	1.2	1.2	4.3	1.6	5.1	5.2
S3	13	16	70	9.7	7	14.3	1.1	0.8	3.9	1.3	3.9	4.8
M1	381	51	122	58	25	6.6	7.8	3.7	3	9.1	14.4	3.1
M2	117	22	255	24	4	13.7	2	1.7	14	2.7	6.1	6.5
M3	768	302	814	201	63	46.5	5.8	6.7	21.2	10.5	19.9	22

NB Units for diuron and Irgarol 1051 are ng/l for water and µg/kg for sediments
 Units for copper and zinc are µg/l for water and mg/kg for sediments

Table D-4 Measured and Predicted Data for River Hamble

Sediment

	Diuron				Irgarol 1051				Copper			Zinc		
Site	Summer	Winter		Predicted	Summer	Winter		Predicted	Summer	Winter	Predicted	Summer	Winter	Predicted
S1	24			33	12			2.6	66	57	132	156	156	41
S2				16	25	37		1.3	69	42	68	175	127	25
S3				9	10			0.7	27	45	49	88	132	20
M1	45			35	16			2.5	92	98	63	191	207	18
M2				2.4		93		0.2	61	47	33	174	130	12

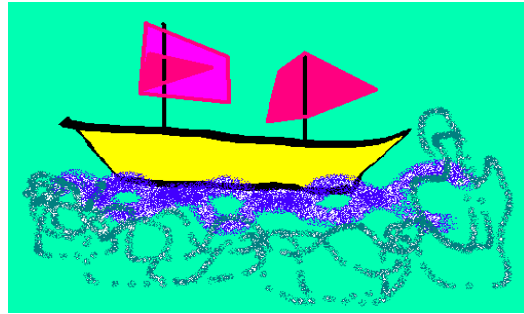
Water

	Diuron				Irgarol 1051				Copper			Zinc		
Site	Summer	Winter	CEFAS	Predicted	Summer	Winter	CEFAS	Predicted	Summer	Winter	Predicted	Summer	Winter	Predicted
S1	264	125	101	984	32	39	31	64	3.1	1.5	28	7.4	7.3	32
S2	254	23	162	480	33	10	42	33	3.1	0.9	15	6.7	3.3	16
S3	77	27	52	240	13	6	13	16	1.2	0.8	7	2.3	3.6	8
M1	355	96	117	546	43	15	47	29	3.7	1.7	14	9.2	8	14
M2	275	11	150	219	61	7	22	12	3.5	0.7	5.3	7.5	3	5.6

NB Units for diuron and Irgarol 1051 are ng/l for water and µg/kg for sediments
 Units for copper and zinc are µg/l for water and mg/kg for sediments

APPENDIX F REMA MODEL USER GUIDANCE

Demonstration of the antifouling model developed by WRc on behalf of HSE and the Environment Agency.



Description of the model

The REMA programme is a mathematical model for estimating the 'Predicted Environmental Concentrations' in marinas and estuaries of active ingredients of biocidal products used for antifouling treatment of boats.

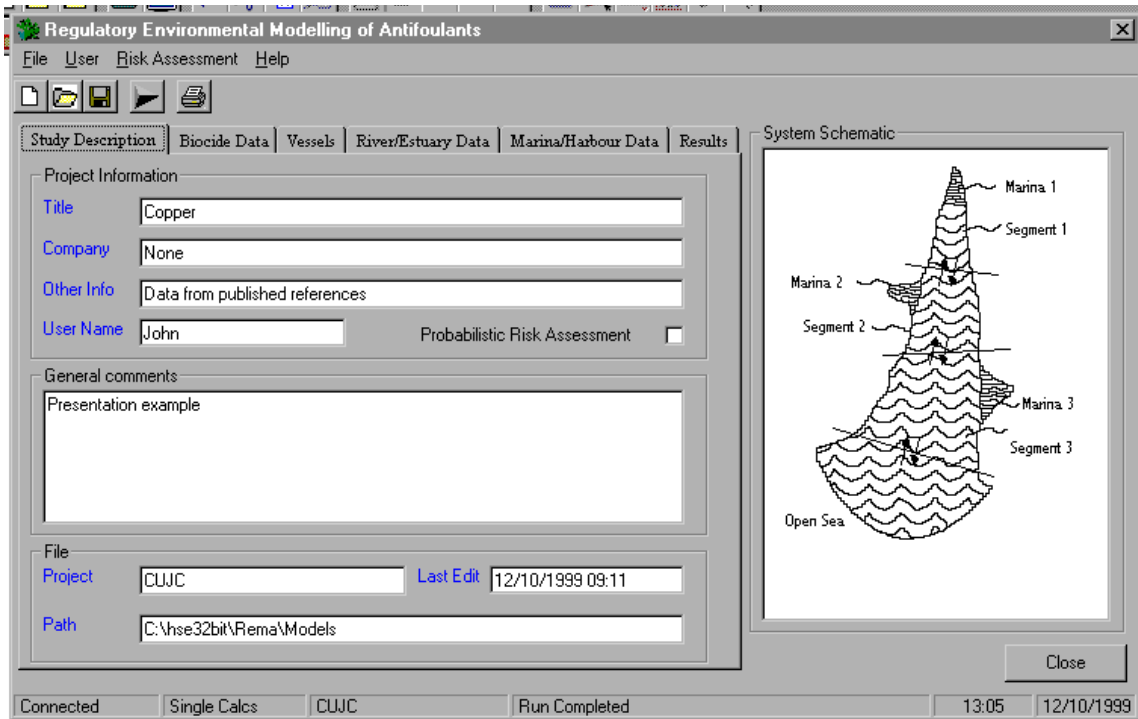
The programme is based on a quantitative water air sediment interaction (QWASI) model employing the fugacity concept for environmental modelling developed by Professor Donald Mackay at Trent University. The QWASI model was developed and validated for selected UK locations using monitoring information for specific antifoulant substances.

The software development project was funded by HSE and the Environment Agency and implemented by WRc. The software was written in Visual Basic by Patrick and Associates.

The REMA screen

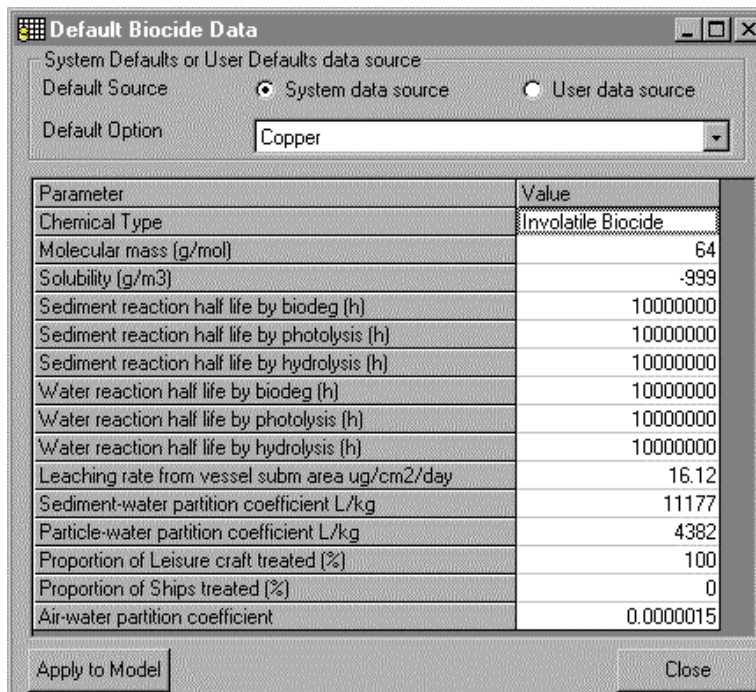
The REMA screen is separated into a number of regions as shown on the next page. At the top of the screen is the title bar, below this is the menu bar containing **File** **User** **Risk Assessment** **Help** menus. Under this is the tool bar containing buttons to create a project, load a project, save a project, run a project and output a project's results. Within each screen are a number of buttons, fields, and check boxes with which the user can interact with the program.

At the bottom of the screen is the status bar which tells the user the present situation and setting of the program. To the right of the screen is the System Schematic, this shows the estuary model. Parts of the model are highlighted when data are being entered or edited in them.



Biocides data

Data for can be selected for an existing biocide, this data can be edited or new biocide data can be added. The data are edited in the **Default Option field**; this field may be blank if no biocides have been added by users.



Once a biocide has been selected pressing **Apply to Model** will close the dialogue box and the biocide selected entered into the model.

Study Description | **Biocide Data** | Vessels | River/Estuary Data | Marina/Harbour Data | Results

Currently selected Default:

Model data

Biocide Type: Organic Biocide Involatible Biocide

Molecular Mass / Relative Atomic Mass: g/mol

Sediment-water partition coeff.: l/kg

Particle-water partition coeff.: l/kg

Solubility: mg/l

Air-water partition:

Leaching rate: ug/cm²/d

Temp.: deg C

	Biodegradation	Photolysis	Hydrolysis	
Half Lives in Water	<input type="text" value="10000000"/>	<input type="text" value="10000000"/>	<input type="text" value="10000000"/>	h
Half Lives in Sediment	<input type="text" value="10000000"/>	<input type="text" value="10000000"/>	<input type="text" value="10000000"/>	h

The Area of hull below the water line information is fixed, based on information collected during the validation of this model. The figures for the Proportion treated with biocide may be set by the user based on known or predicted biocide usage.

Regulatory Environmental Modelling of Antifoulants

File | User | Risk Assessment | Help

Study Description | **Biocide Data** | **Vessels** | River/Estuary Data | Marina/Harbour Data | Results

Default Ship and Leisure craft areas below water line.

Default System-wide Values

Leisure Craft: Area of hull below water line: m²
 Proportion treated with biocide: %

Ships: Area of hull below water line: m²
 Proportion treated with biocide: %

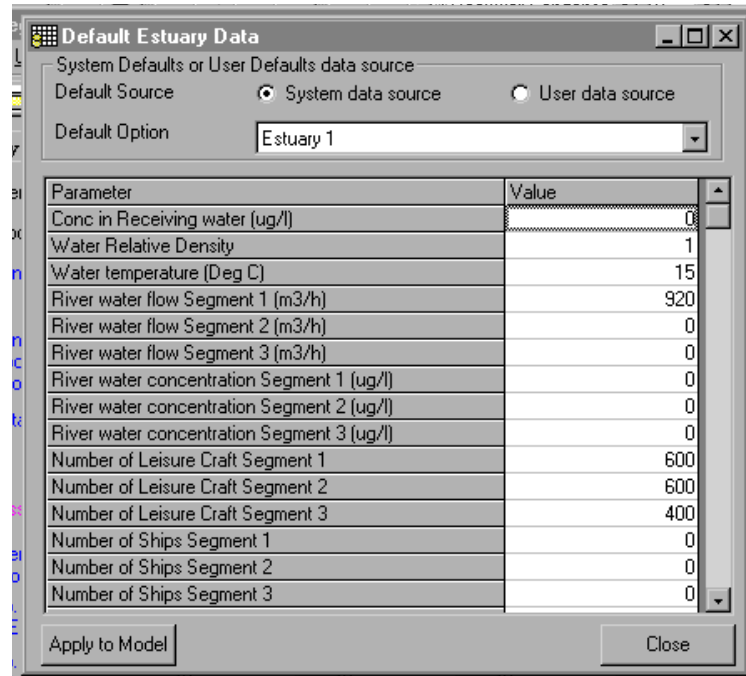
These values are used to calculate the Average Area of vessels in both Marinas/Harbours and Estuaries. The average area of biocide coverage (treated) is calculated by multiplying area of vessels by proportion treated.

