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The Uptake and Depuration of Petroleum Hydrocarbons in Marine Species

A Simulation Study of the Uptake and Depuration of Petroleum Hydrocarbons and Its Effect on Selected Marine Species in the Bristol Bay Ecosystem

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NOTICE

THE UPTAKE AND DEPURATION OF PETROLEUM HYDROCARBONS IN MARINE SPECIES

A simulation study of the uptake and depuration of petroleum hydrocarbons and its effect on selected marine species in the Bristol Bay ecosystem

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1. INTRODUCTION

1.1 Purpose

The purpose of this report is to describe the basic theory and underlying assumptions and provide results from the uptake and depuration algorithm (FEDOIL) of the Biological Impact of an Oil Spill model, BIOS. The BIOS model is a multispecies ecosystem simulation that analyzes the expected impact of hypothetical oil spill scenarios on fishery resources in the eastern Bering Sea. It was developed at the request of the Outer Continental Shelf Environmental Assessment Program (OCSEAP), and is a part of their eastern Bering Sea oil impact study. A full description of the OCSEAP study of which this report is a part is given in Laevastu and Fukuhara (1984a).

As general background, BIOS is a gridded model that simulates the uptake and depuration of oil contaminants in selected marine species (Table 1) resulting from exposure to oil contaminated water and sediments and the consumption of oil contaminated food (submodel FEDOIL). BIOS also simulates the migration of these species over time and space (Swan 1984a, 1984b), studies the expected impact of two hypothetical scenarios (Table 2) (see Laevastu and Fukuhara 1984a, for details), and is applied to three locations in the Bristol Bay area of the eastern Bering Sea: Port Moller, Port Heiden, and Cape Newenham (Figure 1). (The results from Pt. Heiden are emphasized in this report.) Figure 2 provides a diagram of the general sequence of BIOS model computations. Although details are given in Gallagher (1984) and Swan (1984a), the theory and methods described here combine and update the uptake and depuration algorithms described in those preliminary formulations.

Input data for the hydrocarbon concentrations of the water soluable fraction (WSF) of each oil spill scenario were provided by the Rand Corporation in conjunction with Science Applications, Inc. (SAI) (details are given in Laevastu and Fukuhara (1984a)). Hydrocarbon concentration data for the fraction of oil

Table 1.--List of species and input biomass data (by location) used in BIOS[1/].

No.	Species Name	Input Biomass Data (kg/km^2) [2/] Port Moller	Port Heiden	Cape Newenham
1	Herring juveniles	1409	521	1551
2	Herring adults	1121	414	1234
3	Pollock juveniles	3708	2322	3261
4	Pollock adults	11007	6893	9679
5	Pacific cod juveniles	424	279	307
6	Halibut juveniles	730	330	240
7	Yellowfin sole juveniles	722	482	711
8	Other flatfish juveniles	2004	1472	1650
9	Yellowfin sole adults	800	534	789
10	Other flatfish adults	2004	1472	1650
11	Pacific cod adults	861	461	681
12	King and Bairdi crab juveniles	664	222	432
13	King and Bairdi crab adults	1654	553	1078
14	Mobile epifauna	5970	4995	6075
15	Sessile epifauna	13930	11655	14175
16	Infauna	19150	13750	19250

1/ The DYNUMES model (Laevastu and Larkins, 1981) was used to get initial estimates of input biomass data for the three model locations of the BIOS model.

2/ The following assumptions were used to convert the data obtained from the DYNUMES model to biomass fields for use in the BIOS model.

a) Unless noted differently below, the breakdown of species biomass data into juvenile and adult fractions was based on Niggol (1982).

b) DYNUMES species group 5 (halibut) was assumed to be 100% juvenile (i.e., in these shallow waters during this season).

c) Yellowfin sole data were assumed to comprise 75% of DYNUMES species group 7 (yellowfin and rock sole).

d) DYNUMES species group 13 (Pacific and saffron cod) was assumed to be 100% Pacific cod.

e) DYNUMES species groups 7 (rock sole-25%), 6 (flathead sole, flounder), and 8 (other flatfish) were combined to make up the other flatfish group (species 8 and 9) for the BIOS model. These groups were assumed to be equally divided between juveniles and adults.

f) DYNUMES species groups 19 (king crab) and 20 (Tanner crab) were combined, and using available survey data, assumed to be comprised of 71.4% adults and 28.6% juveniles.

g) DYNUMES species group 24 (epifauna) was assumed to be 30% mobile and 70% sessile.

Table 2.--Hypothetical oil spill scenarios.

Scenario	Oil type	Volume	Duration	Temperature	Simulation grid	Locations in Bristol Bay
Well blowout	Prudhoe Bay crude	20,000 bbl/day	15 days	9.3°C	(50 x 50)	Port Moller Port Heiden Cape Newenham
Tanker accident	Automotive diesel	200,000 bbl (instantaneous)	10 days	9.3°C	(32 x 34)	Port Moller Port Heiden Cape Newenham

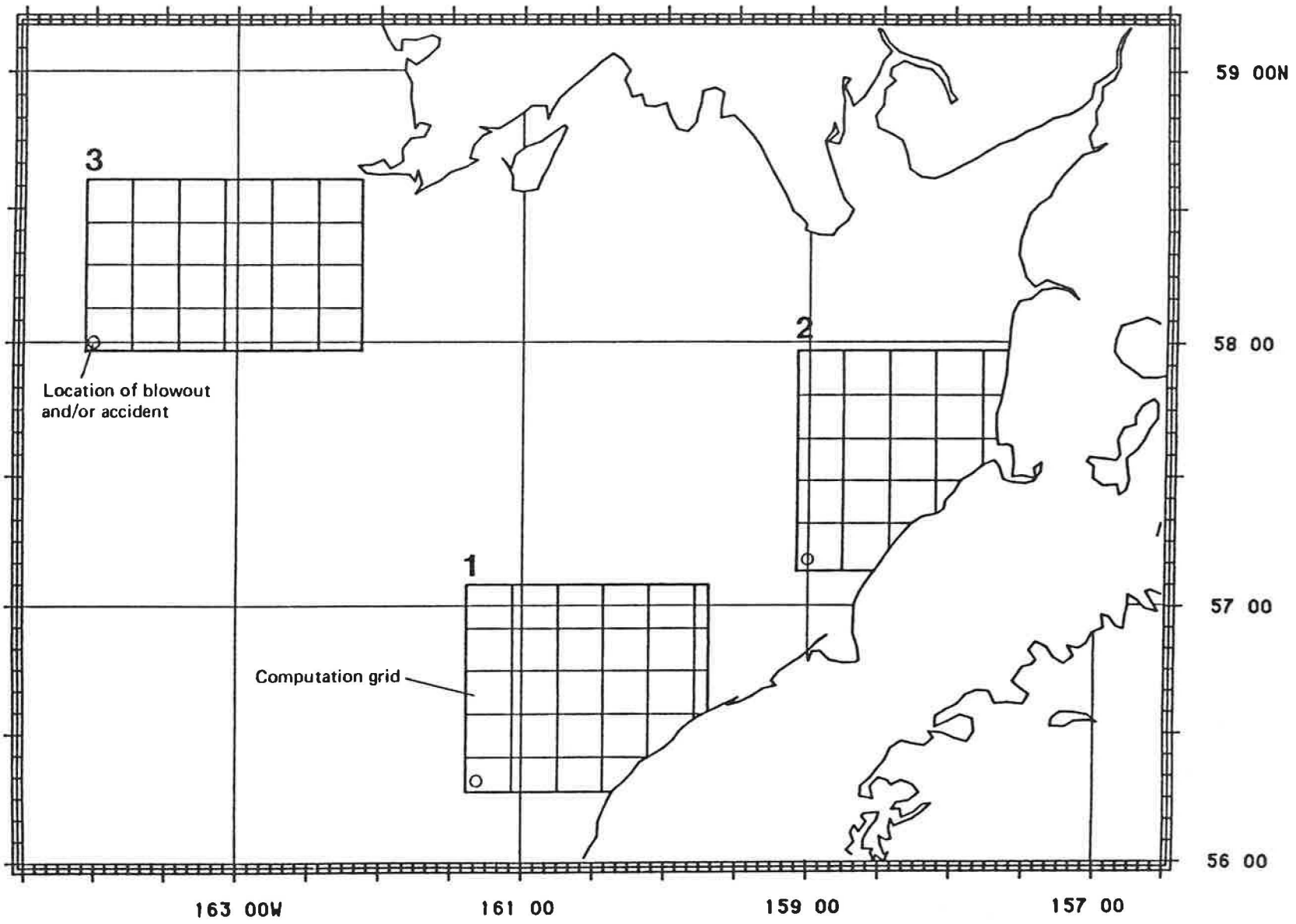
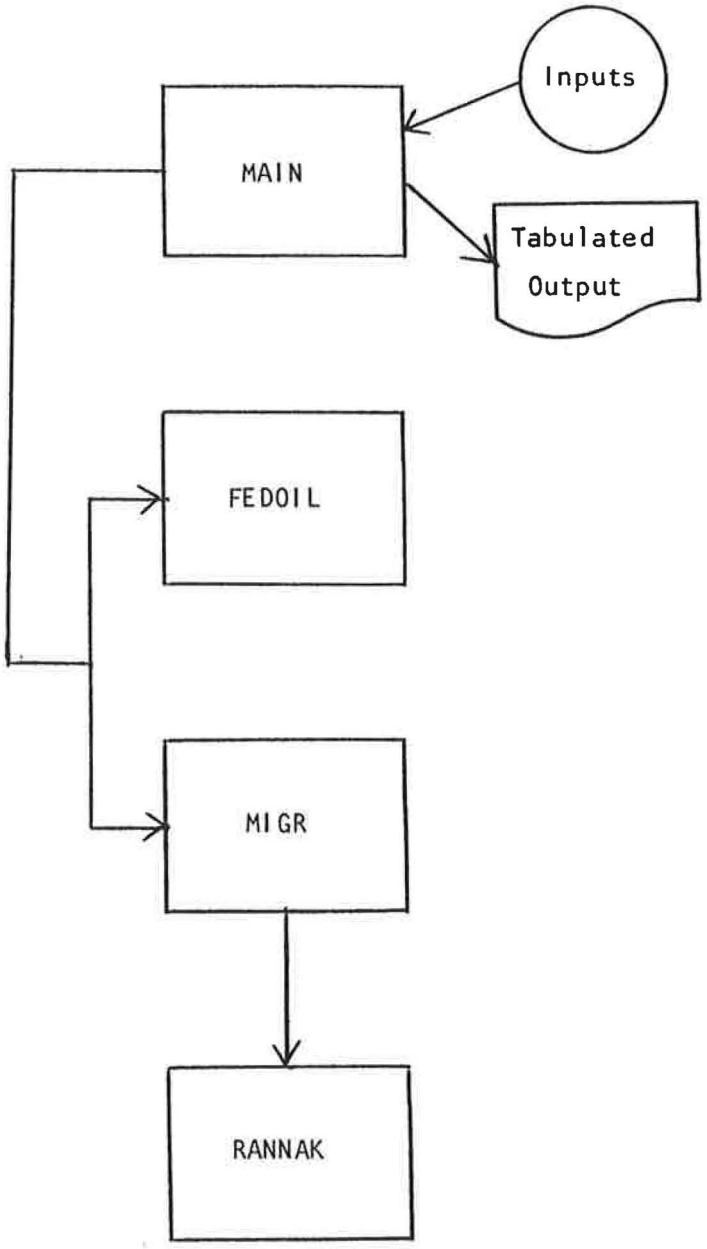


Figure 1.--Locations of hypothetical oil spills, and computational grids in Bristol Bay.



Main Program

Directs sequence of model calculations, reads input and prints output.

Feeding Subroutine

Computes uptake of contaminants through consumption of contaminated food.

Main Migration Subroutine

Directs sequence of migration computations. Sets species-specific parameters and velocities, calculates uptake from exposure to oil and depuration.

Migration Calculation Subroutine

Calculates actual migration and redistributes contamination over model grid. Calculates amount of contaminated biomass leaving the model region.

Figure 2.--Sequence of BIOS model calculations.

reaching the bottom and entering the sediments (referred to here as TARS), were obtained from a simulation model developed by Laevastu and Fukuhara (1984b).

1.2 Selected review of the literature on uptake and depuration of petroleum hydrocarbons.

An extensive literature exists on the fate and effects of petroleum hydrocarbons on marine organisms. Since a variety of authors have recently reviewed this literature (Malins 1977; Wolfe 1977; Connell and Miller 1981a, 1981b; National Academy of Science 1982), this discussion will not attempt to repeat those earlier works. Instead, it will confine itself to reviewing those studies pertinent to the modelling approach used in the BIOS model to simulate the processes of uptake and depuration.