Example:

Ave. Vessel Area treated, Segment 1 = (Proportion Ships treated * No of Ships in Segment 1 * area of Ships hull below water line) + (Proportion Leisure craft treated * No of Leisure craft in Segment 1 * area of Leisure craft hull below water line)

Applying an estuary

To use an estuary model click on the button. This will call up the Default Estuary Data dialogue box shown below.



The dialog box 'Default Estuary Data' contains the following information:

System Defaults or User Defaults data source
Default Source: System data source User data source
Default Option: Estuary 1

Parameter	Value
Conc in Receiving water (ug/l)	0
Water Relative Density	1
Water temperature (Deg C)	15
River water flow Segment 1 (m3/h)	920
River water flow Segment 2 (m3/h)	0
River water flow Segment 3 (m3/h)	0
River water concentration Segment 1 (ug/l)	0
River water concentration Segment 2 (ug/l)	0
River water concentration Segment 3 (ug/l)	0
Number of Leisure Craft Segment 1	600
Number of Leisure Craft Segment 2	600
Number of Leisure Craft Segment 3	400
Number of Ships Segment 1	0
Number of Ships Segment 2	0
Number of Ships Segment 3	0

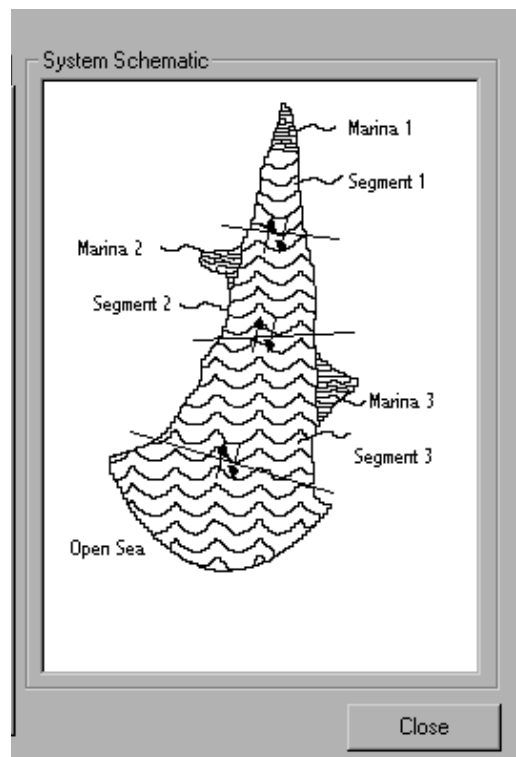
Buttons: Apply to Model, Close

Initially, the centre section of the box will be empty. Clicking on the down arrow on the **Default Options field** will call up a list of default estuaries, from which an estuary can be selected. When the estuary is chosen its parameters are shown in the centre section of the box. By clicking on **Apply to Model** the dialogue box will be closed and the Estuary data selected entered into the model and displayed on the screen as shown below.

The values for **Concentration of biocide in receiving water** and **Concentration of biocide in river water** can be changed based on predictions or measurement of the biocide in question. **The No. of Leisure craft in Estuary** and **No. of Ships in Estuary** can also be changed.

Study Description	Biocide Data	Vessels	River/Estuary Data	Marina/Harbour Data	Results
Currently selected Default		Estuary 1			Defaults
Model data					
Concentration of biocide in receiving water		0 ug/l			
Concentration of biocide in river water inflows		Segment 1	Segment 2	Segment 3	ug/l
		0	0	0	
Total Volume		941600	2321280	2745900	m ³
Vessel Numbers:					
Average treated area below waterline		18420	18420	12280	m ²
No. of Leisure craft in Estuary		600	600	400	
No. of Ships in Estuary		0	0	0	

The four estuaries in the system data are based on data collected in the UK during the last 20 years. Each estuary is divided into three estuary segments each containing one marina. Each estuary segment has an inflow from a river, which itself may have a known concentration of the biocide, set by the user. The model then moves water and sediment between estuary segments and marinas according to the prevailing conditions in the estuary. Each marina has a water flow half time, representing the rate of water exchange between the Marina and adjoining Estuary segment. The whole model is shown in the schematic displayed below.



The individual estuary models can be summarised as: Estuary 1: A small estuary, that dries out. Estuary 2: A well mixed estuary, with a narrow mouth. Estuary 3: A well mixed estuary, with a wide mouth. Estuary 4: A large, complex estuary.

Selecting a marina/harbour model

The **Marina/Harbour Data** used is linked to the **River/Estuary Data**. Although the default model can be selected in this screen by pressing the defaults button, it will also change the values in the **River/Estuary Data** page.


Changing marina/harbour data

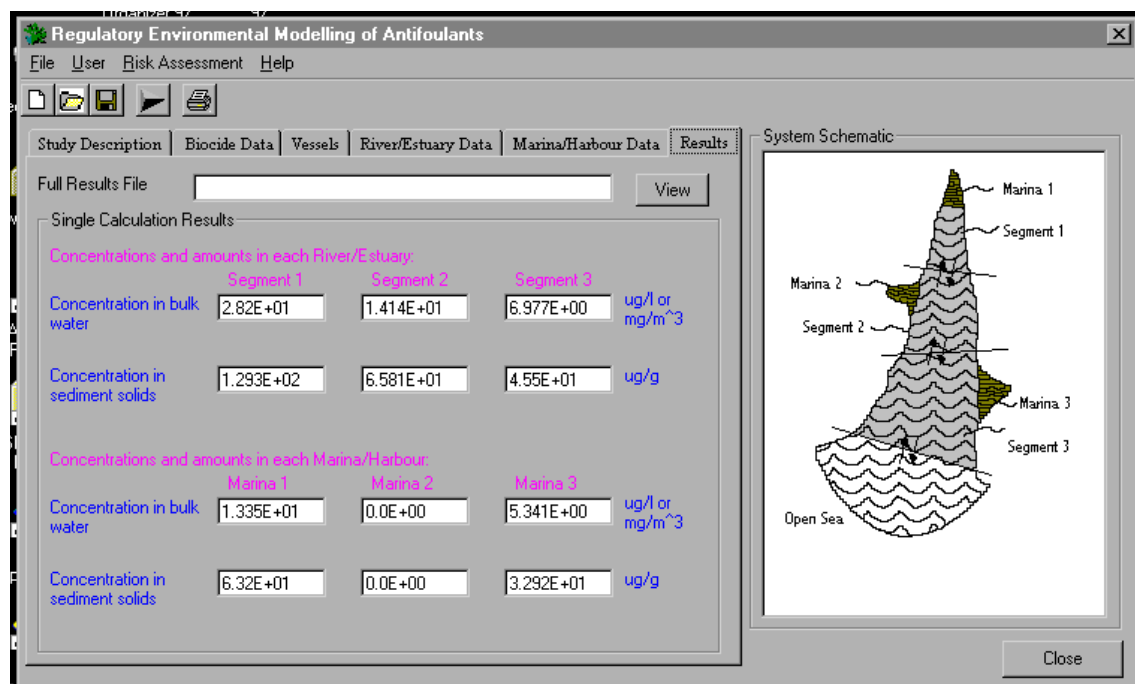
Once an Estuary has been selected the fields shown in black can be changed, those in grey are figures derived from the data given and cannot be changed by the user. Additionally, the name of the Marina/Harbour for Scenario being used cannot be changed by the user.

The **Marina/Harbour Sizes** data can be changed by the user if required, however, this data are based on real situations. The **Water flow half times** indicate the rate of interchange of water between the marina and its adjoining estuary segment. Values other than zero must be placed in the **Water flow half times** fields in order for the model to function correctly. The **Vessel Numbers** field defines the amount of boating/shipping activity in the Marina or Harbour.

	Segment 1	Segment 2	Segment 3	
Marina/Harbour Sizes:				
Area	20000	20000	50000	m ²
Average water depth	4	4	4	m
Total Volume	80000	80000	200000	m ³
Water flow half times:				
Marina/Harbour	12	12	12	h
Vessel Numbers:				
Average treated area below waterline	9210	0	9210	m ²
No. Leisure craft in marina/harbour	300	0	300	
No. Ships in marina/harbour	0	0	0	

Results - Running the model

Once the data has been entered the model may be run by clicking on the  button on the tools bar. In single calculation mode the model should take a few seconds to run, at the end of this time the results will be given as shown overleaf. The results are shown in $\mu\text{g/l}$ and in scientific notation where E represents exponential (times ten to the power). The results shown are for the concentrations of biocide in water and sediment in each of the marinas and estuary segments (no calculations are made for changes in the open sea segment as this is assumed to stay constant).



Probabilistic Risk Assessment - Monte Carlo modelling

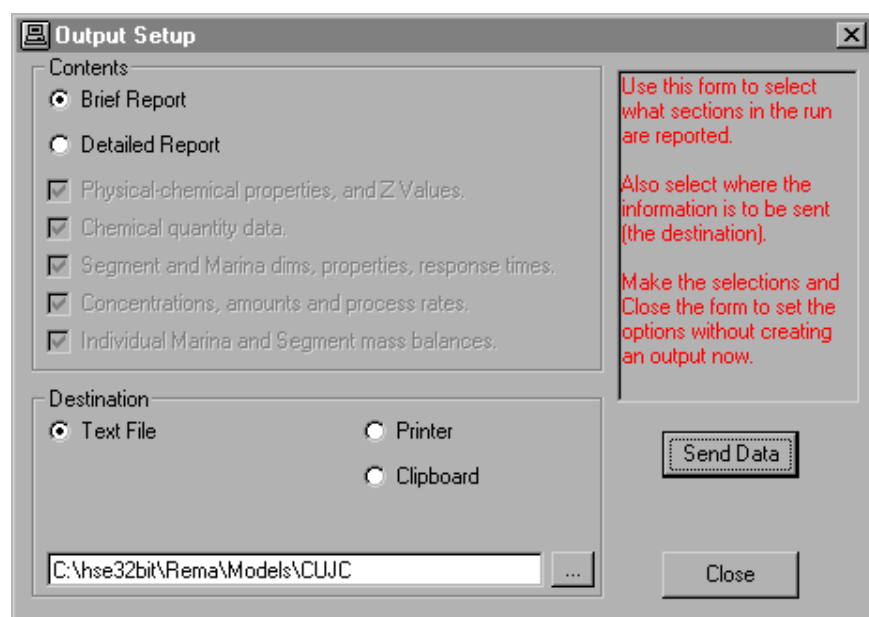
REMA has been developed with probabilistic risk assessment as an additional function. Probabilistic risk assessment allows the user to find the standard deviation and other statistical variations in the results due to uncertainty in the data used, using the Monte Carlo theory. In order to do this the computer generates a large data set of possible solutions to the model. To create each point in the data set the computer applies a random factor to the data to take into account the standard deviation for each datum and then runs the model. By repeating this process the data set slowly builds up into a number of different solutions to the model each using different set of data which have been derived using the standard deviations. Once the data set is produced the computer calculates the mean and standard deviations for each of the results and also allows the user to export the data set it has produced for further analysis. This data can then be examined for factors such as the 95 percentile, however, the maximum and minimum values produced by this method should not be used as the computer has been constrained to the amount of random variation it can apply to the data.