For purposes of this discussion, uptake is defined as the acquisition of petroleum hydrocarbons by an organism either from exposure to oil contaminated water and sediments or from consumption of oil contaminated food. Depuration is defined as the purging of those hydrocarbons from the organisms, both during the uptake process and when the organism is no longer exposed to petroleum contaminants. For a variety of reasons discussed below, no attempt has been made to simulate the disposition of petroleum compounds after uptake; disposition being "what the organism does with a compound (e.g., their conversion to various metabolities)" (Malins and Hodgins 1981).

1.2.1 Uptake

Petroleum hydrocarbons have been shown to accumulate in the tissues and body fluids of many, if not all, marine organisms (Moore and Dwyer 1974, Malins and Hodgins 1981). Although the routes through which hydrocarbons enter marine organisms vary depending on species, life-history stage, and environmental conditions, they can be grouped into two general categories: 1) uptake directly

from contaminated water and sediments; and 2) accumulation through consumption of contaminated food (Connell and Miller 1981a; Thomann and Connolly 1984). The relative importance of each route also varies considerably, both by species group and by the actual bioavailability of the petroleum hydrocarbons involved; e.g., chemical compound, concentration, length of exposure, and medium (i.e., whether the compound is dissolved in the water column, adsorbed on particulate sediments, or bound up in food).

1.2.1.1 Benthic Invertebrates

Benthic invertebrates have been shown to readily uptake petroleum hydrocarbons. Bivalves, which filter large volumes of water when feeding, can uptake and concentrate petroleum hydrocarbons from water, whether in solution or absorbed on suspended particles (see Lee 1977, for review). They have also been shown to bioaccumulate hydrocarbons to a level several orders of magnitude above the external concentration (Stegman and Teal 1973, Fossato and Canzonier 1976). Although bivalves tend to accumulate petroleum hydrocarbons more slowly than fish or crustacea (Neff et al., 1976), several studies show that they continue to do so for as long as they are exposed to oil-contaminated seawater (Stegman and Teal 1973; Neff et al., 1976).

As reviewed by both Connell and Miller (1981a) and the National Academy of Science Report (1982), several uptake experiments with the oyster, Crassostrea virginica demonstrate that oysters tend to accumulate higher concentrations of aromatic hydrocarbons than saturated hydrocarbons relative to their respective concentrations in exposure water during the initial uptake phase. Although similar results have been reported for the clam, Rangia cuneata (Neff et al., 1976), rates of uptake differ between species and appear to be related to differences in

filtering rates and amounts of lipids in the organisms (Lee 1977), and the water solubilities and molecular weights of the specific hydrocarbon pollutants (Lee 1977; Varanasi and Malins 1977). As will be discussed later, however, it is rather difficult to compare data obtained from different studies because of the considerable variability in experimental technique and type and composition of petroleum compounds used. In fact, the review by Varanasi and Malins (1977) is one of the few studies that divides the experiments reviewed into categories reflecting field studies, laboratory studies using oil-in-water dispersions (OWD) and water-soluble fractions (WSF) of oil, and feeding studies involving petroleum contaminated food.

Benthic crustaceans have been shown to rapidly take up petroleum hydrocarbons from either their food or water (Lee et al., 1976, Neff et al., 1976, Rice et al., 1976, Rice et al., 1983). As with bivalves, the rate and amount of petroleum hydrocarbons accumulated appears to be related to internal lipid content and the different solubilities of the individual petroleum constituents (see Connell and Miller 1981a, for review). The present data, however, do not allow for a clear quantitative partitioning of the uptake process between the routes of feeding and exposure to oil-contaminated water or sediments. For example, Rossi et al. (1978), as reported in Connell and Miller (1981a), indicated that it was impossible to establish whether sand crabs, Emerita analoga, incorporated petroleum hydrocarbons into their tissue or superficially entrained contaminated particulate matter. In addition, Lee et al. (1976) have shown that in the case of the blue crab, Callinectes sapidus, most of the hydrocarbons in the food were not assimilated by the tissues, but instead were immediately eliminated from the animal.

The data for benthic worms are no less confusing. Although benthic worms have clearly been shown to uptake petroleum hydrocarbons, the amount and rate of uptake

can vary depending on hydrocarbon constituent and sediment type (Lee 1977, for review). In addition, the actual route of uptake of the hydrocarbons is unclear. Rossi (1977) has reported that most of the aromatic hydrocarbons accumulated by the polycheate, Neanthes arenaceodentata, were derived from water and not sediments, while Prouse and Gordon (1976) indicated that the burrowing activities of the deposit feeding polycheate, Arenicola marina, in sediments may result in uptake from either ingestion of contaminated sediments or through absorption from solution. A variety of other studies indicate that polycheate annelids also vary in sensitivity to fuel-oil soluble fractions at different life stages according to lipid content (e.g., Rossi and Anderson 1976). Moreover, and depending on the study, certain aromatic hydrocarbons (e.g., naphthalenes), have been shown both to accumulate rapidly (Rossi 1977) and not to accumulate to significant levels at all (Anderson et al., 1977).

1.2.1.2 Fish

The principal processes for the uptake of hydrocarbons in fish appear to involve either direct absorption of dissolved and particulate forms via gills or drinking water, or indirect uptake through the ingestion of contaminated food (Connell and Miller 1981a, for review). As in the case of benthic invertebrates, however, the data on uptake in fish are rather contradictory. For example, uptake has been shown to be selective within and between hydrocarbon classes (Connell and Miller 1981a, for review), and within and between species depending on life history stage and ecological niche (i.e., pelagic or demersal) (Korn et al., 1976, Lee 1977; Connell and Miller 1981a, and National Academy of Science 1982, for reviews). In addition, although a variety of authors have concluded that there is a greater storage and persistence of aromatics and polynuclear

aromatic hydrocarbons in lipid-rich than in lipid-poor fish species (Whittle et al., 1977, Connell and Miller 1981a, for review), a study by Roubal et al., (1978) indicates that, for aromatic hydrocarbons, factors other than lipid content may be more influential in determining hydrocarbon accumulation in certain species. Roubal et al., 1978 also indicate that because of the great differences in bioconcentration factors observed for individual aromatic hydrocarbons in both of the species they studied (coho salmon, Oncorhynchus kisutch, and starry flounder, Platichthys stellatus),"these differences may complicate attempts to relate tissue hydrocarbon profiles to hydrocarbon profiles of specific sources of petroleum pollution".

The problem of relating tissue hydrocarbon profiles to sources of hydrocarbon contamination in fish is further complicated by the conflicting reports regarding the relative importance of the uptake routes of feeding and exposure to oil (see Lee 1977 and Connell and Miller 1981a, for reviews). For example, feeding behavior and the presence of oil may be interdependent, as shown by the enhanced weight loss and distinct reduction in food intake by oil exposed flatfish (McCain et al., 1978, Fletcher et al., 1981). Additionally, and with respect to specific feeding studies, Mehrle et al. (1977) have shown that the type and quality of diet fed during chronic toxicity testing can strongly influence the results of the biological parameters being measured (e.g., mortality, growth, development, etc.). Finally, not only is it impossible to compare oil toxicities and animal sensitivities in different studies done prior to 1973 because of the lack of data on the chemical analyses of oil-water solutions (Rice et al., 1979), but results from many of the effects studies have been obtained from experiments using relatively high concentrations that probably would not be encountered in the marine environment (Malins and Hodgins 1981).

1.2.1.3 Summary of uptake studies

The available data on uptake rates and accumulation of petroleum hydrocarbons in marine organisms are confusing, contradictory, and in the case of some studies, provide results that may not be representative of events that occur in the natural, multifaceted conditions found in the marine environment (Malins and Hodgins 1981). Consistent data have been presented, however, that demonstrate the importance of lipid content and petroleum water solubilities in the bioaccumulation of hydrocarbons in both benthic invertebrates and fish. These topics and the general subject of estimating uptake rates will be considered in more detail in Section 2.

1.2.2 Depuration

Depuration of petroleum hydrocarbons from marine organisms is a complex process that varies within and between species and hydrocarbon compounds and with environmental conditions. The actual pathways of depuration are unclear, but seem to be related to the mode of uptake (e.g., absorption from solution, feeding, etc.). Any understanding of the depuration processes is considerably confounded, however, by the degree to which acquired hydrocarbons are accumulated and retained as conversion byproducts. In addition, as in the case of uptake rates, conflicting information on depuration rates seems, oftentimes, to be as much a function of differences in experimental design as it is a function of differences in either hydrocarbon or species specific biochemical processes.

1.2.2.1 Benthic invertebrates

As reviewed by Lee (1977) and Connell and Miller (1981a), most depuration studies indicate that bivalves release accumulated petroleum hydrocarbons when placed in clean or oil-free seawater. After an initial phase of rapid discharge,

there is an extended period of residual hydrocarbon retention. The initial rapid discharge usually results in the calculated short half-lives for accumulated hydrocarbons (Lee 1977). For example, Stegman and Teal (1973) report a 90% loss of petroleum hydrocarbons from high-fat-content oysters (C. virginica) after 14 days of depuration in clean seawater. Stored petroleum hydrocarbon concentration levels, however, were still above the background levels of 1 ppm after 4 weeks. Although several other studies reviewed by Connell and Miller (1981a) also report depuration clearance after 14 days in clean seawater, Fossato and Canzonier's (1976) study of the mussel, Mytilus edulis, indicated that mussels still retained petroleum hydrocarbon concentrations of 30 ppm after 56 days of depuration.

The major difficulty in using depuration rates of petroleum hydrocarbons from bivalves obtained under experimental conditions is the fact that bivalves in oil spill areas generally depurate more slowly. This is due, in part, to the continued input of oil from the sediment. Lee (1977) reports that for oysters, the longer the period of uptake, the slower the depuration of the accumulated petroleum hydrocarbons. In addition, while many calculated biological half-lives from laboratory experiments range between 1 and 7 days, results from field experiments suggest considerably longer half-lives (i.e., 48-60 days; DiSalvo et al., 1975) for aromatic hydrocarbons in particular. Although this increased retention time for aromatic hydrocarbons may be related to passive diffusion between lipids and the aqueous phase, as expressed by lipid/water partition coefficients (Stegman and Teal 1973, Neff et al., 1976), an additional hypothesis has been proposed by Stegman and Teal (1973) that suggests that for chronically exposed bivalves the same accumulated hydrocarbons enter a stable tissue compartment where they are retained and released slowly during depuration in clean seawater.

Connell and Miller (1981a) reviewed studies by several other workers (e.g., Neff et al., 1976) that also suggest this latter explanation for the rapid initial loss of hydrocarbons and retention of a small persistent fraction in depuration studies.

The more important factor in the storage of aromatic hydrocarbons in bivalves, however, is probably the absence of detectable aryl hydrocarbon hydroxylases (AHH) activity. As reviewed in Varanasi and Malins (1977), it is generally accepted that the metabolism of aromatic hydrocarbons is mediated by cytochrome P_{450}-dependent enzyme systems (mixed-function oxidases; MFO), and that these oxygenases, or drug-metabolizing enzymes, are believed to account for the formation of virtually all of the primary metabolic products of aromatic hydrocarbon degradation. Since it appears that mollusks do not possess the systems necessary for the metabolism of aromatic hydrocarbons and their subsequent excretion as the more water-soluble hydroxylation products, the ability of bivalves to store and retain petroleum hydrocarbons for considerable periods of time is probably directly related to this apparent lack of MFO activity. As discussed below, such biological and biochemical complexity only further complicates the already difficult task of modelling the uptake and depuration of petroleum hydrocarbons in marine organisms.

Benthic crustaceans have been generally shown to depurate petroleum hydrocarbons rather rapidly when placed in clean seawater (i.e., in 2 to 10 days). The information is not as clear, however, with respect to the depuration of petroleum hydrocarbons in an oil-spill area. Lee et al. (1976) have suggested that crabs should not retain petroleum hydrocarbons in an oil-spilled area, except for very recent uptake, due to their high metabolic and excretion rates. This

position is supported by results from their experiments with the blue crab, Callinectes sapidus, in which they found no evidence of storage of hydrocarbons by any crab tissue. Rice et al. (1983), however, report preliminary results from their studies with king crab, Paralithodes camtschatica, exposed to water soluble fractions (WSF) of crude oil that indicate site specific uptake and retention of petroleum hydrocarbons; i.e., although the crabs had virtually no naphthalene in their gill tissues, viscera concentrations of naphthalene were 1200 times the naphthalene concentrations in the WSF. In addition, Burns (1976), as reported in Lee (1977), noted that the fuel-oil hydrocarbon body burden in intertidal fiddler crabs, Uca pugnax, lasted for up to four years in an area where sediments were contaminated by an actual oil spill. This suggests that the crabs continued to take up oil from either the contaminated sediments or from oil released from the sediments. In either case, the complex nature of hydrocarbon retention and depuration in crabs in the natural environment makes it difficult to directly extrapolate experimental findings on depuration rates to field situations.

The depuration of petroleum hydrocarbons in benthic worms is generally rapid. Depending on species and hydrocarbon compound, tissue body burdens of petroleum hydrocarbons have been shown to drop to background levels in 14 to 24 days when benthic worms were placed in clean seawater (Lee 1977, Connell and Miller 1981a, for reviews). Although neither reviewer provided information on depuration rates in the presence of oil contaminated sediments, each indicated that benthic worms have well developed enzyme systems that rapidly metabolize petroleum hydrocarbons. One study by Anderson et al. (1977), however, reports that tissue concentrations of naphthalenes in sediment-exposed sipunculid worms, Phascolosonia

agassizii, were comparable to those found in the contaminated sediments. Thus, despite the fact that both the water- and sediment-exposed worms from the Anderson et al. (1978) study released accumulated naphthalenes to background levels after 14 days depuration, the long term effects of continued hydrocarbon exposure on depuration rates is left unclear.

1.2.2.2 Fish

The depuration of petroleum hydrocarbons from fish usually takes between 7 to 14 days when organisms are placed in clean seawater (Lee 1977). As in the case of uptake, however, depuration has been shown to be selective within and between species and hydrocarbon classes (Korn et al., 1976, Roubal et al., 1978). Korn et al. (1976), for example, reported that when fish were placed in clean seawater substantial depuration occurred within 7 to 14 days but, for some naphthalenes and higher-molecular-weight aromatics, a significant residual fraction (about 1 to 10%) was retained for longer periods (see Connell and Miller 1981a, for a review of this topic).

Fish have active enzyme systems (MFO) that can metabolize aromatic hydrocarbons rather rapidly to water-soluble compounds. This process facilitates the removal of toxic hydrocarbons from the body, and as Rice (1981) points out, these already active enzyme systems have been shown to increase after exposure to petroleum hydrocarbons. Several studies, however, have shown that some of the resulting metabolities persist in tissues longer than the parent hydrocarbons (Roubal et al., 1977, Varanasi et al., 1979). Varanasi et al. (1979) has shown also that the extent of biotransformation of naphthalene and the types of metabolities remaining in tissues of flatfish are greatly influenced by both mode of exposure and the time elapsed after the exposure is initiated.

In a follow-up study, Varanasi et al. (1981) further indicated that, in general, lower water temperature increased tissue concentrations of both the parent hydrocarbon (naphthalene) and its metabolities. They pointed out, however, that the actual magnitude of the increase was dependent upon the hydrocarbon compound, the tissue, and the time after the initiation of the exposure. Clearly, the complex nature of the process of retention of petroleum hydrocarbons and their conversion byproducts only further complicates attempts at understanding the depuration process in marine fish.

1.2.2.3 Summary of Depuration Studies

The complex nature of the depuration process and the variability in reported depuration rates, particularly between field and laboratory data, makes any simulation of the depuration of petroleum hydrocarbons a fundamentally qualitative undertaking. This is particularly apparent when one considers the facts upon which most investigators agree; i.e., that depuration rates under actual oil spill conditions are most likely altered and determined by complex interactions between the size of the spill, type of oil, the species and its physiological state, and the existing environmental and hydrodynamic regimes (Lee 1977, Connell and Miller 1981a). As discussed in Section 2, such a complex of factors considerably limits the set of reasonable approaches available for modelling the depuration process.

2. METHODS

2.1 Modelling approaches to the uptake and depuration of petroleum

The various approaches taken in modelling the uptake and depuration of organic compounds in marine species have ranged from simple and direct methods based on first-order kinetics (e.g., Branson et al., 1975), to more complex methods based on the coupling of pollutant biokinetics with fish bioenergetics (e.g., Norstrom et al., 1976). Although each of these approaches has a certain elegance in theory (the latter models in particular), each has been "frought with difficulty because of the paucity of some parameter values" (Hallam and deLuma 1984). In addition, the confusing and oftentimes conflicting results of laboratory and field investigations with respect to the relative importance of uptake from feeding and uptake from exposure to oil-contaminated water or sediments (see Section 1 above), has further complicated the problem of modelling the marine system.

In order to simplify the modelling approach taken here, the uptake of an oil pollutant is assumed to represent the uptake from both feeding and exposure to oil-contaminated water and sediments. Although this approach ignores the predator-prey dynamics of the ecosystem, it circumvents the problem of estimating the many bioenergetic rate parameters needed for the model, recognizing that these rate constants may vary with environmental conditions. In addition, since "we have more gaps than knowledge about the foodweb transfer of hydrocarbons in the ocean" (Teal 1977), the approach taken here further avoids the problem of trying to partition pollutant uptake between feeding and exposure to oil contaminants, a process already complicated by the fact that marine organisms have been shown to have decreased feeding rates when exposed to sublethal concentrations of petroleum.

The model used in this analysis, submodel FEDOIL, will study the total bioaccumulation of a pollutant in an organism. Bioaccumulation is defined to occur when the rates of uptake and redistribution exceed the rates of metabolism and elimination. The modelling approach is based on simple first-order kinetics (Atkins 1969, Moriarity 1975, and Wilson 1975), and can be described by a simple two-compartment (water and organism) reversible reaction model (Branson et al., 1975, Eberhardt 1975, Blanchard et al., 1978). (Banerjee (1984) uses the same approach but refers to it as a one-compartment pharmacokinetic model.) It is given as:

$$C_w \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C_f \qquad (1)$$

where C_w is the concentration in the water, C_f is the concentration in the fish (or other marine organism), and k_1 and k_2 are rate constants for the movement of the pollutant into and out of the fish, respectively (see Figures 3 and 4).

As Moriarity (1975) points out, this approach, although mathematically convenient, is unrealistic in that it assumes a whole organism can be considered as a single compartment. This criticism has been voiced also by Atkins (1969), Wilson (1975), and a variety of field workers such as Stegman and Teal (1973), as reviewed in Connell and Miller (1981a). Most of the available data, however, can only be fitted to an equation with a single exponential (Moriarity 1975), a point borne out by Eberhardt's (1975) inability to fit the "more complex models thus required to data of the kind reported" in the studies he reviewed. MacKay and Hughes (1984) also found that "model complexity greatly exceeds the detail of the experimental information", and thus found it necessary to

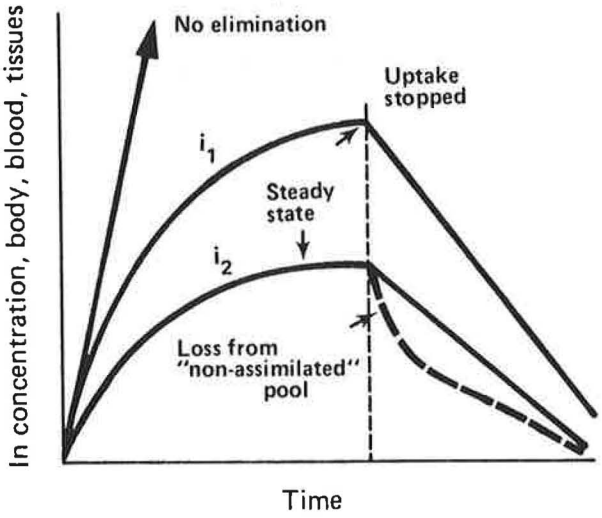


Figure 3.--Generalized relations of uptake and depuration with time at different levels of exposure. $i_1 > i_2$. Broken line indicates depuration from two (or more) compartments (from Moriarity 1975).

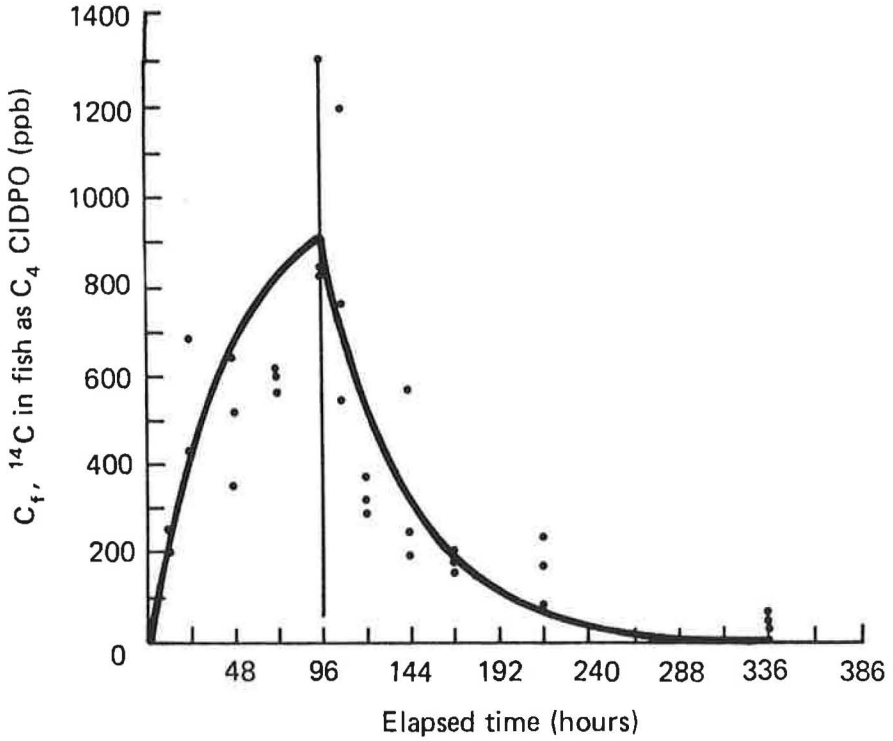


Figure 4.--Uptake and clearance curve of high exposure of C_4ClDPO in trout as linear plot with rate constants from nonlinear regression analysis. Points are concentrations in individual fish. The average concentration in water was 3.6 ppb. The vertical line at 96 hrs indicates the boundary between uptake and clearance. $k_1 = 6.05 \pm 0.98$; $k_2 = 0.0207 \pm 0.0041$. Bioconcentration factor, BCF = 292 ± 75 (from Blanchard et al., 1977).

"introduce simplifying assumptions to reduce the number of parameters". Given the lack of data available for parameterizing the more complex multi-compartment models, the one-compartment model used here seems reasonable as a first order approximation.

The change over time of the internal concentration, C_f, is given by:

$$dC_f/dt = (k_1)(C_w) - (k_2)(C_f) \quad (2)$$

with the solution (for C_w constant):

$$C_f(t) = (k_1/k_2)(C_w)(1-\exp(-k_2 t)); \; C_f(0) = 0 \quad (3)$$

If the initial concentration of the organism, $C_f(0)$, is not zero, then we have:

$$C_f(t) = (k_1/k_2)(C_w)(1-\exp(-k_2 t)) + C_f(0)\exp(-k_2 t) \quad (4)$$

This equation assumes a steady state condition as t approaches infinity, such that when $dC_f/dt = 0$, Equation 2 becomes:

$$\frac{C_f}{C_w} = \frac{k_1}{k_2} = BCF \quad (5)$$

where BCF defines the bioconcentration factor (bioaccumulation rate) at steady state.

One of the disadvantages of using this steady state approach is the assumption of a constant external concentration, C_w. Since the simulated external oil concentration data used in this study (as supplied by the Rand corporation; see Laevastu and Fukuhara 1984a, for a discussion) change over time and space, Equation 4 was adjusted to better reflect the dynamic nature of the system. The form used in the BIOS model is given as:

$$C_f(t) = (k_1/k_2(C_w(t))(1-\exp(-k_2)) + C_f(t-1)\exp(-k_2) \quad (6)$$

$$C_f(0) = 0 \quad (7)$$

By replacing the initial concentration, $C_f(0)$, of Equation 4 by the internal concentration of the previous time step, $C_f(t-1)$, and then removing the variable of time, t, in the exponent of the exponential, the Equation Set 6-7 gives a reasonable finite difference approximation of the uptake and depuration of oil contaminants when the external concentration, C_w, is not constant. Test runs of the BIOS model comparing simulation outputs from Equation 4 with those of the Equation Set 6-7 give identical results for the case $C_w(t) = C_w$, constant. Since Equation 4 is clearly not applicable to the case where C_w is changing over time ($C_w = C_w(t)$), the Equation Set 6-7 seems appropriate for the case when the external concentration is time dependent.