RESULTS OUTPUT

In order to define the type of output required use File > Print setup from the menu bar to call up the dialogue box shown below.

The dialogue box is in three parts. The first sets the **Contents** of the output file. The second sets the **Destination**. This gives a list of check box options (both Printer and Clipboard have been disabled in this application). The lower field in this section shows the path and filename to which the output will be sent, this can be changed by the user if required. Further information on these sections is given below

The third area contains the **Send Data** and **Close** buttons. **Send Data** will send the output data to the specified file immediately, **Close** put the requested setting in place for data to be sent later. Please note, data can only be sent once a model has been run.



Outputs from Single Calculations

Single calculations can be **Output** as **Text files** only. A summary can be obtained by clicking on the **Brief Report** box. Detailed reports can be obtained by pressing the **Detailed Reports** check box and pressing the options check boxes beneath it as required.

Outputs from Probabilistic Calculations

Results from probabilistic calculations can be output as **Brief Reports** in the **Text File** format or as a **Special CSV Results File** (Comma-separated values format) which can be read by spreadsheet packages. The CSV file contains the full dataset produced if **Write input data** to file was selected in the dialogue box then the Probabilistic input data will also be written to this file.

Writing outputs

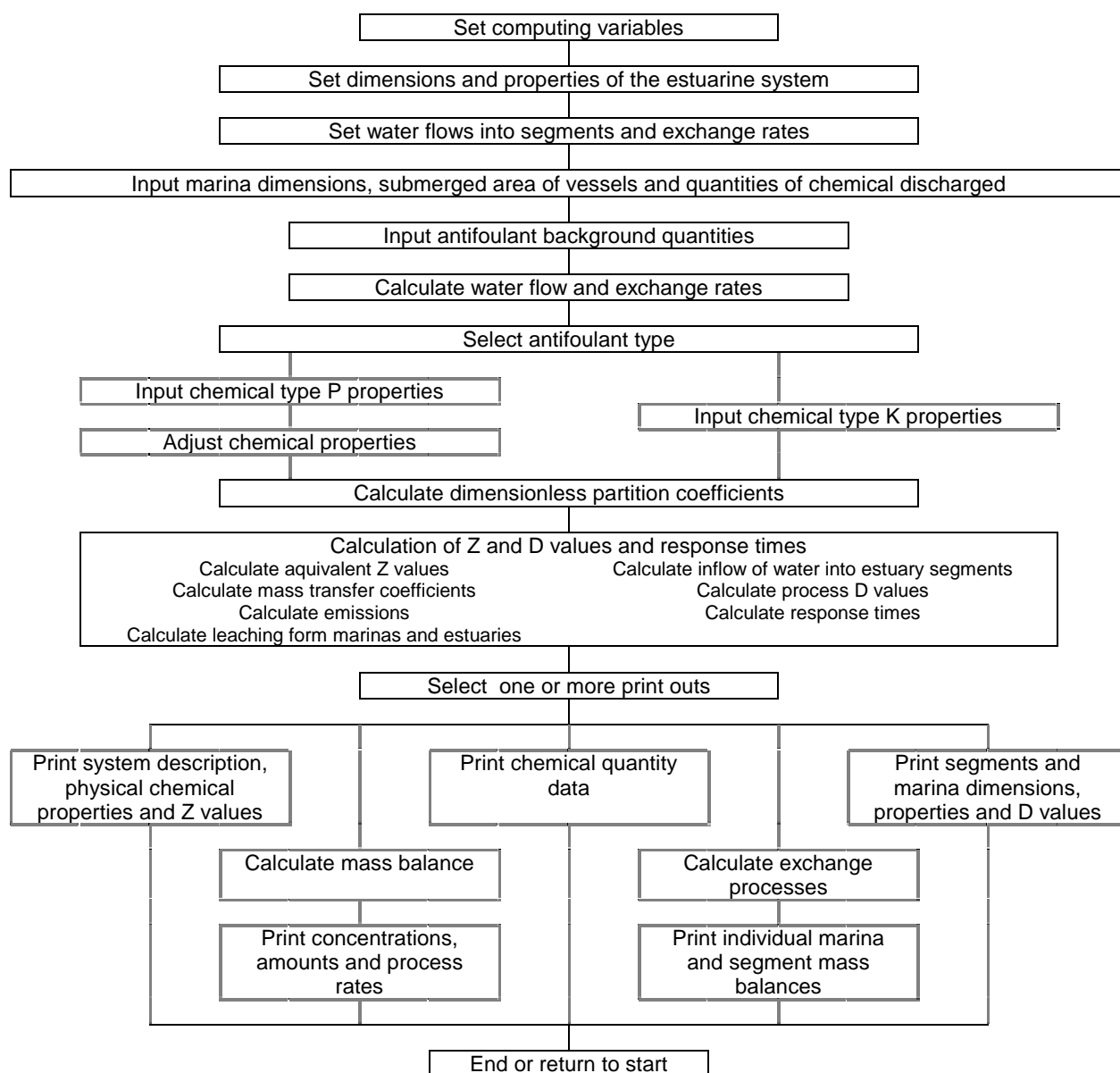
The **Output** can be obtained in a number of ways from the **Output Setup** dialogue box by clicking on **Send Data**, from File > Print on the menu bar or by clicking on the button on the tool bar.

Viewing outputs

Text outputs can be viewed by clicking on the button on the **Results** page, this starts up the notepad program with the output file displayed. Other outputs can be viewed by opening them in an appropriate package.

APPENDIX G GWBASIC PROGRAM

The REMA (Regulatory Environmental Modelling of Antifoulant) software is based on a QWASI fugacity model which was initially programmed in GWBASIC. The QWASI model has been placed in user-friendly shell programmed in visual basic, but all of the key calculations are performed by the GWBASIC part of the software. This Appendix provides a flow diagram of the GWBASIC program routines (Figure F-1) and a full listing of the program source code.



Type P = Organic antifoulants

Type K = Non-volatile antifoulants

Figure F-1 GWBasic program

LISTING OF GWBASIC SOURCE CODE FOR THE QWASI MODEL – REMA

```

10  REM A Steady State Model of an Antifoulant Chemical Fate in a 3 Segment
    Air-Water-Sediment System, Based on the QWASI Fugacity Modelling
    Approach
20  REM For details see Chapter 8 of "Multimedia Environmental Models" by
    D. Mackay CRC Press/Lewis Publishers. 1991
30  REM SET COMPUTING VARIABLES
40  DIM P$(20),H$(25),Y(25,10),DP(15,15)
50  DIM GPM(4),GWM(4),VFPM(4),CSPM(4)
60  OPEN "output.txt" FOR OUTPUT AS #1
70  REM Nomenclature Conventions
80  N$(1)="Upstream Zone           "
90  N$(2)="Middle Zone            "
100 N$(3)="Downstream Zone        "
110 N$(4)="Ultimate receiving water"
120 REM Identify processes
130 P$(1)="| Sediment burial       |"
140 P$(2)="| Sediment transformation |"
150 P$(3)="| Sediment resuspension  |"
160 P$(4)="| Sediment-water diffusion|"
170 P$(5)="| Sediment deposition    |"
180 P$(6)="| Water transformation  |"
190 P$(7)="| Water-air diffusion    |"
200 REM DIMENSIONS AND PROPERTIES OF THE ESTUARINE SYSTEM
210 REM Segment Dimensions
220 II=3:III=II+1                                'number of segments
230 AW(1)=843000! : AW(2)=3879000! : AW(3)=5760000! 'water areas m2
240 HW(1)=3.76 : HW(2)=2.27 : HW(3)=3.42          'water depths m
250 HS(1)=.08 : HS(2)=.05 : HS(3)=.03            'sediment active
                                                    depths m

260 FOR I = 1 TO II
270 AAS(I)=AW(I)                                  'Sediment areas m2
280 VW(I)=AW(I)*HW(I)                             'Water volume m3
290 VS(I)=AAS(I)*HS(I)                            'Active sediment
                                                    volumes m3

300 NEXT I
310 REM Phase densities (kg/L or g/cm3)
320 DENW=1                                         'Water
330 DENP(1)=1.8: DENP(2)=1.8: DENP(3)=1.8:DENP(4)=1.8 'Suspended
                                                    particles
340 DENS(1)=2: DENS(2)=2: DENS(3)=2!             'Sediment solids
350 ORGP(1)=.05 : ORGP(2)=.05 : ORGP(3)=.05     'Organic content of
                                                    suspended particles
360 ORGS(1)=.02: ORGS(2)=.02: ORGS(3)=.02       'Organic content of
                                                    sediment solids

370 REM Particle Concentrations
380 VFS(1)=.05: VFS(2)=.05: VFS(3)=.05          'Volume fraction
                                                    sediment solids
390 VFMS(1)=.05: VFMS(2)=.05: VFMS(3)=.05      'Volume fraction
                                                    sediment solids
400 CSP(1)=21! : CSP(2)=24!: CSP(3)=28!:CSP(4)=30 'Suspended solids
                                                    conc in water g/m3
                                                    or mg/L

410 FOR I = 1 TO III
420 VFP(I)=CSP(I)/(DENP(I)*10^6)                 'Vol fraction of
                                                    susp particles
430 NEXT I

```

```

440 FOR I = 1 TO III                                'set all water
                                                    exchanges to zero
                                                    initially

450 FOR J=1 TO III
460 GW(I,J)=0:GP(I,J)=0:GI(I)=0:GX(I)=0
470 NEXT J
480 NEXT I
490 REM SET WATER FLOWS INTO SEGMENTS AND EXCHANGE RATES
500 GI(1)=4833!:GI(2)=0!:GI(3)=0!                'Water inflow rates
                                                    ie rivers m3/h
510 GW(2,1)=7630!:GW(3,2)=198000!:GW(4,3)=324000! 'Set water exchange
                                                    rates m3/h
520 DEP(1)=20 :DEP(2)=10: DEP(3)=8                'Particle
                                                    deposition rates
                                                    g/m2/day
530 RES(1)=15 :RES(2)=7 :RES(3)=3                'Particle
                                                    resuspension rates
                                                    g/m2/day
540 BUR(1)=3! :BUR(2)=2! :BUR(3)=2!              'Particle burial
                                                    rates g/m2/day

550 FOR I=1 TO II
560 GD(I)=DEP(I)*AAS(I)/24/DENP(I)/1000000!      'rates in m3/h
570 GR(I)=RES(I)*AAS(I)/24/DENS(I)/1000000!
580 GB(I)=BUR(I)*AAS(I)/24/DENS(I)/1000000!
590 NEXT I
600 REM INPUT DATA CONCERNING MARINA DIMENSIONS, SUBMERGED AREA OF VESSELS
AND QUANTITIES OF CHEMICAL DISCHARGED
610 AWM(1)=20000!:AWM(2)=20000:AWM(3)=50000!    'marina areas
620 AASM(1)=AWM(1):AASM(2)=AWM(2):AASM(3)=AWM(3) 'sediment areas
630 HWM(1)=4 :HWM(2)=4:HWM(3)=4                 'marina water
                                                    depths (m)
640 HSM(1)=.1:HSM(2)=.1:HSM(3)=.1               'marina sediment
                                                    depths (m)
650 DENPM(1)=1.8:DENPM(2)=1.7:DENPM(3)=1.8      'Suspended
                                                    particles
660 DENSM(1)=2:DENSM(2)=2.1:DENSM(3)=2.2        'Sediment solids
670 CSPM(1)=13:CSPM(2)=25:CSPM(3)=25            'suspended solids
                                                    mg/L
680 VSPM(1)=.05:VSPM(2)=.06:VSPM(3)=.4         'sediment solids
                                                    volume fractions
690 TFWM(1)= 12:TFWM(2)=12:TFWM(3)=12           'water flow half
                                                    times (h)
700 TFSM(1)=30000:TFSM(2)=50000!:TFSM(3)=60000! 'sediment flow half
                                                    times (h)
710 ORGPM(1)=.1:ORGPM(2)=.1:ORGPM(3)=.1         'organic carbon
                                                    content of
                                                    particles
720 ORGSM(1)=.05:ORGSM(2)=.05:ORGSM(3)=.05      'organic carbon
                                                    content of sediment
                                                    solids
730 AVESE(1)=6140:AVESE(2)=7337:AVESE(3)=553    'total submerged
                                                    area of vessels in
                                                    estuary (m2)
740 AVESM(1)=2763:AVESM(2)=6140:AVESM(3)=15350 'total submerged
                                                    area of vessels in
                                                    marinas (m2)

750 FOR I=1 TO II
760 VFPM(I)=CSPM(I)/(DENPM(I)*1000000!)
770 VWM(I)=AWM(I)*HWM(I)
780 VSM(I)=AASM(I)*HSM(I)
790 GBM(I)=BUR(I)*AASM(I)/24/DENSM(I)/1000000!  'rates in m3/h
800 GDM(I)=DEP(I)*AASM(I)/24/DENPM(I)/1000000!