External concentration data, $C_w(t)$, are given for both the water soluable fraction (WSF), $C_w(t)_{WSF}$, and for the fraction of the oil that sedimentizes to the bottom (TARS), $C_w(t)_{TARS}$. Since marine organisms may be affected by either one or both of these pollutant levels depending on life history, it was necessary to compute a composite value of external concentration that reflected the relative exposure of a species to the two types of external concentration data. Since a species' feeding behavior can be generalized into the fraction of pelagic and demersal food in its diet, this composite value was also adapted to address the differential feeding behavior of an individual species. Before discussing this topic further, however, it is necessary to make some additional comments regarding the rate constants k_1 and k_2.

Methods for obtaining realistic parameter values for the uptake and depuration rate constants, k_1 and k_2, were complicated by a variety of factors. First, species-specific rates often are lacking and, when available, are usually limited

to the specific experimental situation (i.e., time of exposure, experimental system design, temperature), making it difficult to transfer the results to field situations (Malins and Hodgins 1981). Second, most studies work with only very small fish when studying uptake and depuration rates (Eberhardt 1974, Hamelink 1977). Several studies, however, suggest that experiments with larger fish will give substantially different results (Hamelink and Waybrant 1976, Anderson and Weber 1975, Thomann 1981, Thomann and Connolly 1984). Third, although lower water temperature has been shown to increase tissue concentrations of both parent hydrocarbons and their metabolities (Varanasi et al., 1981), no direct function has been developed relating the magnitude of accumulation with temperature (Fossato and Canzonier 1976, Rice et al., 1977). In addition, several studies have shown that the lowering of water temperature significantly influences the rate of elimination of individual hydrocarbons such as naphthalene (Collier et al., 1978, Varanasi et al., 1981). Fourth, the conversion of accumulated hydrocarbons to byproducts that may also accumulate but go undetected limits any attempts to simulate the depuration process. Finally, and most importantly, the considerable differences in bioconcentration factors observed for individual aromatic hydrocarbons seriously complicate attempts to relate tissue hydrocarbon profiles to hydrocarbon profiles of specific sources of petroleum pollution (Roubal et al., 1978).

In order to address these problems, particularly the latter, it was necessary to make several simplifying assumptions in estimating the values of k_1 and k_2. As shown in Equation 5, the bioconcentration factor, BCF, can be estimated from the ratio of k_1 to k_2. Similarly, $k_1(k_2)$ can be estimated if values for BCF and $k_2(k_1)$ are available. Since k_1 values were the most difficult to obtain from the

literature, it was decided not to use explicit uptake rates in this analysis but instead to rewrite equation (6) as:

$$C_f(t) = \text{VALUE}\ (1-\exp(-k_2)) + C_f(t-1)\exp(-k_2) \qquad (8)$$

where the variable VALUE is calculated according to the pelagic or demersal nature of the species. For the general case, VALUE is given as:

$$\text{VALUE} = (\text{PEL})(\text{BCFPEL})(C_w(t)_{WSF}) + (\text{DEM})(\text{BCFDEM})(C_w(t)_{TARS}) \qquad (9)$$

where PEL and DEM are the fraction of pelagic and demersal food, respectively, in a species diet (PEL is set equal to FODCMP, the fraction of pelagic food, and DEM = 1.0 - PEL), and BCFPEL and BCFDEM are the pelagic and demersal bioconcentration factors, respectively (see discussion below).

The depuration parameter, k_2, can now be estimated from either the reported total depuration time of all hydrocarbons from an organism after being placed in clean water via the equation:

$$k_2 = [-\ \ln(C_f(0)/C_f(t)_c)]/t \qquad (10)$$

where $C_f(t)_c$ is the total concentration in the organism just prior to being placed in clean water; or from data on the biological half-life of the hydrocarbon contaminant via the equation:

$$k_2 = \frac{\ln 2}{t(1/2)} \qquad (11)$$

where t(1/2) is the biological half-life (Wilson 1975, Connell and Miller 1981a). (See Table 3).

With regards to the bioconcentration factor, BCF, and its pelagic and demersal components, BCFPEL and BCFDEM, a variety of investigators have shown that BCF can be estimated from either the n-octanol water partition coefficient (Neely et al., 1974, Veith et al., 1979), or from the water solubility (Chiou et al., 1977,

Table 3.--Depuration rate (k_2) data used in submodel FEDOIL.

Species type	Depuration half-life or total time in days	Estimated k_2 value used in FEDOIL	Source of data
Pelagic juvenile	2-7 a)	.1980	a) total time - Korn et al. 1976
Pelagic adult	7-14 a)	.1320	a) total time - Lee 1977
Semi-pelagic juvenile	2-7 a)	.1980	a) total time - Korn et al. 1976
Semi-pelagic adult	7-14 a)	.1320	a) total time - Lee 1977
Flatfish juvenile	4.2 a) $\leq$ 51 b)	.1664	a) half-life - Roubal et al. 1978 b) total time - McCain et al. 1978
Flatfish adult	$\leq$ 51 a)	.1109	a) total time - McCain et al. 1978
King crab juvenile	2.1 a) 2-10 b)	.3342	a) half-life - Lee et al. 1978 b) total time - Lee 1977
King crab adult	2-10 a)	.2228	a) total time - Lee 1977
Mobile epifauna	3-4 a)	.1980	a) total time - Anderson 1977
Sessile epifauna	16 a) 28-35 b)	.0346	a) half-life - Lee 1977 b) total time - Lee 1977
Infauna	10 a) 12-14 b)	.06930	a) half-life - Lee 1977 b) total time - Lee 1977

Spacie et al., 1979) of the hydrocarbon. Since "water solubility is usually the most available measured parameter and probably the most practical for early assessment of potential bioconcentration hazard" (Kenaga and Goring 1980), the BCF values used in this analysis are estimated according to Kenaga and Goring (1980) via the equation:

$$\log BCF = 2.791 - 0.564(\log WS) \qquad (12)$$

where WS is the water solubility in parts per million (ppm) of the specific hydrocarbon in question (for a review of the relevant theory of partition coefficients and water solubility, see Chiou 1981). The BCFPEL and BCFDEM values are then set equal to the calculated BCF of Equation 12. Each value could, of course, be set individually if the data so indicated; for example, BCFDEM is set equal to twice BCF for mobile and sessile epifauna, species 14 and 15, due to their high bioconcentration rates.

Since different hydrocarbon compounds have order of magnitude differences in their water solubilities (see Tables 4 and 5), a water solubility index (WS) was used to compute the BCF from Equation 12 (Table 6). This water solubility index represents those hydrocarbon compounds that are the most significant oil contaminant fractions resulting from an oil spill and that have been demonstrated to be most toxic to, and accumulated by, marine organisms (i.e., naphthalenes). Using data from several sources (Clark and Brown 1977, Payne et al., 1984), the naphthalene fraction of the total hydrocarbons reported in the WSF external concentration data supplied by the Rand Corporation (a breakdown of hydrocarbon components was not provided), was assumed to be approximately 50% of the total for both scenarios. The naphthalene fraction of total hydrocarbons simulated for the TARS external concentration data (Laevastu and Fukuhara 1984b), was

Table 4.--Solubility of selected aromatic petroleum hydrocarbon in water [a].

Compound	Carbon number	Solubility[b] (ppm)
Benzene	6	1,780
Toluene	7	515
O-Xylene	8	175
Ethylbenzene	8	152
Naphthalene	10	31.3
		22.0 (SW)
1 - Methylnaphthalene	11	25.8
2 - Methylnaphthalene	11	24.6
2 - Ethylnaphthalene	12	8.00
1,5 - Dimethylnaphthalene	12	2.74
2,3 - Dimethylnaphthalene	12	1.99
2,6 - Dimethylnaphthalene	12	1.30

a) - Adapted from Clark and McLeod (1977).

b) - In distilled water, except where noted by (SW), indicating filtered seawater, usually corrected to a salinity of 35 °/oo (parts per thousand); ppm=parts per million - micrograms per gram.

Table 5.--Hydrocarbon content of water-soluble fractions of four test oils [a].

Compound	Hydrocarbon content of water-soluble fraction (ppm) S. Louisiana crude oil	Kuwait crude oil	No. 2 fuel oil	Bunker C residual oil
Alkanes				
Ethane	0.54	0.23	-[b]	-
Propane	3.01	3.30	-	-
Butane	2.36	3.66	-	-
Isobutane	1.69	0.90	0.39	0.05
Pentane	0.49	1.31	-	-
Isopentane	0.70	0.98	-	-
Cyclopentane + 2-methylpentane	0.38	0.59	0.02	0.005
Methylcyclopentane	0.23	0.19	0.019	0.004
Hexane	0.09	0.29	0.014	0.004
Methylcyclohexane	0.22	0.08	0.03	0.002
Heptane	0.06	0.09	0.02	0.004
C_{16} n-Paraffin	0.012	0.0006	0.008	0.0012
C_{17} n-Paraffin	0.009	0.0008	0.006	0.0019
Total C_{12}-C_{24} n-paraffins	0.089	0.004	0.047	0.012
Aromatics				
Benzene	6.75	3.36	0.55	0.04
Toluene	4.13	3.62	1.04	0.08
Ethylbenzene + m-, p-xylenes	1.56	1.58	0.95	0.09
O-Xylene	0.40	0.67	0.32	0.03
Trimethylbenzenes	0.76	0.73	0.97	0.11
Naphthalene	0.12	0.02	0.84	0.21
1-Methylnaphthalene	0.06	0.02	0.34	0.19
2-Methylnaphthalene	0.05	0.008	0.48	0.20
Dimethylnaphthalenes	0.06	0.02	0.24	0.20
Trimethylnaphthalenes	0.008	0.003	0.03	0.10
Biphenyl	0.001	0.001	0.011	0.001
Methylbiphenyls	0.001	0.001	0.014	0.001
Dimethylbiphenyls	0.001	0.001	0.003	0.001
Fluorene	0.001	0.001	0.009	0.005
Methylfluorenes	0.001	0.001	0.009	0.004
Dimethylfluorenes	0.001	0.001	0.002	0.002
Dibenzothiophene	0.001	0.001	0.004	0.001
Phenanthrene	0.001	0.001	0.010	0.009
Methylphenanthrenes	0.002	0.001	0.007	0.011
Dimethylphenanthrenes	0.001	0.001	0.003	0.003
Total saturates	9.86	11.62	0.54	0.081
Total aromatics	13.90	10.03	5.74	1.28
Total dissolved hydrocarbons measured	23.76	21.65	6.28	1.36

a) Adapted from Varanasi and Malins (1977).

b) Showed unresolved GC peaks, probably includes some olefins.

Table 6.--Water solubility index (WS) of total naphthalenes used in computing BCF in Equation 12 [a].

Hydrocarbon	Water solubility (ppm) [b]
Naphthalene	22.0
1 - Methylnaphthalene	17.23
2 - Methylnaphthalene	16.43
1,5 - Dimethylnaphthalene	1.83
2,3 - Dimethylnaphthalene	1.33
2,6 - Dimethylnaphthalene	.868
Mean	9.949

Mean water solubility index (WS) = 9.949

log (WS) = .9978

log BCF = 2.228 (from Equation 12)

BCF = 170

a) Concept of total naphthalenes taken from Anderson et al., 1977.

b) Estimated to represent water solubility in filtered seawater; i.e., see Table 4.

assumed to be 10% of the total for both scenarios. Although this use of a water solubility index for naphthalenes further underscores the qualitative nature of this analysis, the lack of data available on the specific hydrocarbon composition of each oil spill scenario made a finer analysis impossible and, if attempted, would have contributed little to making the results more precise.

Although the methods used in Equations 10-12 for estimating the parameters k_2 and BCF are approximations, they do lend themselves to addressing many of the difficulties discussed previously. In addition to making use of the best available, if somewhat limited, data, they also circumvent the need to directly address such factors as metabolic rate, fat content, body size, and dietary intake. In addition, although Laevastu and Fukuhara (1984b) have developed a method of relating temperature to depuration rate, the approach taken here avoids the accompanying problem of estimating both species-specific and temperature-specific depuration rates. This seems appropriate given the facts that 1) there is only "about a 25% change in either the (n-octanol/water) partition coefficient or the aqueous solubility for every 1° variation in temperature" (Chiou et al., 1977); and 2) temperature is assumed constant in this analysis (i.e., 9.3°C).