```

```

810 GRM(I)=RES(I)*AASM(I)/24/DENSM(I)/1000000!
820 GJM(I)=VWM(I)*.693/TFWM(I)
830 GYM(I)=GJM(I)*VFPM(I)
840 NEXT I
850 REM INPUT ANTI-FOULANT BACKGROUND QUANTITIES
860 PRINT "Specify background data"
870 PRINT "Input discharge and background quantities, any previous values
in parentheses ( )
880 FOR I=1 TO II
890 PRINT "Background concentration in river input (g/m3 or mg/L) to
segment ";I;"(";"CGI(I);")":INPUT CGI(I)
900 NEXT I
910 PRINT "Background concentration (g/m3 or mg/L) in ultimate receiving
water (";"CGI(III);")":INPUT CGI(III)
920 ETGT=0:ETT=0:ETKT=0
930 FOR I=1 TO II
940 EWG(I)=CGI(I)*GI(I)                                'g/h in inflow
                                                         water
950 NEXT I
960 REM CALCULATE WATER FLOW AND EXCHANGE RATES
970 GW(1,2)=GI(1)+GW(2,1)
980 GW(2,3)=GI(2)+GW(3,2)+GW(1,2)-GW(2,1)
990 GW(3,4)=GI(3)+GW(4,3)+GW(2,3)-GW(3,2)
1000 FOR I=1 TO III
1010 FOR J=1 TO III
1020 GP(I,J)=GW(I,J)*VFP(I)
1030 NEXT J
1040 NEXT I
1050 REM Total water and particle outflows
1060 FOR I=1 TO II
1070 GJT(I)=GW(I,1)+GW(I,2)+GW(I,3)+GW(I,4)
1080 GYT(I)=GJT(I)*VFP(I)
1090 NEXT I
1100 REM INPUT OF BIOFOULANT PROPERTIES
1110 PRINT " A steady state model of the fate of a chemical antifoulant in a
3 segment estuarine system"
1120 PRINT " "
1130 PRINT "There are two methods of entering the antifoulant chemical
properties:"
1140 PRINT "Method P is to enter physical chemical properties "
1150 PRINT "(This method is normally applied to organic chemicals)"
1160 PRINT "Method K is to enter partition coefficients "
1170 PRINT "(This method is normally applied to involatile chemicals such as
metals)"
1180 PRINT "Specify a chemical by entering one of the following"
1190 PRINT "A chemical to be user-specified by method P 1"
1200 PRINT "A chemical to be user-specified by method K 2"
1210 PRINT "Please enter 1 or 2"
1220 INPUT QQ
1230 ON QQ GOTO 1240,1570
1240 REM INPUT TYPE P CHEMICAL PROPERTIES
1250 PRINT "Input antifoulant properties, any previous values in parentheses
( )
1260 PRINT "Chemical name (preferably in CAPITALS)(";"C$;")":INPUT C$
1270 PRINT "Temperature deg C (";"TC;")":INPUT TC
1280 PRINT "Melting point deg C (for liquids input system temp above)
(";"TM;")":INPUT TM
1290 PRINT "Molecular weight g/mol (";"WM;")":INPUT WM
1300 PRINT "Water solubility g/m3 (";"SOLY;")":INPUT SOLY
1310 PRINT "Vapour pressure Pa (";"VP;")":INPUT VP
1320 PRINT "Log organic carbon-water partition coefficient KOC
(";"LKOC;")":INPUT LKOC

```



```

1330 PRINT "Biodegradation half life in sediment hours (";TDS1;")":INPUT
      TDS1
1340 PRINT "Photolysis half life in sediment hours (";TDS2;")":INPUT TDS2
1350 PRINT "Hydrolysis half life in sediment hours (";TDS3;")":INPUT TDS3
1360 PRINT "Biodegradation half life in water hours (";TDW1;")":INPUT TDW1
1370 PRINT "Photolysis half life in water hours (";TDW2;")":INPUT TDW2
1380 PRINT "Hydrolysis half life in water hours (";TDW3;")":INPUT TDW3
1390 PRINT "Leaching rate from vessel surfaces eg 10 ug/cm2.day
      (";EVESG;")":INPUT EVESG
1400 REM Adjust chemical properties
1410 TK = TC + 273                                     'temperature in
                                                         degrees Kelvin

1420 TMK=TM+273
1430 R=8.314
1440 IF TMK<TK THEN FRAT=1 ELSE FRAT=EXP(6.79*(1-TMK/TK)) 'fugacity ratio
1450 VPL=VP/FRAT                                     'subcooled liquid
                                                         vapour pressure
                                                         'solubility
                                                         (mol/m^3)
1460 SOLM = SOLY/WM                                     'Henry's Law
                                                         constant
                                                         (Pa m^3/mol)
1470 H = VP/SOLM                                     'organic carbon-
                                                         water partition
                                                         coefficient
1480 KOC = 10^LKOC                                     'dimensionless air-
                                                         water partition
                                                         coefficient

1490 KDAW=H/R/TK

1500 FOR I=1 TO III
1510 KPPW(I)=KOC*ORGP(I)
1520 KPPWM(I)=KOC*ORGPM(I)
1530 KPSW(I)=KOC*ORGS(I)
1540 KPSWM(I)=KOC*ORGSM(I)
1550 NEXT I
1560 GOTO 1790
1570 REM INPUT TYPE K CHEMICAL PROPERTIES
1580 PRINT "Input chemical properties, any previous values in parentheses (
      )
1590 PRINT "Chemical name (preferably in CAPITALS)(";C$;")":INPUT C$
1600 PRINT "Temperature deg C (";TC;")":INPUT TC
1610 PRINT "Molecular weight g/mol (";WM;")":INPUT WM
1620 PRINT "Partition coefficients are common to all segments"
1630 PRINT "Air-water partition coefficient KDAW (";KDAW;")":INPUT KDAW
1640 PRINT "Sediment-water partition coefficient KPSWC L/kg
      (";KPSWC;")":INPUT KPSWC
1650 PRINT "Particle-water partition coefficient KPPWC L/kg
      (";KPPWC;")":INPUT KPPWC
1660 PRINT "Biodegradation half life in sediment hours (";TDS1;")":INPUT
      TDS1
1670 PRINT "Photolysis half life in sediment hours (";TDS2;")":INPUT TDS2
1680 PRINT "Hydrolysis half life in sediment hours (";TDS3;")":INPUT TDS3
1690 PRINT "Biodegradation half life in water hours (";TDW1;")":INPUT TDW1
1700 PRINT "Photolysis half life in water hours (";TDW2;")":INPUT TDW2
1710 PRINT "Hydrolysis half life in water hours (";TDW3;")":INPUT TDW3
1720 PRINT "Leaching rate from vessel surfaces eg 10 ug/cm2.day
      (";EVESG;")":INPUT EVESG
1730 FOR I= 1 TO III
1740 KPSW(I)=KPSWC
1750 KPSWM(I)=KPSWC
1760 KPPW(I)=KPPWC
1770 KPPWM(I)=KPPWC
1780 NEXT I