In general, the methods described here, particularly the necessity of using the naphthalenes component of total hydrocarbons as a water solubility index, seem useful as a first order approximation and qualitative measure of "bioaccumulation potential" for the oil concentration data used in this analysis.

2.2 Sensitivity analysis

An important aspect of model evaluation is validation. Since the submodel FEDOIL is the major component of the BIOS model that is used in simulating uptake and depuration, it seemed appropriate to provide information on the validity of

submodel results. Although a model's results normally can be validated by comparison with field data, such an analysis limits the comparison to a specific set of field conditions, which, in the case of oil spill impacts on marine organisms, are usually only available in very broad and qualitative terms. A more general and less restrictive method is a sensitivity analysis where model input parameters are perturbed one at a time and model response to the changes is compared with a base model run which contains best estimates of input parameters. If the input parameters are perturbed within their range of uncertainty, then the sensitivity analysis should give an indication of the amount of uncertainty in model output estimates. The sensitivity analysis can also indicate those particular input parameters that cause the most change in model output, and relatedly, the degree to which model structure (i.e., specific model equations) contribute to model output.

Such a sensitivity analysis was conducted for the submodel FEDOIL. The analysis only considers the non-migration case (i.e., there is no spatial resolution in the submodel FEDOIL), and uses specified external concentration levels (i.e., for both constant and time dependent concentration data) in place of the actual oil spill scenario data used in the larger BIOS model.

The sensitivity analysis involved estimating the absolute error, E, in model input parameters, k_2, BCFPEL, BCFDEM, and FODCMP from a survey of the literature (Table 7). A series of model runs were then made in which each set of parameters were increased and then decreased by the amount of the error. Base parameter values are as given previously. Following the discussion of Livingston (1980), the perturbed value, P_i' of a parameter P_i is given as:

$$P_i' = P_i \ (1 \pm E') \qquad (13)$$

Table 7.--Model input parameters, P_i, and their estimated error, E, used in FEDOIL sensitivity tests [a].

	Parameter - P_i	Error - E
P_1	k_2	± 50%
P_2	BCFPEL	± 50%
P_3	BCFDEM	± 50%
P_4	FODCMP	± 20%

a) Errors estimated from general review of literature.

where E' is the fractional error ($E'=E/100$) of the relevant input parameter. The model output measured for sensitivity to parameter changes was the maximum internal hydrocarbon concentration, C_f, for each species.

The sensitivity of a dependent variable X to a small change in a parameter P_i is usually expressed as:

$$S_i = \frac{\partial X}{\partial P_i} \tag{14}$$

which can be approximated as:

$$S_i = \frac{X_i - X_B}{\Delta P_i} \tag{15}$$

where X_B is the value of the dependent variable X from a base model run and X_i is the value of the dependent variable X when the i^{th} parameter, P_i is perturbed (Livingston 1980).

Following Rivard and Doubleday (1979) and Wiens and Innis (1974), Livingston (1980) uses relative sensitivity, R_i, to denote the change in the dependent variable due to a parameter perturbation. Relative sensitivity relates a percent change in the dependent variable to a percent change in the parameter value and is calculated as:

$$R_i = \frac{\Delta X}{X \cdot E'} = \frac{X_i - X_B}{X_B \cdot E'} \tag{16}$$

or in simpler terms,

$$R_i = \frac{\% \text{ change in dependent variable}}{\% \text{ change in parameter value}} \tag{17}$$

As Livingston (1980) points out, the advantage of a relative sensitivity measurement is that it is less influenced by the orders of magnitude of the dependent variable and the input parameters. The relative sensitivity, R_i, is used to represent the results from the submodel FEDOIL sensitivity tests.

Rivard and Doubleday (1979) describe the following way to interpret relative sensitivity values:

1.) a negative R_i means that a decrease (increase) of the parameter P_i causes an increase (decrease) of the dependent variable X_i;

2.) a positive R_i means that an increase (decrease) of P_i causes an increase (decrease) in X_i;

3.) $R_i = 0$ means that the change in P_i does not affect X_i;

4.) $0 < |R_i| < 1$ the amount of change in P_i causes a lesser amount of change in X_i (i.e., a 10% change in P_i causes a 5% change in X_i);

5.) $|R_i| = 1$ implies that a change in P_i causes a corresponding change in X_i. (The degree of nonlinearity in the model may affect the exactness of this relationship for large parameter changes.)

6.) $|R_i| > 1$ the amount of change in P_i causes a greater amount of change in X_i.

3. RESULTS

3.1 Sensitivity results of submodel FEDOIL

A summary of the relative sensitivity values, R_i, of the submodel output (maximum internal concentration) is given in Tables 8 and 9. The data in Table 8 reflect the case of a constant external concentration of 1 ppm for 10 days, followed by 100% depuration (i.e., organisms assumed in oil free water). Table 9 reflects the case of an initial external concentration of 1 ppm that is decreased exponentially at a rate of approximately 55% per day (Figure 5). The simulation results from the submodel for both concentrations and for various parameter perturbations are illustrated graphically for a semi-demersal species (e.g., Pacific cod) in Figures 6 to 13.

The relative sensitivities, R_i, were generally less than unity for all species studied and independent of the parameter perturbed. The only exceptions were for changes in the bioconcentration factors for pelagic (BCFPEL) and demersal (BCFDEM) species when the species under study were either a 100% pelagic feeder (i.e., Species 1) or a 100% demersal feeder (i.e., Species 14, 15, and 16). In each of these cases the sensitivity of model output was approximately proportional to the changes in the relevant parameter; i.e., $|R_i| = 1$.

The relative sensitivities of changes in the bioconcentration factors (BCFPEL, BCFDEM) and the fraction of pelagic food in the diet (FODCMP) were the same, independent of either the external concentration or the positive or negative perturbation in the given parameter. The specific values varied by species, however, and seem related to their relative pelagic or demersal nature; e.g., the more pelagic (demersal) a species, the greater the relative sensitivity of submodel output given a percentage change in the pelagic (demersal) bioconcentration factor.

Table 8.--Relative sensitivity, R_i, of maximum internal concentration index to parameter perturbations in submodel FEDOIL. (Constant external concentration of 1 ppm.)

	Parameter varied							
	k_2		BCFPEL		BCFDEM		FODCMP	
Species group	-50	+50	-50	+50	-50	+50	-20	+20
Pelagic adults	.681	.352	.990	.990	.010	.010	.792	.208
Semipelagic adults	.681	.352	.682	.682	.318	.318	.545	.545
Flatfish adults	.730	.419	.469	.469	.531	.531	.375	.375
Crab adults	.494	.162	.357	.357	.643	.643	.286	.286
Sessile epifauna	.912	.768	-	-	1.00	1.00	-	-

Table 9.--Relative sensitivity, R_i, of maximum internal concentration index to parameter perturbations in submodel FEDOIL. (Decreasing external concentration starting at 1 ppm.)

Species group	Parameter varied							
	k_2		BCFPEL		BCFDEM		FODCMP	
	-50	+50	-50	+50	-50	+50	-20	+20
Pelagic adults	.835	.670	.990	.990	.010	.010	.792	.208
Semipelagic adults	.835	.670	.682	.682	.318	.318	.545	.545
Flatfish adults	.847	.717	.469	.469	.531	.531	.375	.375
Crab adults	.782	.606	.357	.357	.643	.643	.286	.286
Sessile epifauna	.929	.825	-	-	1.00	1.00	-	-

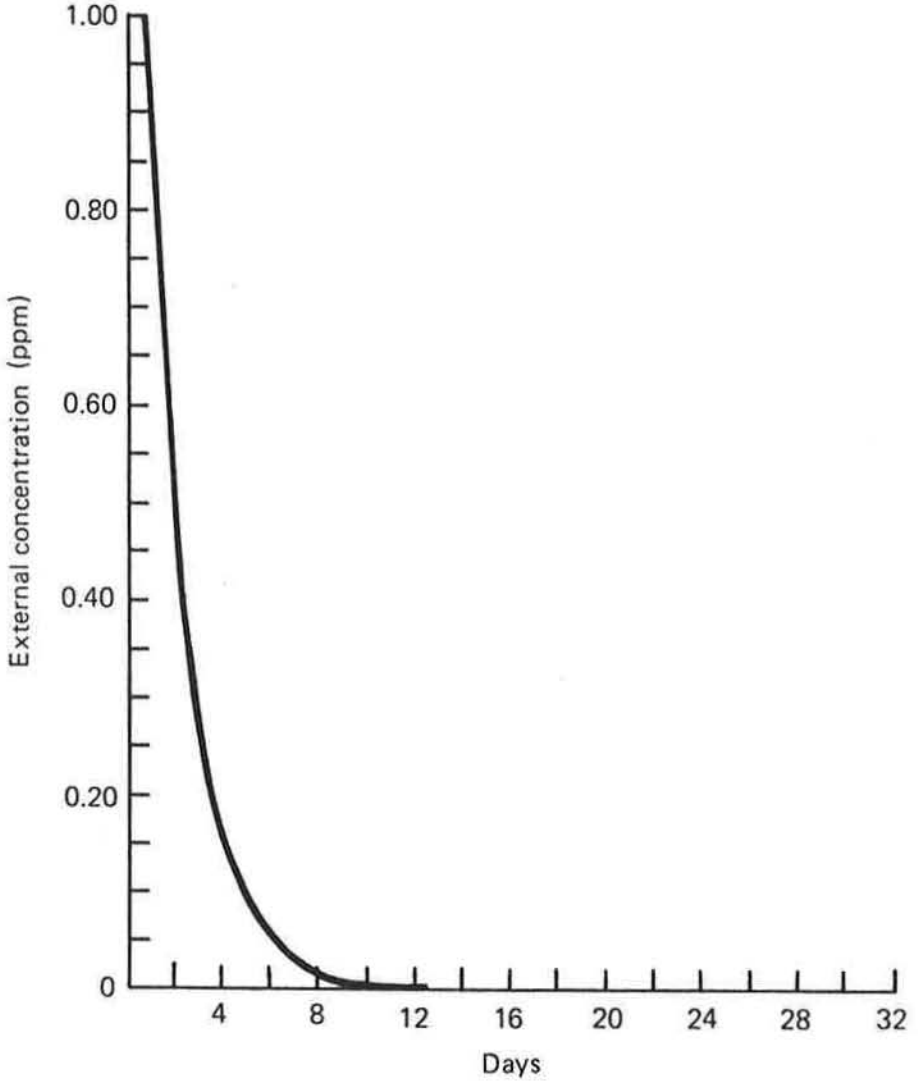


Figure 5.--External concentration (ppm) with time. Data used in sensitivity analysis of submodel FEDOIL.

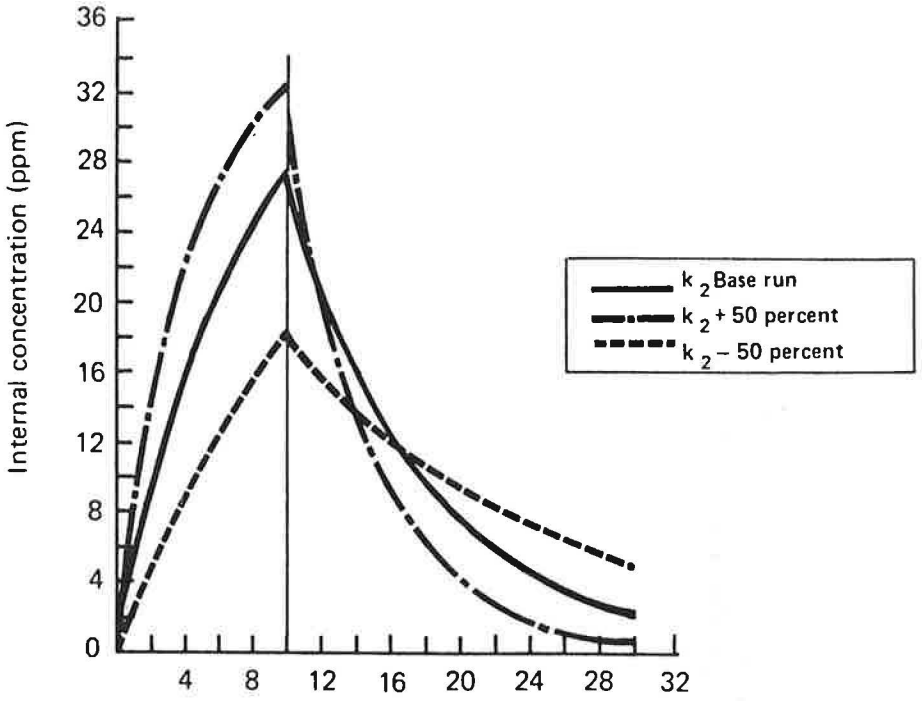


Figure 6.--Variation in internal concentration (ppm) of semi-pelagic species (Species No. 11) given perturbation of model parameter, k_2. External concentration as described in text. The vertical line at day 10 indicates the boundary between uptake and depuration and depuration only.