```

```

1790 REM CALCULATE DIMENSIONLESS PARTITION COEFFICIENTS
1800 FOR I=1 TO III
1810 KDPW(I)=KPPW(I)*DENP(I)
1820 KDPWM(I)=KPPWM(I)*DENP(I)
1830 KDSW(I)=KPSW(I)*DENS(I)
1840 KDSWM(I)=KPSWM(I)*DENS(I)
1850 NEXT I
1860 TK=TC+273
1870 R=8.314
1880 REM Reaction rate constants (h^-1) calculated from total half lives
1890 TDS=1/(1/TDS1+1/TDS2+1/TDS3)
1900 TDW=1/(1/TDW1+1/TDW2+1/TDW3)
1910 KS = .693/TDS           'total sediment
                             reaction rate
                             constant
1920 KW = .693/TDW         'total water
                             reaction rate
                             constant

1930 REM CALCULATION OF Z AND D VALUES AND RESPONSE TIMES
1940 REM Calculate aquivalent Z values
1950 ZW = 1                 'Z for water
1960 ZA = KDAW             'Z for air
1970 FOR I= 1 TO III
1980 ZP(I) = KDPW(I)       'Z for water
                             particles
1990 ZPM(I) = KDPWM(I)    'Z for water
                             particles in marina
2000 ZS(I) = KDSW(I)      'Z for sediment
                             particles
2010 ZSM(I) = KDSWM(I)    'Z for sediment
                             particles in marina
2020 ZST(I)=ZW*(1-VFS(I))+ZS(I)*VFS(I) 'Z for bulk
                             sediment
2030 ZSTM(I)=ZW*(1-VFSM(I))+ZSM(I)*VFSM(I) 'Z for bulk
                             sediment
2040 ZWT(I) = ZW*(1-VFP(I))+ZP(I)*VFP(I) 'Z for bulk water
2050 ZWTM(I) = ZW*(1-VFPM(I))+ZPM(I)*VFPM(I) 'Z for bulk water
2060 NEXT I
2070 REM Mass Transfer Coefficients (m/h)
2080 KVA = 3!              'volatilization:
                             air side
2090 KVV = .03            'volatilization:
                             water side
2100 KV = 1/(1/KVV + 1/(KVA*KDAW)) 'overall water side
2110 KT = .0002          'sediment-water
                             diffusion

2120 REM Calculate emissions
2130 ETGT=0:ETT=0:ETKT=0
2140 EVES=EVESG*.000001*10000!/24/WM 'leaching rate
                                         mol/m2/h from
                                         ug/cm2/day

2150 FOR I=1 TO II
2160 REM leaching rates from vessels in estuaries and marinas
2170 EVE(I)=EVES*AVESE(I) 'leaching rate from
                             vessels in estuary
                             mol/h
2180 EVM(I)=EVES*AVESM(I) 'leaching rate from
                             vessels in marinas
                             mol/h
2190 EVEG(I)=EVE(I)*WM    'rate in g/h
2200 EVMG(I)=EVM(I)*WM    'rate in g/h
2210 EVEK(I)=EVEG(I)*8760/1000 'rate in kg/year

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2220 EVMK(I)=EVMG(I)*8760/1000 'rate in kg/year
2230 REM input rates by inflow in water to estuary segments
2240 EWG(I)=CGI(I)*GI(I) 'g/h in inflow
water
2250 EW(I)=EWG(I)/WM 'mol/h in inflow
water
2260 EWK(I)=EWG(I)*8760/1000 'kg/year in inflow
water

2270 REM total rates for each segment
2280 ET(I)=EVE(I)+EVM(I)+EW(I)
2290 ETG(I)=ET(I)*WM
2300 ETK(I)=ETG(I)*8760/1000
2310 REM grand total rates
2320 ETT=ETT+ET(I) 'mol/h
2330 ETTG=ETT*WM 'g/h
2340 ETTK=ETT*8760/1000 'kg/year
2350 NEXT I
2360 REM Calculation of process D values DP(I,J) and DPM(I,J) and response
times
2370 FOR I=1 TO II
2380 DP(1,I) = GB(I) * ZS(I) 'burial
2390 DPM(1,I) = GBM(I) * ZSM(I) 'burial
2400 DP(2,I) = VS(I) * ZST(I) * KS 'sediment
transformation
2410 DPM(2,I) = VSM(I) * ZSTM(I) * KS 'sediment
transformation
2420 DP(3,I) = GR(I) * ZS(I) 'sediment
resuspension
2430 DPM(3,I) = GRM(I) * ZSM(I) 'sediment
resuspension
2440 DP(4,I) = KT * AAS(I) * ZW 'sediment-water
diffusion
2450 DPM(4,I) = KT * AASM(I) * ZW 'sediment-water
diffusion
2460 DP(5,I) = GD(I) * ZP(I) 'sediment
deposition
2470 DPM(5,I) = GDM(I) * ZPM(I) 'sediment
deposition
2480 DP(6,I) = VW(I) * ZWT(I) * KW 'water
transformation
2490 DPM(6,I) = VWM(I) * ZWTM(I) * KW 'water
transformation
2500 DP(7,I) = KV * AW(I) * ZW 'volatilization
2510 DPM(7,I) = KV * AWM(I) * ZW 'volatilization
2520 NEXT I
2530 FOR I = 1 TO III
2540 FOR J=1 TO III
2550 DJ(I,J)=GW(I,J)*ZW 'water flow
2560 DJM(I)=GJM(I)*ZW 'water flow
2570 DY(I,J)=GP(I,J)*ZP(I) 'particle flow
2580 DYM(I)=GYM(I)*ZPM(I) 'particle flow
2590 D(I,J)=DJ(I,J)+DY(I,J) 'total flow
2600 DM(I)=DJM(I)+DYM(I) 'total flow
2610 NEXT J
2620 NEXT I
2630 REM Calculate response times in years
2640 FOR I=1 TO II
2650 TYS(1,I)=VS(I)*ZST(I)/DP(1,I)/8760
2660 TYS(2,I)=VS(I)*ZST(I)/DP(2,I)/8760
2670 TYS(3,I)=VS(I)*ZST(I)/DP(3,I)/8760:TYW(3,I)=VW(I)*ZWT(I)/DP(3,I)/8760
2680 TYS(4,I)=VS(I)*ZST(I)/DP(4,I)/8760:TYW(4,I)=VW(I)*ZWT(I)/DP(4,I)/8760
2690 TYS(5,I)=VS(I)*ZST(I)/DP(5,I)/8760:TYW(5,I)=VW(I)*ZWT(I)/DP(5,I)/8760

```

```

2700 TYW(6,I)=VW(I)*ZWT(I)/DP(6,I)/8760
2710 TYW(7,I)=VW(I)*ZWT(I)/DP(7,I)/8760
2720 NEXT I
2730 FW(III)=CGI(III)/WM/ZWT(III)           'aquivalence in
                                           receiving water

2740 FOR I = 1 TO II
2750 FWI(I)=CGI(I)/WM/ZWT(I)
2760 REM DE includes losses by reaction, burial and volatilization
2770 REM DT is DE plus advective losses
2780 DE(I)=DP(4,I)+DP(5,I)+DP(6,I)+DP(7,I)-
      (DP(3,I)+DP(4,I))*(DP(4,I)+DP(5,I))/(DP(1,I)+DP(2,I)+DP(3,I)+DP(4,I))
2790 DEM(I)=DPM(4,I)+DPM(5,I)+DPM(6,I)+DPM(7,I)-
      (DPM(3,I)+DPM(4,I))*(DPM(4,I)+DPM(5,I))/(DPM(1,I)+DPM(2,I)+DPM(3,I)+DPM
      (4,I))
2800 DT(I)=DE(I)+D(I,1)+D(I,2)+D(I,3)+D(I,4)
2810 DTM(I)=DEM(I)+DJM(I)+DYM(I)
2820 NEXT I
2830 REM PRINT-OUT OF INPUT DATA
2840 PRINT "Input printing requirements ; zero for 'No',1 for 'Yes'"
2850 PRINT "Physical-chemical requirements, and Z values "
2860 INPUT P1
2870 PRINT "Chemical quantity data "
2880 INPUT P2
2890 PRINT "Segment and marina dimensions, properties, D values and response
      times"
2900 INPUT P3
2910 PRINT "Concentrations, amounts and process rates"
2920 INPUT P4
2930 PRINT "Individual marina and segment mass balances"
2940 INPUT P5
2950 PRINT#1, " "
2960 REM PRINT OUT SYSTEM DESCRIPTION
2970 " PRINT#1, "Estimated fate of ";C$";:PRINT#1 ," in an estuarine system
      consisting of three segments or zones and marinas "
2980 PRINT#1, "Steady-state fate model in a series of three water, sediment
      segments "
2990 PRINT #1," "
3000 IF P1=0 GOTO 3710
3010 PRINT#1,"Physical-chemical and Partitioning Properties of ";C$
3020 PRINT#1,"These are input data, some values may be zero "
3030 PRINT#1," -----
      --"
3040 PRINT#1, USING "| Temperature (deg C) |
      ### |";TC |
3050 PRINT#1, USING "| Gas constant (J/mol K) |
      #.### |";R |
3060 PRINT#1, USING "| Molecular mass (g/mol) |
      ##### |";WM |
3070 PRINT#1, USING "| Melting point (deg C) (system temp. for liquids) |
      ##### |";TM |
3080 PRINT#1, USING "| Solubility (g/m3) |
      ##.##^ ^ ^ ^ |";SOLY |
3090 PRINT#1, USING "| Vapour pressure (Pa) |
      ##.##^ ^ ^ ^ |";VP |
3100 PRINT#1, USING "| Subcooled liquid vapour pressure (Pa) |
      ##.##^ ^ ^ ^ |";VPL |
3110 PRINT#1, USING "| Fugacity ratio |
      ##.##^ ^ ^ ^ |";FRAT |
3120 PRINT#1, USING "| Henry's Law constant (Pa m3/mol) |
      ##.##^ ^ ^ ^ |";H |
3130 PRINT#1, USING "| Air water partition coefficient (dim'less) |
      ##.##^ ^ ^ ^ |";KDAW |

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```

3140 PRINT#1, USING "| Log organic carbon water partition coefficient |
      ##.## |";LKOC
3150 PRINT#1, USING "| Organic carbon-water partition coefficient |
      ##.##^^^^ |";KOC
3160 PRINT#1, USING "| Water reaction half life by biodeg (hours) |
      ##.##^^^^ |";TDW1
3170 PRINT#1, USING "| Water reaction half life by photolysis (h) |
      ##.##^^^^ |";TDW2
3180 PRINT#1, USING "| Water reaction half life by hydrolysis (h) |
      ##.##^^^^ |";TDW3
3190 PRINT#1, USING "| Water reaction half life (total) (h) |
      ##.##^^^^ |";TDW
3200 PRINT#1, USING "| Sediment reaction half life by biodeg (hours) |
      ##.##^^^^ |";TDS1
3210 PRINT#1, USING "| Sediment reaction half life by photolysis (h) |
      ##.##^^^^ |";TDS2
3220 PRINT#1, USING "| Sediment reaction half life by hydrolysis (h) |
      ##.##^^^^ |";TDS3
3230 PRINT#1, USING "| Sediment reaction half life (total) (h) |
      ##.##^^^^ |";TDS
3240 PRINT#1, USING "| Emission rate from vessel ug/cm2/day |
      ##.##^^^^ |";EVESG
3250 PRINT#1, USING "| Sediment-water partition coefficient L/kg |
      ##.##^^^^ |";KPSWC
3260 PRINT#1, USING "| Particle-water partition coefficient L/kg |
      ##.##^^^^ |";KPPWC
3270 PRINT#1, USING "| Leaching rate from vessel subm area ug/cm2/day |
      ##.##^^^^ |";EVESG
3280 PRINT#1, " -----
      ---"
3290 PRINT#1, " "
3300 PRINT#1, " Z Values common to all segments "
3310 PRINT#1, " -----"
3320 PRINT#1, USING "| Z for air | ##.##^^^^
      |";ZA
3330 PRINT#1, USING "| Z for water | ##.##^^^^
      |";ZW
3340 PRINT#1, " -----"
3350 PRINT#1, " "
3360 H$(1)="| Z for water particles | "
3370 H$(2)="| Z for sediment solids | "
3380 H$(3)="| Z for bulk water | "
3390 H$(4)="| Z for bulk sediment | "
3400 H$(5)="| Particle-water partition coefficient (L/kg) | "
3410 H$(6)="| Sediment-water partition coefficient (L/kg) | "
3420 FOR I= 1 TO II
3430
      Y(1,I)=ZP(I):Y(2,I)=ZS(I):Y(3,I)=ZWT(I):Y(4,I)=ZST(I):Y(5,I)=KPPW(I):Y
      (6,I)=KPSW(I)
3440 NEXT I
3450 PRINT#1, " Segment Z Values which may be segment specific (Pa.m3/mol) "
3460 PRINT#1, " Property Segment No 1
      2 3 "
3470 PRINT#1, " -----
      -----"
3480 FOR J=1 TO 6
3490 PRINT#1, H$(J);
3500 FOR I= 1 TO II
3510 PRINT#1, USING "##.##^^^^ |";Y(J,I);
3520 NEXT I
3530 PRINT#1, " "
3540 NEXT J