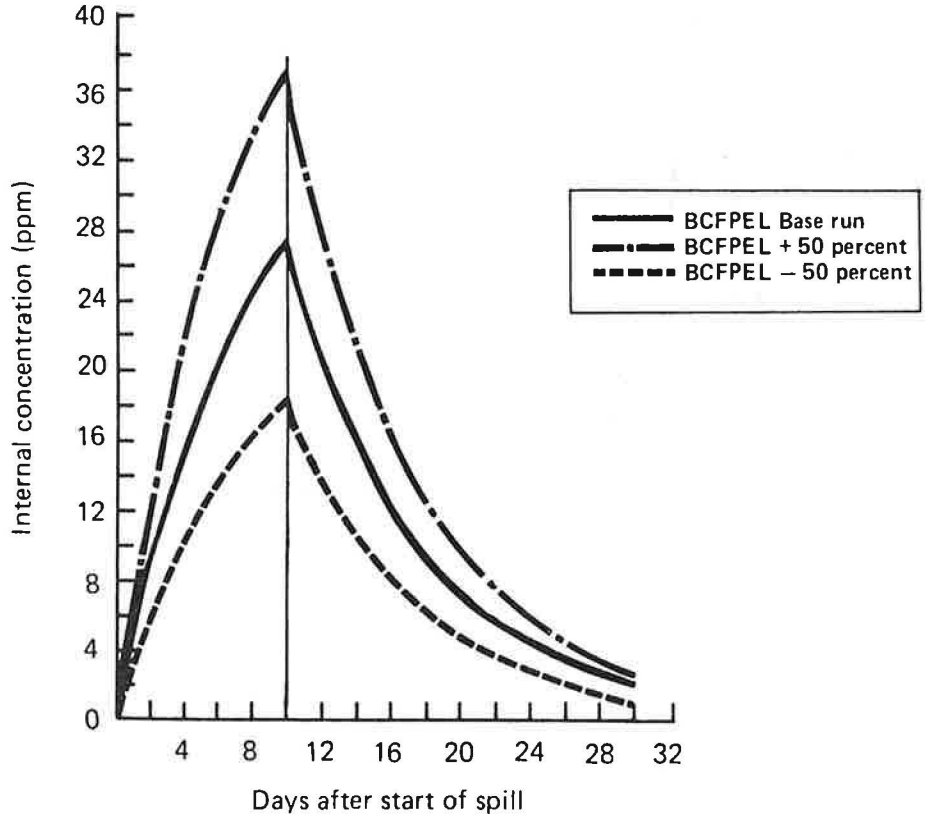


Figure 7.--Variation in internal concentration (ppm) of semi-pelagic species (Species No. 11) given perturbation of model parameter, BCFPEL. External concentration as described in text. The vertical line at day 10 indicates the boundary between uptake and depuration and depuration only.

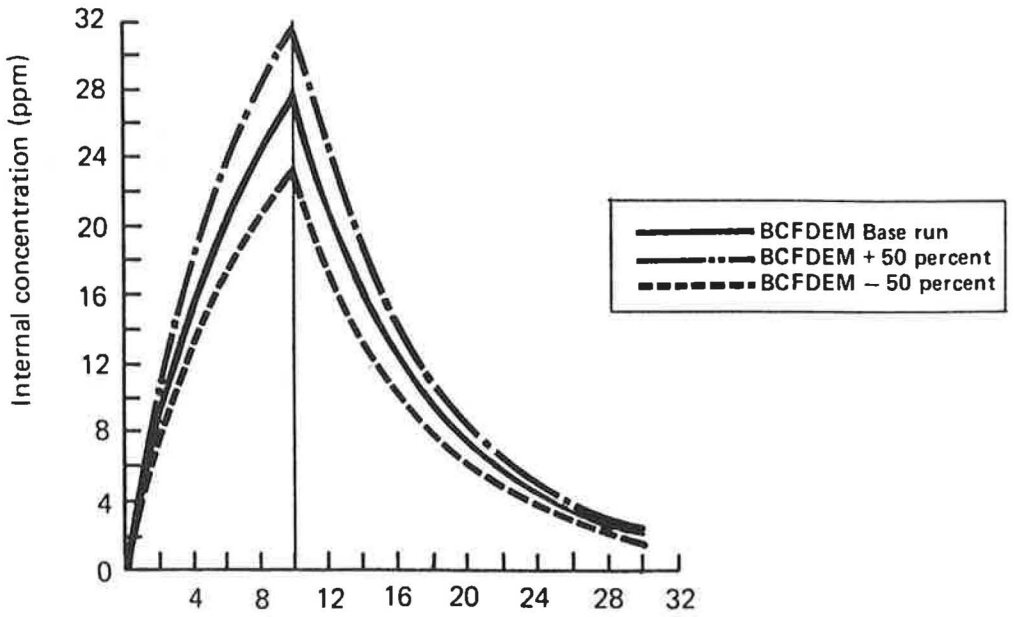


Figure 8.--Variation in internal concentration (ppm) of semi-pelagic species (Species No. 11) given perturbation of model parameter, BCFDEM. External concentration as described in text. The vertical line at day 10 indicates the boundary between uptake and depuration and depuration only.

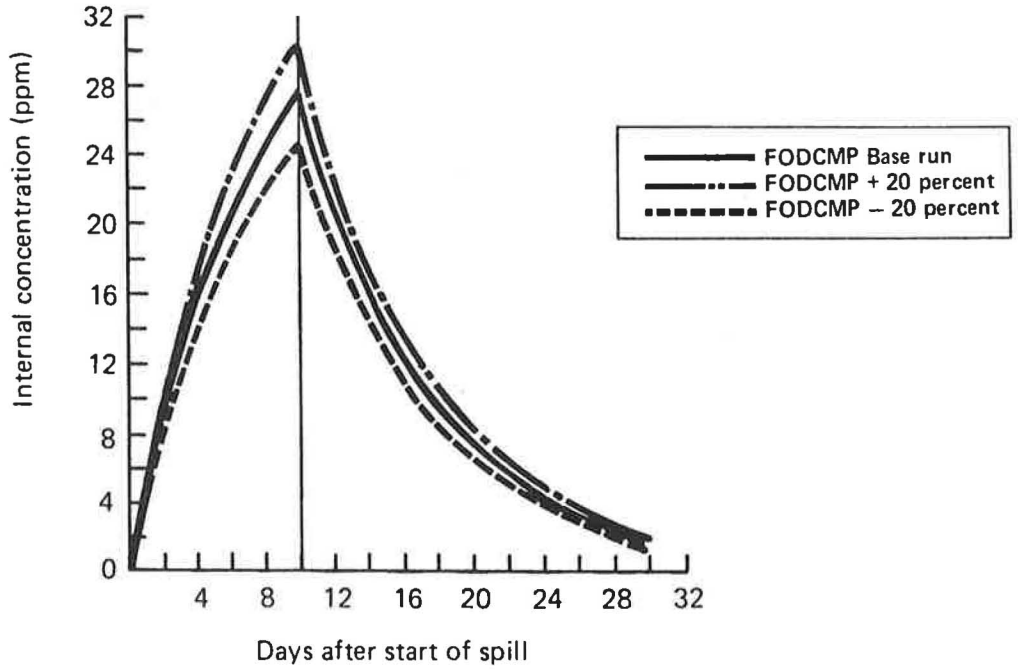


Figure 9.--Variation in internal concentration (ppm) of semi-pelagic species (Species No. 11) given perturbation of model parameter, FODCMP. External concentration as described in text. The vertical line at day 10 indicates the boundary between uptake and depuration and depuration only.

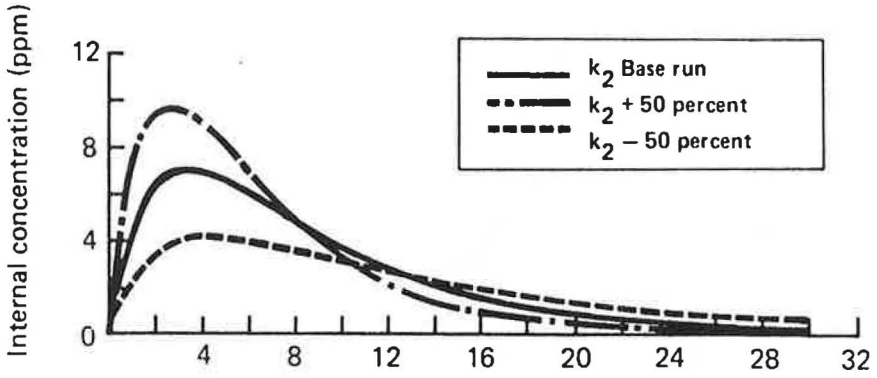


Figure 10.--Variation in internal concentration (ppm) of semi-pelagic species (Species No. 11) given perturbation of model parameter, k_2. External concentration as described in text and shown in Figure 5.

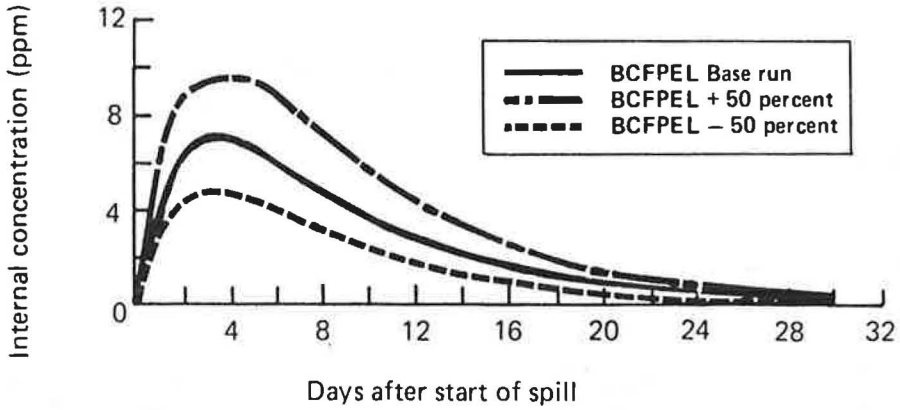


Figure 11.--Variation in internal concentration (ppm) of semi-pelagic species (Species No. 11) given perturbation of model parameter, BCFPEL. External concentration as described in text and shown in Figure 5.

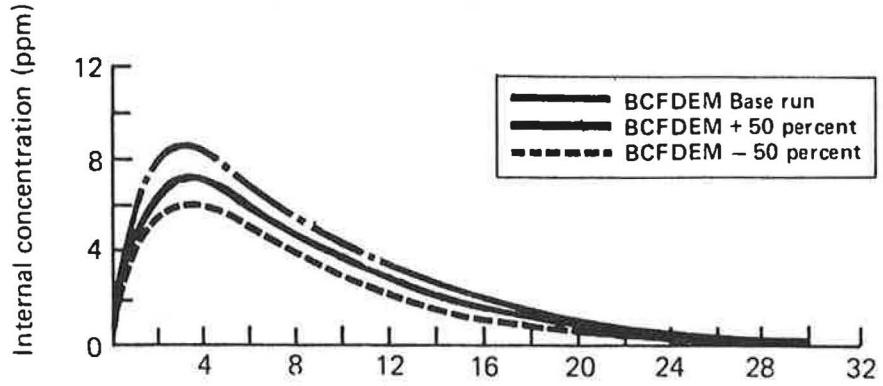


Figure 12.--Variation in internal concentration (ppm) of semi-pelagic species (Species No. 11) given perturbation of model parameter, BCFDEM. External concentration as described in text and shown in Figure 5.