```

```

3550 PRINT#1, " -----
----- "
3560 PRINT#1, " "
3570 FOR I= 1 TO II
3580     Y(1,I)=ZPM(I):Y(2,I)=ZSM(I):Y(3,I)=ZWTM(I):Y(4,I)=ZSTM(I):Y(5,I)=KPPWM
        (I):Y(6,I)=KPSWM(I)
3590 NEXT I
3600 PRINT#1, " Marina Z Values which may be marina specific (Pa.m3/mol) "
3610 PRINT#1, " Property                               Marina No      1
        2                3 "
3620 PRINT#1, " -----
----- "
3630 FOR J=1 TO 6
3640 PRINT#1, H$(J);
3650 FOR I= 1 TO II
3660 PRINT#1, USING "##.##^ ^ ^ ^ |";Y(J,I);
3670 NEXT I
3680 PRINT#1, " "
3690 NEXT J
3700 PRINT#1, " -----
----- "
3710 PRINT#1, " "
3720 PRINT #1,CHR$(12)
3730 IF P2=0 GOTO 4240
3740 PRINT#1, " Chemical quantity data"
3750 PRINT#1, " -----"
3760 PRINT#1, USING " | Conc in receivg water (g/m3) | ##.##^ ^ ^ ^ |";CGI(III)
3770 PRINT#1, USING " | Aquivalence in receivg water | ##.##^ ^ ^ ^ |";FW(III)
3780 PRINT#1, " -----"
3790 PRINT #1,CHR$(12)
3800 PRINT#1, " "
3810 H$(3)=" | A-F input from vessels in marina g/h | "
3820 H$(4)=" | A-F input from vess in marina kg/year | "
3830 H$(5)=" | A-F input from vess in marina mol/h | "
3840 H$(6)=" | A-F input from vessels in estuary g/h | "
3850 H$(7)=" | A-F input from vess in estuary kg/year | "
3860 H$(8)=" | A-F input from vess in estuary mol/h | "
3870 H$(9)=" | River water flow m3/h | "
3880 H$(10)=" | River water concentration g/m3 | "
3890 H$(11)=" | River chemical input g/h | "
3900 H$(12)=" | River chemical input kg/year | "
3910 H$(13)=" | River chemical input mol/h | "
3920 H$(14)=" | " | "
3930 H$(15)=" | Total input g/h | "
3940 H$(16)=" | Total input kg/year | "
3950 H$(17)=" | Total input mol/hour | "
3960 H$(18)=" | " | "
3970 H$(19)=" | Approx river fugacity/aquiv | "
3980 H$(20)=" | Vessel area in marina m2 | "
3990 H$(21)=" | Vessel area in estuary m2 | "
4000 FOR I = 1 TO II
4010 Y(3,I)=EVMG(I):Y(4,I)=EVMK(I):Y(5,I)=EVM(I)
4020 Y(6,I)=EVEG(I):Y(7,I)=EVEK(I):Y(8,I)=EVE(I)
4030 Y(9,I)=GI(I):Y(10,I)=CGI(I):Y(11,I)=EWG(I)
4040 Y(12,I)=EWK(I):Y(13,I)=EW(I):Y(14,I)=0:Y(15,I)=ETG(I)
4050 Y(16,I)=ETK(I):Y(17,I)=ET(I):Y(18,I)=0:Y(19,I)=FWI(I)
4060 Y(20,I)=AVESM(I):Y(21,I)=AVESE(I)
4070 NEXT I
4080 PRINT#1, " Discharges to marinas & segments 1 2
        3 "

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4090 PRINT#1, " -----
-----"
4100 FOR J= 3 TO 21
4110 PRINT#1, H$(J);
4120 FOR I=1 TO II
4130 PRINT#1, USING "##.##^ ^ ^ ^ |";Y(J,I);
4140 NEXT I
4150 PRINT#1, " "
4160 NEXT J
4170 PRINT#1, " -----
-----"
4180 PRINT#1, " "
4190 PRINT#1, " -----"
4200 PRINT#1, USING " | Grand total mol/h | ##.##^ ^ ^ ^ | ";ETT
4210 PRINT#1, USING " | Grand total g/h | ##.##^ ^ ^ ^ | ";ETTg
4220 PRINT#1, USING " | Grand total kg/year | ##.##^ ^ ^ ^ | ";ETTkg
4230 PRINT#1, " -----"
4240 IF P3=0 GOTO 6280
4250 REM Print out segment properties
4260 FOR I=1 TO II
4270
    Y(1,I)=ORGP(I):Y(2,I)=ORGS(I):Y(3,I)=DENP(I):Y(4,I)=DENS(I):Y(5,I)=VFP
    (I)
4280 Y(6,I)=CSP(I):Y(7,I)=VFS(I)
4290
    Y(8,I)=AW(I):Y(9,I)=AAS(I):Y(10,I)=VW(I):Y(11,I)=VS(I):Y(12,I)=HW(I):Y
    (13,I)=HS(I)
4300 Y(14,I)=GJT(I):Y(15,I)=GYT(I)
4310 NEXT I
4320 H$(1)=" | Fraction OC in water column particles | "
4330 H$(2)=" | Fraction OC in sediment particles | "
4340 H$(3)=" | Density of particles in water (g/cm3) | "
4350 H$(4)=" | Density of surficial sediment particles (g/cm3) | "
4360 H$(5)=" | Volume fraction water particles | "
4370 H$(6)=" | Concentration: water column particles (mg/L) | "
4380 H$(7)=" | Volume fraction of solids in sediment | "
4390 H$(8)=" | Water area (square metres) | "
4400 H$(9)=" | Sediment area (square metres) | "
4410 H$(10)=" | Water volume (cubic metres) | "
4420 H$(11)=" | Sediment volume (cubic metres) | "
4430 H$(12)=" | Mean water depth (metres) | "
4440 H$(13)=" | Mean active sediment depth (metres) | "
4450 H$(14)=" | Water inflow and outflow rate (m3/h) | "
4460 H$(15)=" | Particle outflow rate (m3/h) | "
4470 PRINT#1, " "
4480 PRINT#1, " Segment properties Segment No 1
    2 3 "
4490 PRINT#1, " -----
-----"
4500 FOR J= 1 TO 15
4510 PRINT#1, H$(J);
4520 FOR I=1 TO II
4530 PRINT#1, USING "##.##^ ^ ^ ^ |";Y(J,I);
4540 NEXT I
4550 PRINT #1, " "
4560 NEXT J
4570 PRINT#1, " -----
-----"
4580 REM Print out marina properties
4590 FOR I=1 TO II

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4600      Y(1,I)=ORGPM(I):Y(2,I)=ORGS(M(I):Y(3,I)=DENPM(I):Y(4,I)=DENSM(I):Y(5,I)
      =VFPM(I)
4610 Y(6,I)=CSPM(I):Y(7,I)=VSPM(I)
4620      Y(8,I)=AWM(I):Y(9,I)=AASM(I):Y(10,I)=VWM(I):Y(11,I)=VSM(I):Y(12,I)=HWM
      (I):Y(13,I)=HSM(I)
4630 Y(14,I)=GJM(I):Y(15,I)=GYM(I)
4640 NEXT I
4650 PRINT#1, " "
4660 PRINT#1, " Marina properties                      Segment No      1
      2              3 "
4670 PRINT#1, " -----"
      -----"
4680 FOR J= 1 TO 15
4690 PRINT#1, H$(J);
4700 FOR I=1 TO III
4710 PRINT#1, USING "##.##^ ^ ^ ^ |";Y(J,I);
4720 NEXT I
4730 PRINT #1, " "
4740 NEXT J
4750 PRINT#1, " -----"
      -----"
4760 PRINT #1,CHR$(12)
4770 PRINT#1, " Inter-segment D values (water)          "
4780 PRINT#1, "              1              2              3              4 "
4790 PRINT#1, " -----"
4800 FOR I=1 TO III
4810 PRINT#1, USING "|  ## |";I ;
4820 FOR J=1 TO III
4830 PRINT#1, USING " ##.##^ ^ ^ ^ |";DJ(I,J);
4840 NEXT J
4850 PRINT#1, " "
4860 NEXT I
4870 PRINT#1, " -----"
4880 PRINT#1, " "
4890 PRINT#1, " Inter-segment D values (particles)          "
4900 PRINT#1, " Source              Destination "
4910 PRINT#1, "              1              2              3              4 "
4920 PRINT#1, " -----"
4930 FOR I=1 TO III
4940 PRINT#1, USING "|  ## |";I ;
4950 FOR J=1 TO III
4960 PRINT#1, USING " ##.##^ ^ ^ ^ |";DY(I,J);
4970 NEXT J
4980 PRINT#1, " "
4990 NEXT I
5000 PRINT#1, " -----"
5010 PRINT#1, " "
5020 PRINT#1, " "
5030 PRINT#1, " Inter-segment D values (total)          "
5040 PRINT#1, " Source              Destination "
5050 PRINT#1, "              1              2              3              4 "
5060 PRINT#1, " -----"
5070 FOR I=1 TO III
5080 PRINT#1, USING "|  ## |";I ;
5090 FOR J=1 TO III
5100 PRINT#1, USING " ##.##^ ^ ^ ^ |";D(I,J);
5110 NEXT J
5120 PRINT#1, " "
5130 NEXT I
5140 PRINT#1, " -----"

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5150 PRINT#1, " "
5160 PRINT#1, " "
5170 PRINT#1, " Sediment-water exchange processes"
5180 PRINT#1, " Property                Segment No      1
      2                3 "
5190 PRINT#1, " -----"
      "
5200 H$(1)=" | Sediment deposition g/m2/day      | "
5210 H$(2)=" | Sediment resuspension g/m2/day     | "
5220 H$(3)=" | Sediment burial g/m2/day           | "
5230 H$(4)=" | Sediment deposition m3/h             | "
5240 H$(5)=" | Sediment resuspension m3/h              | "
5250 H$(6)=" | Sediment burial m3/h                | "
5260 FOR I = 1 TO II
5270 Y(1,I)=DEP(I):Y(2,I)=RES(I):Y(3,I)=BUR(I)
5280 Y(4,I)=GD(I):Y(5,I)=GR(I):Y(6,I)=GB(I)
5290 NEXT I
5300 FOR J= 1 TO 6
5310 PRINT#1, H$(J);
5320 FOR I=1 TO II
5330 PRINT#1, USING "##.##^ ^ ^ ^ |";Y(J,I);
5340 NEXT I
5350 PRINT#1, " "
5360 NEXT J
5370 PRINT#1, " -----"
      "
5380 PRINT#1, " "
5390 PRINT#1, " Mass Transfer Coefficients (m/h)      "
5400 PRINT#1, " -----"
5410 PRINT#1, USING " | Volatilization:  Air side      | ##.##^ ^ ^ ^
      |";KVA
5420 PRINT#1, USING " | Volatilization:  Water side   | ##.##^ ^ ^ ^
      |";KVA
5430 PRINT#1, USING " | Overall water side           | ##.##^ ^ ^ ^
      |";KV
5440 PRINT#1, USING " | Sediment-water diffusion     | ##.##^ ^ ^ ^
      |";KT
5450 PRINT#1, " -----"
5460 PRINT#1, " "
5470 PRINT #1,CHR$(12)
5480 PRINT#1, " D Values for transport and transformation processes"
5490 PRINT#1, " Process                Segment No      1          2          3 "
5500 PRINT#1, " -----"
      "
5510 FOR J= 1 TO 7
5520 PRINT#1, P$(J);
5530 FOR I =1 TO II
5540 PRINT#1, USING " ##.##^ ^ ^ ^ |";DP(J,I);
5550 NEXT I
5560 PRINT#1, " "
5570 NEXT J
5580 PRINT#1, " -----"
      "
5590 PRINT#1, " | Total D values DE(I)      |";
5600 FOR I =1 TO II
5610 PRINT#1, USING " ##.##^ ^ ^ ^ |";DE(I);
5620 NEXT I
5630 PRINT#1, " "
5640 PRINT#1, " | Total D value DT(I)      | " ;
5650 FOR I =1 TO II
5660 PRINT#1, USING " ##.##^ ^ ^ ^ |";DT(I);
5670 NEXT I