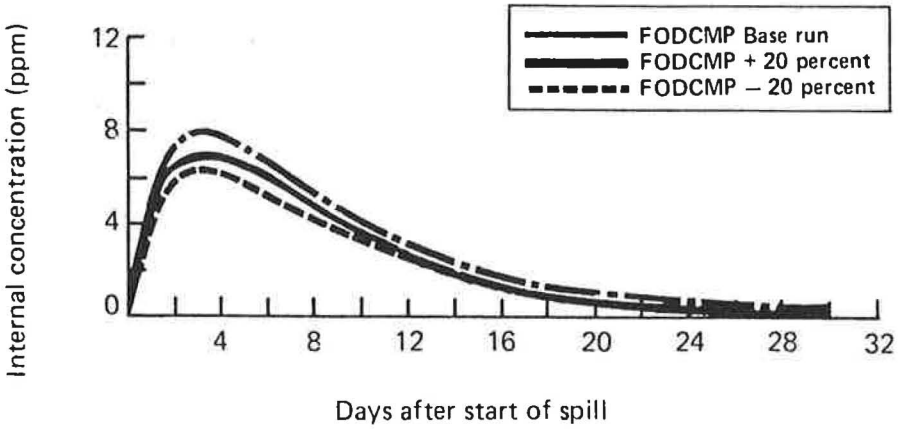


Figure 13.--Variation in internal concentration (ppm) of semi-pelagic species (Species No. 11) given perturbation of model parameter, FODCMP. External concentration as described in text and shown in Figure 5.

Changes in the depuration rate, k_2, produced a mixture of sensitivity results. Although all sensitivity values, $|R_i|$, were less than unity, they varied among species and between external concentration levels, and were dependent on the positive or negative perturbation of the parameter. The greatest effects were on 100% demersal species (e.g., sessile epifauna), independent of external concentration. The results further suggest that species specific sensitivity values following a percentage change in the depuration rate also are related to the relative pelagic or demersal nature of the species. In addition, changes in the depuration rate produced higher $|R_i|$ values for all species for the case of a time dependent (and decreasing) external concentration.

Although the submodel FEDOIL is necessarily qualitative given the limits to the available data and to our knowledge of the uptake and depuration processes, the results of the sensitivity analysis suggest that the submodel is fairly robust with respect to the relative errors associated with the various parameter values. Simulation results of the internal concentrations of five representative species for both the constant and time dependent external concentration data are shown in Figures 14 and 15, respectively.

3.2 Results from BIOS

Time dependent changes in the external concentration data used in this study are illustrated graphically in Figures 16 to 19. These data represent the percentages of the total area at the Pt. Heiden location covered by various levels of the water-soluble fraction (WSF) and oil on the bottom fractions (TARS) of external contamination. Since the external concentration data (WAF) provided by the Rand Corporation were only available for a maximum of 15 days, these data were decreased exponentially at 55% per day from day 10 (accident) and day 15 (blowout), respectively, in order to provide external concentration data to day 30.

In the case of the "blowout scenario", neither the WSF nor the TARS concentrations (Figures 16 and 17) exceeded 1 ppm during the time period of the simulation. Approximately 24 hours following the blowout the WSF concentration (Figure 16)

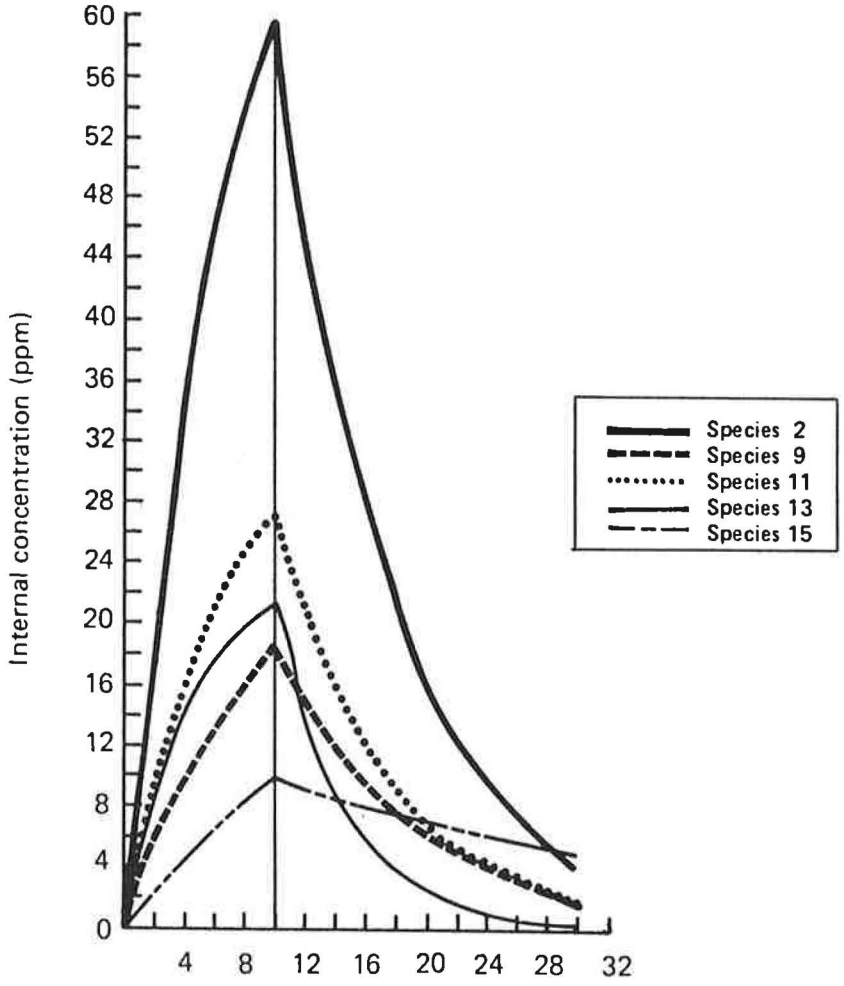


Figure 14.--Variation in internal concentration (ppm) of selected marine species (see text). External concentration as described in text. The vertical line at day 10 indicates the boundary between uptake and depuration and depuration only.

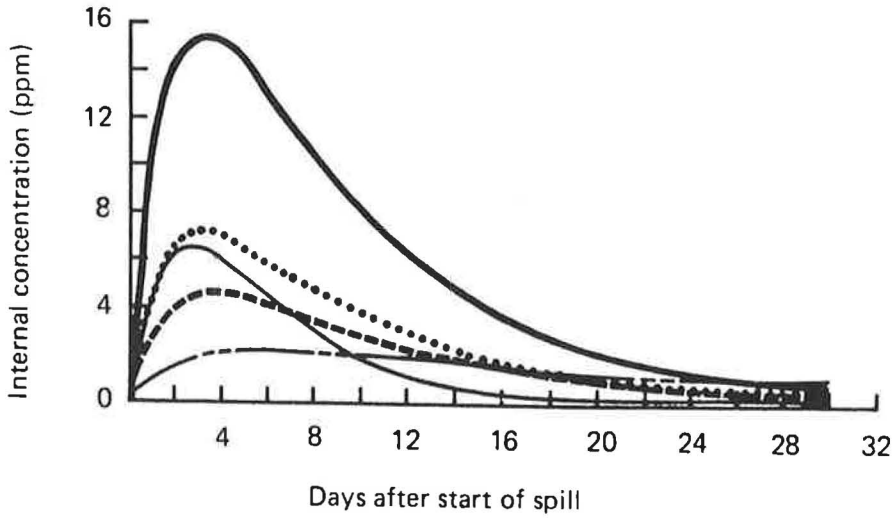


Figure 15.--Variation in internal concentration (ppm) of selected marine species (see text). External concentration as described in text and shown in Figure 5.

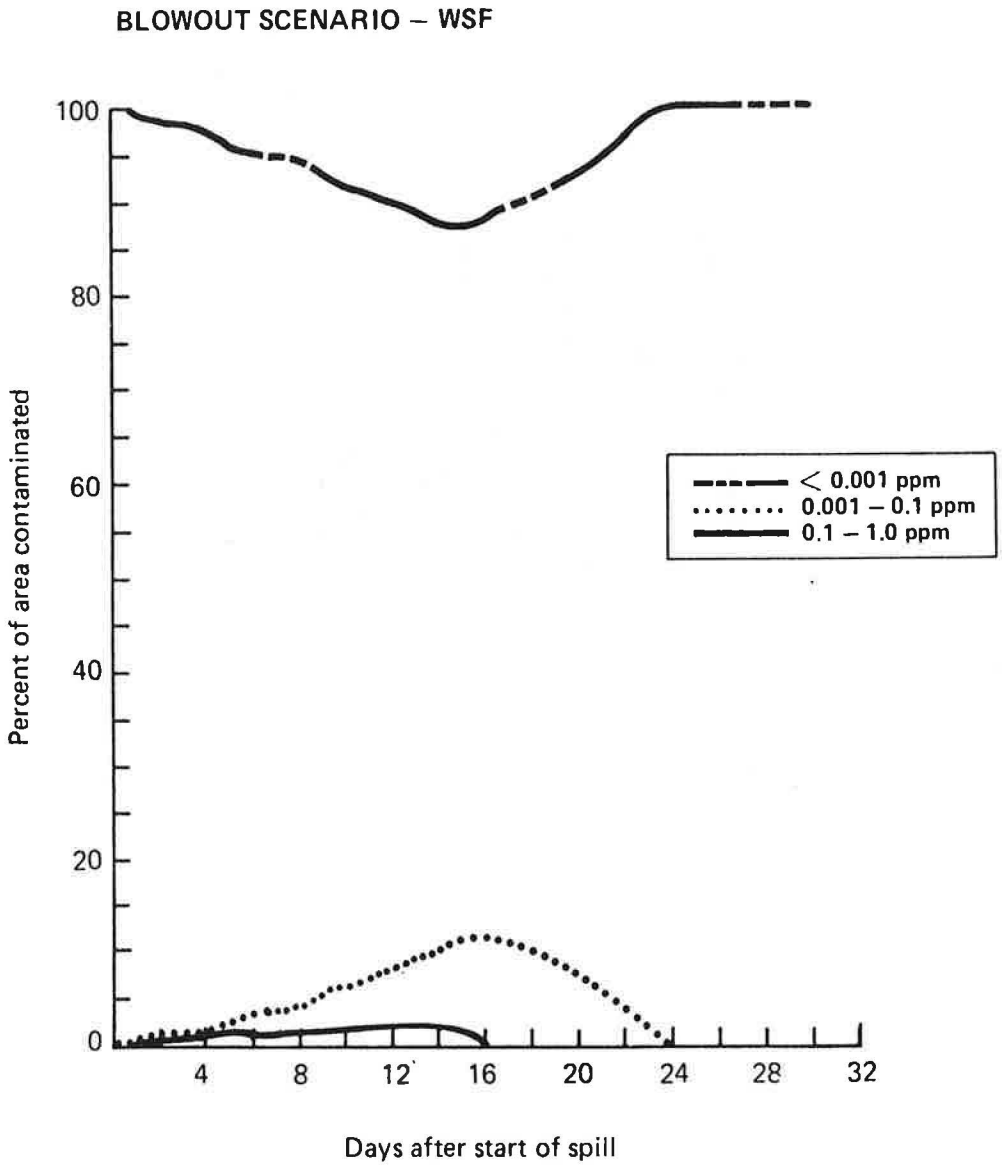


Figure 16.--External concentration of WSF from "blowout scenario" at Pt. Heiden as percent of total area contaminated. Data as used in BIOS model.