```

```

5680 PRINT#1, " "
5690 PRINT#1, " -----
      -"
5700 PRINT#1, " "
5710 PRINT#1, " D Values for transport and transformation processes"
5720 PRINT#1, " Process          Marina No          1          2          3 "
5730 PRINT#1, " -----
      -"
5740 FOR J= 1 TO 7
5750 PRINT#1, P$(J);
5760 FOR I =1 TO II
5770 PRINT#1, USING " ##.##^ ^ ^ ^ |";DPM(J,I);
5780 NEXT I
5790 PRINT#1, " "
5800 NEXT J
5810 PRINT#1, " -----
      -"
5820 PRINT#1, "| Total D values DEM(I) |";
5830 FOR I =1 TO II
5840 PRINT#1, USING " ##.##^ ^ ^ ^ |";DEM(I);
5850 NEXT I
5860 PRINT#1, " "
5870 PRINT#1, "| Total D value DTM(I) |" ;
5880 FOR I =1 TO II
5890 PRINT#1, USING " ##.##^ ^ ^ ^ |";DTM(I);
5900 NEXT I
5910 PRINT#1, " "
5920 PRINT#1, "| Water outflow DJM(I) |" ;
5930 FOR I =1 TO II
5940 PRINT#1, USING " ##.##^ ^ ^ ^ |";DJM(I);
5950 NEXT I
5960 PRINT#1, " "
5970 PRINT#1, "| Particle outf DYM(I) |" ;
5980 FOR I =1 TO II
5990 PRINT#1, USING " ##.##^ ^ ^ ^ |";DYM(I);
6000 NEXT I
6010 PRINT#1, " "
6020 PRINT#1, " -----
      -"
6030 PRINT#1, " Sediment response times in segments ie VZ/D (years) "
6040 PRINT#1, " Process          Segment No          1          2          3 "
6050 PRINT#1, " -----
      -"
6060 FOR J = 1 TO 5
6070 PRINT#1, P$(J);
6080 FOR I= 1 TO II
6090 PRINT#1, USING " ##.##^ ^ ^ ^ |";TYS(J,I);
6100 NEXT I
6110 PRINT#1, " "
6120 NEXT J
6130 PRINT#1, " -----
      -"
6140 PRINT#1, " "
6150 PRINT#1, " Water response times in segments ie VZ/D (years) "
6160 PRINT#1, " Process          Segment No          1          2          3 "
6170 PRINT#1, " -----
      -"
6180 FOR J = 3 TO 7
6190 PRINT#1, P$(J);
6200 FOR I= 1 TO II
6210 PRINT#1, USING " ##.##^ ^ ^ ^ |";TYW(J,I);
6220 NEXT I

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6230 PRINT#1, " "
6240 NEXT J
6250 PRINT#1, " -----"
      -"
6260 PRINT#1, " "
6270 PRINT #1,CHR$(12)
6280 REM MASS BALANCE CALCULATION
6290 FOR I=1 TO II
6300 FWM(I)=EVM(I)/DTM(I)
6310 FSM(I)=FWM(I)*(DPM(4,I)+DPM(5,I))/(DPM(1,I)+DPM(2,I)+DPM(3,I)+DPM(4,I))
6320 RJYM(I)=FWM(I)*(DJM(I)+DYM(I))
6330 I(I)=EVE(I)+EW(I)+RJYM(I) 'inputs from vessels, water inflow and
      marinas
6340 NEXT I
6350 REM Calculate J and D groups, and solve steady state condition
6360 J1=DT(1)
6370 J2=DT(2)-D(1,2)*D(2,1)/J1
6380 J3=DT(3)-D(2,3)*D(3,2)/J2
6390 FW(3)=(I(3)+D(2,3)*(I(2)+I(1)*D(1,2)/J1)/J2+FW(4)*D(4,3))/J3
6400 FW(2)=(I(2)+I(1)*D(1,2)/J1+FW(3)*D(3,2))/J2
6410 FW(1)=(I(1)+D(2,1)*FW(2))/J1
6420 FOR I = 1 TO II
6430 FS(I)=FW(I)*(DP(4,I)+DP(5,I))/(DP(1,I)+DP(2,I)+DP(3,I)+DP(4,I))
6440 NEXT I
6450 MTT=0:MTTK=0
6460 MTTM=0:MTTKM=0
6470 FOR I =1 TO II
6480 CWT(I)=FW(I)*ZWT(I)
6490 CWTG(I)=CWT(I)*WM
6500 CST(I)=FS(I)*ZST(I)
6510 CSTG(I)=FS(I)*ZS(I)*WM/DENS(I)
6520 MWT(I)=FW(I)*VW(I)*ZWT(I)
6530 MWTK(I)=MWT(I)*WM/1000
6540 MST(I)=FS(I)*VS(I)*ZST(I)
6550 MSTK(I)=MST(I)*WM/1000
6560 MT(I)=MWT(I)+MST(I)
6570 MTK(I)=MT(I)*WM/1000
6580 MTT=MTT+MT(I):MTTK=MTTK+MTK(I)
6590 CWTM(I)=FWM(I)*ZWTM(I)
6600 CWTGM(I)=CWTM(I)*WM
6610 CSTM(I)=FSM(I)*ZSTM(I)
6620 CSTGM(I)=FSM(I)*ZSM(I)*WM/DENSM(I)
6630 MWTM(I)=FWM(I)*VWM(I)*ZWTM(I)
6640 MWTKM(I)=MWTM(I)*WM/1000
6650 MSTM(I)=FSM(I)*VSM(I)*ZSTM(I)
6660 MSTKM(I)=MSTM(I)*WM/1000
6670 MTM(I)=MWTM(I)+MSTM(I)
6680 MTKM(I)=MTM(I)*WM/1000
6690 MTTM=MTTM+MTM(I):MTTKM=MTTKM+MTKM(I)
6700 NEXT I
6710 REM Calculate process rates
6720 FOR I = 1 TO II
6730 FOR J = 1 TO 3
6740 R(J,I)=FS(I)*DP(J,I) :RK(J,I)=R(J,I)*WM*8760/1000
6750 RM(J,I)=FSM(I)*DPM(J,I) :RKM(J,I)=RM(J,I)*WM*8760/1000
6760 NEXT J
6770 R(4,I)=(FS(I)-FW(I))*DP(4,I) :RK(4,I)=R(4,I)*WM*8760/1000
6780 RM(4,I)=(FSM(I)-FWM(I))*DPM(4,I) :RKM(4,I)=RM(4,I)*WM*8760/1000
6790 FOR J = 5 TO 6
6800 R(J,I)=FW(I)*DP(J,I) :RK(J,I)=R(J,I)*WM*8760/1000
6810 RM(J,I)=FWM(I)*DPM(J,I) :RKM(J,I)=RM(J,I)*WM*8760/1000
6820 NEXT J

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6830 R(7,I)=FW(I)*DP(7,I) :RK(7,I)=R(7,I)*WM*8760/1000
6840 RM(7,I)=FWM(I)*DPM(7,I) :RKM(7,I)=RM(7,I)*WM*8760/1000
6850 RSW(I)=FS(I)*(DP(3,I)+DP(4,I)) :RSWK(I)=RSW(I)*WM*8760/1000
6860 RSWM(I)=FSM(I)*(DPM(3,I)+DPM(4,I)) :RSWKM(I)=RSWM(I)*WM*8760/1000
6870 RWS(I)=FW(I)*(DP(4,I)+DP(5,I)) :RWSK(I)=RWS(I)*WM*8760/1000
6880 RWSM(I)=FWM(I)*(DPM(4,I)+DPM(5,I)) :RWSKM(I)=RWSM(I)*WM*8760/1000
6890 NEXT I
6900 FOR I = 1 TO III
6910 FOR J = 1 TO III
6920 RJY(I,J)=D(I,J)*FW(I) :RJYK(I,J)=RJY(I,J)*WM*8760/1000
6930 NEXT J
6940 NEXT I
6950 FOR I = 1 TO III
6960 RI(I)=0 :RX(I)=0
6970 RIM(I)=0 :RXM(I)=0
6980 FOR J= 1 TO III
6990 RX(I)=RX(I)+RJY(I,J)
7000 RI(I)=RI(I)+RJY(J,I)
7010 NEXT J
7020 RXK(I)=RX(I)*WM*8760/1000
7030 RIK(I)=RI(I)*WM*8760/1000
7040 RXM(I)=FWM(I)*DM(I)
7050 RIM(I)=EVM(I)
7060 RXKM(I)=RXM(I)*WM*8760/1000
7070 RIKM(I)=RIM(I)*WM*8760/1000
7080 NEXT I
7090 REM PRINT-OUT RESULTS
7100 IF P4=0 GOTO 8360
7110 PRINT#1, " Concentrations and amounts in each segment"
7120 H$(1)=" |Aquivalence in water column |"
7130 H$(2)=" |Aquivalence in sediment |"
7140 H$(3)=" |Concentration in bulk water (mol/m3) |"
7150 H$(4)=" |Concentration in bulk water (mg/L or g/m3) |"
7160 H$(5)=" |Concentration in bulk sediment (mol/m3) |"
7170 H$(6)=" |Concentration in sediment solids (ug/g) |"
7180 H$(7)=" |Amount in water column (mol) |"
7190 H$(8)=" |Amount in water column (kg) |"
7200 H$(9)=" |Amount in sediment (mol) |"
7210 H$(10)=" |Amount in sediment (kg) |"
7220 H$(11)=" |Total amount in segment (mol) |"
7230 H$(12)=" |Total amount in segment (kg) |"
7240 FOR I= 1 TO II
7250 Y(1,I)=FW(I) :Y(2,I)=FS(I) :Y(3,I)=CWT(I) :Y(4,I)=CWTG(I) :Y(5,I)=CST(I)
7260 Y(6,I)=CSTG(I) :Y(7,I)=MWT(I)
7270 Y(8,I)=MWTK(I) :Y(9,I)=MST(I) :Y(10,I)=MSTK(I) :Y(11,I)=MT(I) :Y(12,I)=MTK
(I)
7280 NEXT I
7290 PRINT#1, " Property Segment No 1
2 3 "
7300 PRINT#1, " -----
----- "
7310 FOR J= 1 TO 12
7320 PRINT#1, H$(J);
7330 FOR I=1 TO II
7340 PRINT#1, USING "##.##^ ^ ^ |";Y(J,I);
7350 NEXT I
7360 PRINT#1, " "
7370 NEXT J
7380 PRINT#1, " -----
----- "
7390 PRINT#1, " "

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7400 PRINT#1, " Grand total mol      ";MTT
7410 PRINT#1, " Grand total kg       ";MTTK
7420 PRINT#1, " "
7430 PRINT#1, " Concentrations and amounts in each marina "
7440 H$(1)="|Aquivalence in water column      |"
7450 H$(2)="|Aquivalence in sediment          |"
7460 H$(3)="|Concentration in bulk water (mol/m3) |"
7470 H$(4)="|Concentration in bulk water (mg/L or g/m3) |"
7480 H$(5)="|Concentration in bulk sediment (mol/m3) |"
7490 H$(6)="|Concentration in sediment solids (ug/g) |"
7500 H$(7)="|Amount in water column (mol) |"
7510 H$(8)="|Amount in water column (kg) |"
7520 H$(9)="|Amount in sediment (mol) |"
7530 H$(10)="|Amount in sediment (kg) |"
7540 H$(11)="|Total amount in segment (mol) |"
7550 H$(12)="|Total amount in segment (kg) |"
7560 FOR I= 1 TO II
7570
      Y(1,I)=FWM(I):Y(2,I)=FSM(I):Y(3,I)=CWTM(I):Y(4,I)=CWTGM(I):Y(5,I)=CSTM
      (I)
7580 Y(6,I)=CSTGM(I):Y(7,I)=MWTM(I)
7590
      Y(8,I)=MWTKM(I):Y(9,I)=MSTM(I):Y(10,I)=MSTKM(I):Y(11,I)=MTM(I):Y(12,I)
      =MTKM(I)
7600 NEXT I
7610 PRINT#1, " Property                Marina No      1
      2                3 "
7620 PRINT#1, " -----
      ----- "
7630 FOR J= 1 TO 12
7640 PRINT#1, H$(J);
7650 FOR I=1 TO II
7660 PRINT#1, USING "##.##^ ^ ^ |";Y(J,I);
7670 NEXT I
7680 PRINT#1, " "
7690 NEXT J
7700 PRINT#1, " -----
      ----- "
7710 PRINT#1, " "
7720 PRINT#1, " Grand total mol      ";MTTM
7730 PRINT#1, " Grand total kg       ";MTTKM
7740 PRINT#1, " "
7750 PRINT#1, " "
7760 REM Print out transport and transformation rates for segments
7770 FOR I=1 TO II
7780 Y(1,I)=R(1,I):Y(2,I)=R(2,I):Y(3,I)=R(3,I):Y(4,I)=R(4,I):Y(5,I)=R(5,I)
7790 Y(6,I)=R(6,I):Y(7,I)=R(7,I):Y(8,I)=R(8,I)
7800
      Y(9,I)=RK(1,I):Y(10,I)=RK(2,I):Y(11,I)=RK(3,I):Y(12,I)=RK(4,I):Y(13,I)
      =RK(5,I)
7810 Y(14,I)=RK(6,I):Y(15,I)=RK(7,I):Y(16,I)=RK(8,I)
7820 NEXT I
7830 PRINT#1, " "
7840 PRINT#1, " Process rates in Segments kg/year"
7850 PRINT#1, " Process      Segment No      1                2                3 "
7860 PRINT#1, " -----
      ----- "
7870 FOR J= 1 TO 7
7880 PRINT#1, P$(J);
7890 FOR I=1 TO II
7900 PRINT#1, USING "##.##^ ^ ^ |";Y(J+8,I);
7910 NEXT I
7920 PRINT#1, " "

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7930 NEXT J
7940 PRINT#1, " -----"
7950 PRINT#1, " "
7960 PRINT#1, " Inter-segment transfers kg/year      "
7970 PRINT#1, " Source          Destination "
7980 PRINT#1, "           1           2           3           4 "
7990 PRINT#1, " -----"
8000 FOR I=1 TO III
8010 PRINT#1, USING "| ## |";I ;
8020 FOR J=1 TO III
8030 PRINT#1, USING " ##.##^ ^ ^ |";RJK(I,J);
8040 NEXT J
8050 PRINT#1, " "
8060 NEXT I
8070 PRINT#1, " -----"
8080 PRINT#1, " "
8090 REM Print out transport and transformation rates for marinas
8100 FOR I=1 TO II
8110     Y(1,I)=RM(1,I):Y(2,I)=RM(2,I):Y(3,I)=RM(3,I):Y(4,I)=RM(4,I):Y(5,I)=RM(
5,I)
8120 Y(6,I)=RM(6,I):Y(7,I)=RM(7,I):Y(8,I)=RM(8,I)
8130     Y(9,I)=RKM(1,I):Y(10,I)=RKM(2,I):Y(11,I)=RKM(3,I):Y(12,I)=RKM(4,I):Y(1
3,I)=RKM(5,I)
8140 Y(14,I)=RKM(6,I):Y(15,I)=RKM(7,I):Y(16,I)=RKM(8,I)
8150 NEXT I
8160 PRINT#1, " "
8170 PRINT#1, " Process rates in marinas kg/year"
8180 PRINT#1, " Process          Segment No          1          2          3 "
8190 PRINT#1, " -----"
8200 FOR J= 1 TO 7
8210 PRINT#1, P$(J);
8220 FOR I=1 TO II
8230 PRINT#1, USING "##.##^ ^ ^ |";Y(J+8,I);
8240 NEXT I
8250 PRINT#1, " "
8260 NEXT J
8270 PRINT#1, " | Total chemical outflow | " ;
8280 FOR I=1 TO II
8290 PRINT#1, USING "##.##^ ^ ^ |";RXM(I);
8300 NEXT I
8310 PRINT#1, " "
8320 PRINT#1, " -----"
8330 PRINT#1, " "
8340 PRINT#1, " "
8350 PRINT#1,CHR$(12)
8360 REM PRINT-OUT INDIVIDUAL SEGMENT MASS BALANCES
8370 IF P5=0 GOTO 8890
8380 FOR I = 1 TO II
8390 PRINT#1, " " : PRINT#1, "
Segment          Marina "
8400 PRINT#1, " Segment No ";I;N$(I);"          mol/h          kg/year          mol/h
kg/year"
8410 PRINT#1, " "
8420 PRINT#1, USING "          River inflow discharges
###.#####          #####.###";EW(I), EWK(I)
8430 PRINT#1, USING "          Total inflow from adjacent segments
###.#####          #####.###";RI(I), RIK(I)
8440 PRINT#1, USING "          Total outflow to adjacent segments
###.#####          #####.###          #####.###";RX(I),
RXK(I),RXM(I),RXKM(I)

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8450 PRINT#1, USING "          Vessel emissions
      ###.#####      #####.###      #####.###
      #####.###";EVE(I),EVEK(I),EVM(I),EVMK(I)
8460 PRINT#1, USING "          Evaporation
      ###.#####      #####.###      #####.###
      #####.###";R(7,I),RK(7,I),RM(7,I),RKM(7,I)
8470 PRINT#1, USING "          Water transformation
      ###.#####      #####.###      #####.###
      #####.###";R(6,I),RK(6,I),RM(6,I),RKM(6,I)
8480 PRINT#1, USING "          Water to sediment transfer
      ###.#####      #####.###      #####.###
      #####.###";RWS(I),RWSK(I),RWSM(I),RWSKM(I)
8490 PRINT#1, USING "          Sediment to water transfer
      ###.#####      #####.###      #####.###
      #####.###";RSW(I),RSWK(I),RSWM(I),RSWKM(I)
8500 PRINT#1, USING "          Sediment transformation
      ###.#####      #####.###      #####.###
      #####.###";R(2,I),RK(2,I),RM(2,I),RKM(2,I)
8510 PRINT#1, USING "          Sediment burial
      ###.#####      #####.###      #####.###
      #####.###";R(1,I),RK(1,I),RM(1,I),RKM(I,I)
8520 PRINT#1, " "
8530 PRINT#1, "          Details of exchange processes"
8540 RVN=DP(7,I)*(FW(I)-FA): RVNK=RVN*WM*8760/1000
8550 RTN=DP(4,I)*(FS(I)-FW(I)): RTNK=RTN*WM*8760/1000
8560 RSWD=DP(4,I)*FS(I): RSWDK=RSWD*WM*8760/1000
8570 RWSD=DP(4,I)*FW(I): RWSDK=RWSD*WM*8760/1000
8580 RV=DP(7,I)*FW(I): RVK=RV*WM*8760/1000
8590 SUMWI=EVE(I)+EW(I)+RI(I)+RSW(I)+RJYM(I):SUMWIK=SUMWI*WM*8760/1000
8600 SMMWI=EVM(I)+RSWM(I):SMMWIK=SMMWI*WM*8760/1000 'marina water input
8610 SUMWX=R(7,I)+R(6,I)+RX(I)+RWS(I) :SUMWXK=SUMWX*WM*8760/1000
8620 SMMWX=RM(7,I)+RM(6,I)+RJYM(I)+RWSM(I):SMMWXK=SMMWX*WM*8760/1000
8630 SUMSI=RWS(I) :SUMSIK=SUMSI*WM*8760/1000
8640 SMMSI=RSWM(I) :SMMSIK=SMMSI*WM*8760/1000
8650 SUMSX=RSW(I)+R(2,I)+R(1,I) :SUMSXK=SUMSX*WM*8760/1000
8660 SMMSX=RSWM(I)+RM(2,I)+RM(1,I) :SMMSXK=SMMSX*WM*8760/1000
8670 PRINT#1, USING "          Volatilization
      ###.#####      #####.###";RV, RVK
8680 PRINT#1, USING "          Sediment deposition
      ###.#####      #####.###";R(5,I),RK(5,I)
8690 PRINT#1, USING "          Sediment resuspension
      ###.#####      #####.###";R(3,I),RK(3,I)
8700 PRINT#1, USING "          (Net sediment to water diffusion)
      ###.#####      #####.###";RTN, RTNK
8710 PRINT#1, USING "          Sediment to water diffusion
      ###.#####      #####.###";RSWD, RSWDK
8720 PRINT#1, USING "          Water to sediment diffusion
      ###.#####      #####.###";RWSD, RWSDK
8730 PRINT#1, USING "          Inflow from upstream segment
      ###.#####      #####.###";RJY(I-1,I),RJYK(I-1,I)
8740 PRINT#1, USING "          Inflow from downstream segment
      ###.#####      #####.###";RJY(I+1,I),RJYK(I+1,I)
8750 PRINT#1, USING "          Outflow to upstream segment
      ###.#####      #####.###";RJY(I,I-1),RJYK(I,I-1)
8760 PRINT#1, USING "          Outflow to downstream segment
      ###.#####      #####.###";RJY(I,I+1),RJYK(I,I+1)
8770 PRINT#1, " "
8780 PRINT#1, USING "          Total input to water column
      ###.#####      #####.###      #####.###      #####.###";SUMWI, SUMWIK,SMMWI,SMMWIK
8790 PRINT#1, USING "          Total output from water column
      ###.#####      #####.###      #####.###      #####.###";SUMWX, SUMWXK,SMMWX,SMMWXK
8800 PRINT#1, " "

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8810 PRINT#1, USING "          Total input to sediment
      ###.#####      #####.###  #####.###  #####.###";SUMSI, SUMSIK,SMMSI,SMMSIK
8820 PRINT#1, USING "          Total output from sediment
      ###.#####      #####.###  #####.###  #####.###";SUMSX, SUMSXK,SMMSX,SMMSXK
8830 PRINT#1, " "
8840 PRINT#1, USING "          Total amount in water mol and kg
      ###.#####      #####.###  #####.###
      #####.###";MWT(I),MWTK(I),MWTM(I),MWTKM(I)
8850 PRINT#1, USING "          Total amount in sediment mol and kg
      ###.#####      #####.###  #####.###
      #####.###";MST(I),MSTK(I),MSTM(I),MSTKM(I)
8860 PRINT#1, " "
8870 PRINT#1,CHR$(12)
8880 NEXT I
8890 PRINT " If you wish to return to the start enter Y, to end enter N"
8900 INPUT Y$
8910 IF Y$="Y" OR Y$="y" GOTO 1100
8920 END

```




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