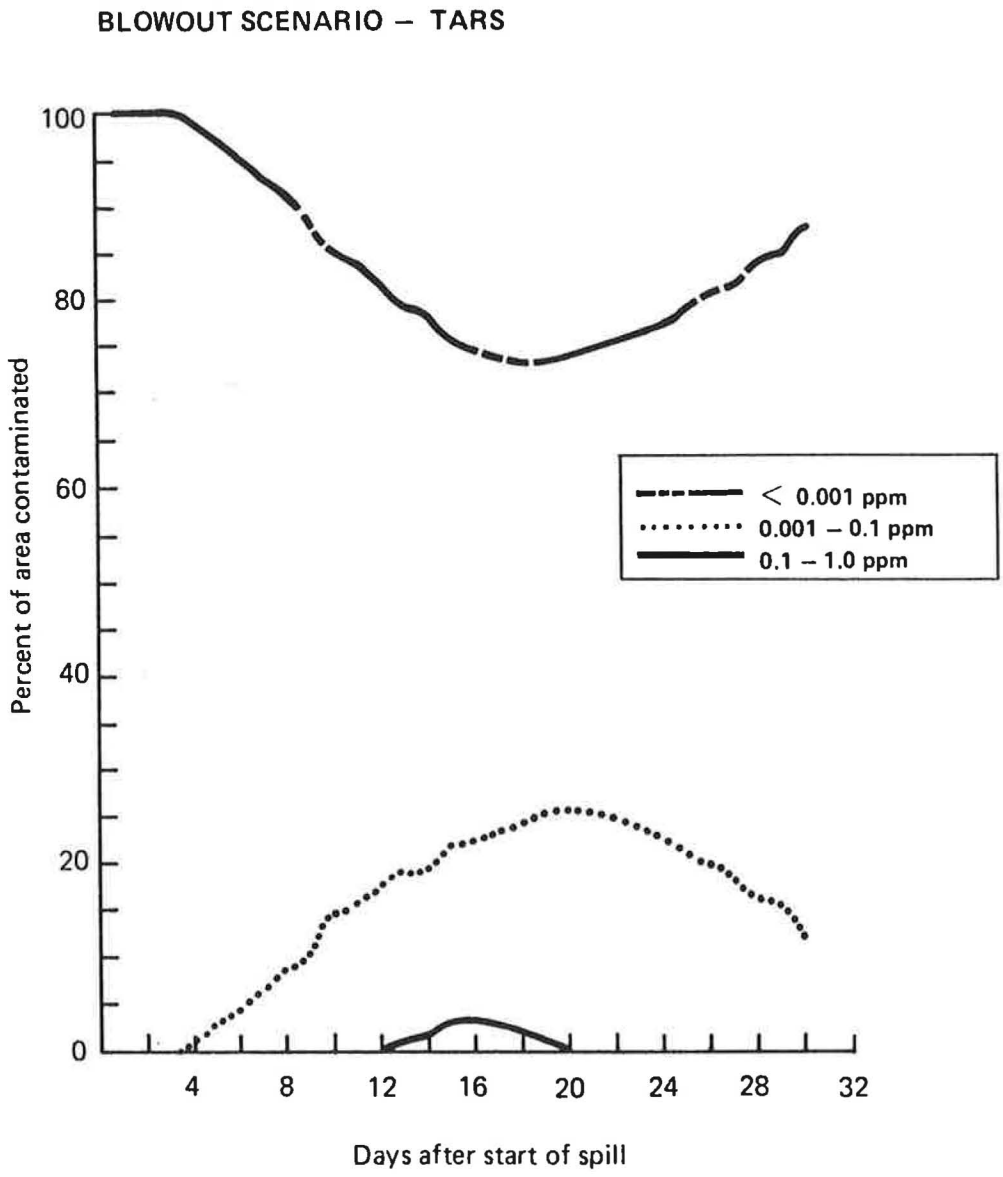


Figure 17.--External concentration of TARS from "blowout scenario" at Pt. Heiden as percent of total area contaminated. Data as used in BIOS model.

is less than .001 ppm over 100% of the spill area. Thirty (30) days after the blowout the TARS concentration (Figure 17) is between .001 and .1 ppm in less than 14% of the spill area.

In the case of the "accident scenario", both WSF and TARS concentrations (Figures 18 and 19) exceeded 5 ppm, although for only 4 days and covering less than 2% of the spill area for the WSF concentration, and for only 12 days and covering less than 5% of the spill area for the TARS concentration. After 23 days the WSF concentration from the accident (Figure 18) is less than .001 ppm over 100% of the spill area, and after 30 days less than 28% of the area has a TARS concentration between .01 and 1 ppm (Figure 19).

These data on the percentage of the total area that is contaminated can be compared to the data on soluble aromatic derivatives (SAD) given in Table 10. to roughly assess the mortality caused by the oil spill scenarios analyzed in this study. The results from the blowout scenario suggest that external concentration data are too low to cause sufficient direct mortalities in either larval or adult life-history stages. The concentrations would be sufficient, however, to disrupt both feeding and reproduction behavior (i.e., effects have been noticed at concentration levels as low as 10-100 ppb; Moore and Dwyer 1974). In addition, since SAD concentrations lower than 0.1-1 ppm may cause sub-lethal toxic effects (Moore and Dwyer 1974), there is a potential for limited but uncertain sub-lethal toxic effects to occur in about 2 to 5% of the available biomasses in the first 20 days following the initial blowout. The effects would, of course, be species specific with demersal species being affected to a greater degree than pelagic species.

The results from the accident scenario suggest the potential for more serious impacts on the marine environment, benthic organisms in particular. As Figure 19

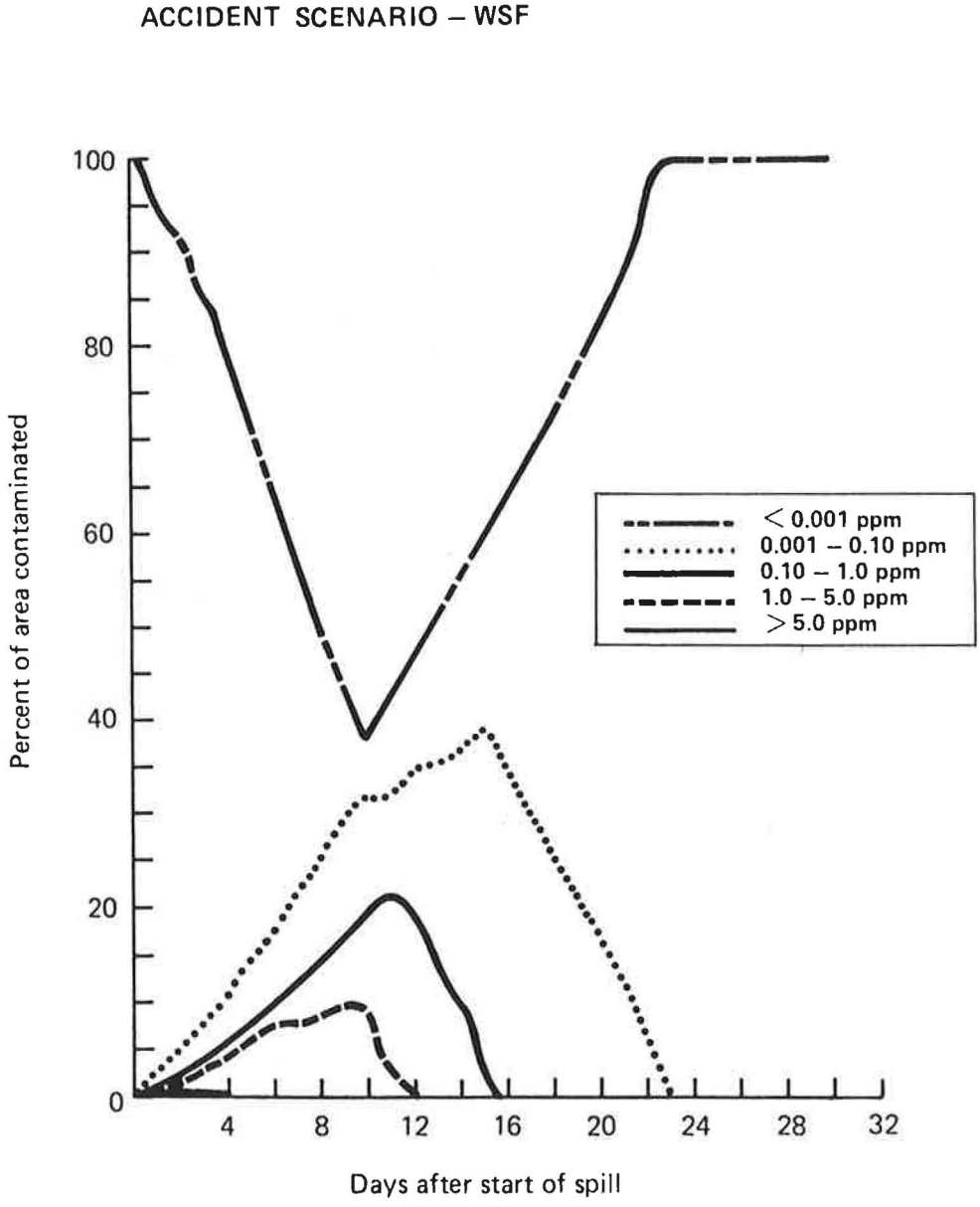


Figure 18.--External concentration of WSF from "accident scenario" at Pt. Heiden as percent of total area contaminated. Data as used in BIOS model.

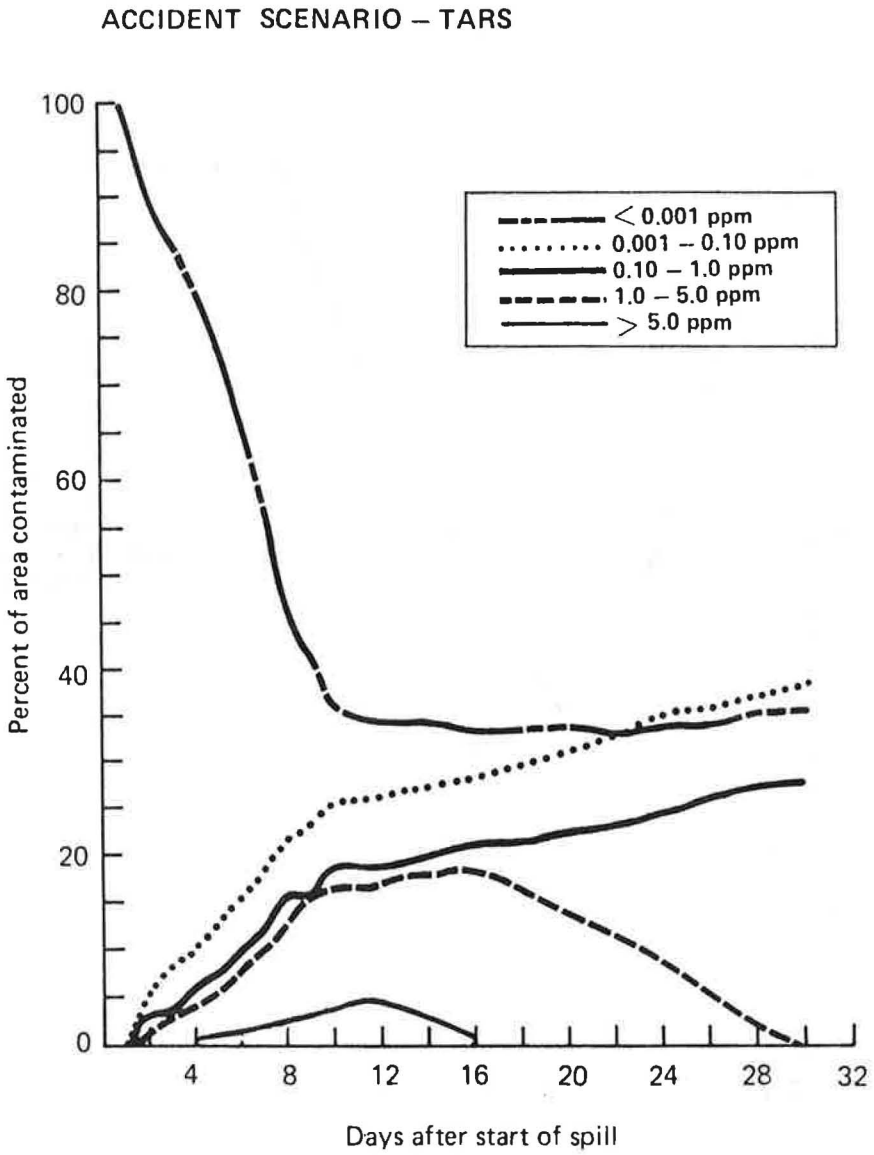


Figure 19.--External concentration of TARS from "accident scenario" at Pt. Heiden as percent of total area contaminated. Data as used in BIOS model.

Table 10.--Summary of toxicity data.[a)]

Class of Organism	Estimated concentrations (ppm) of soluble aromatics causing toxicity
Finfish	5 - 50
Larvae (all species)	0.1 - 1.0
Pelagic crustacens	1 - 10
Bivalves	5 - 50
Benthic crustaceans (e.g., crabs)	1 - 10
Other benthic invertebrates (e.g., worms)	1 - 10

a) Adapted from Moore and Dwyer 1974

illustrates, the external concentrations of TARS are between 1 to 5 ppm for almost 30 days and cover a maximum of approximately 19% of the total area. In addition, the potential for sub-lethal toxic effects and the disruption of feeding and reproduction is also considerably higher in the "accident scenario" than from the "blowout scenario". Since the subject of oil-induced mortalities and their resultant effects on year class strength will be discussed in detail in the final report (Laevastu and Fukuhara, in preparation), the topic will not be considered further in this report. It should be pointed out, however, that the area and species biomasses affected by the oil contamination referred to in this study are only a small fraction of the total area and biomasses of the eastern Bering Sea (see Figure 1 and Table 11).

Figure 20 shows the percentage of the total biomass of 5 representative species that is tainted (internal concentration >5 ppm) from both the blowout and accident scenarios. For the "blowout scenario" only 2 species showed internal concentrations greater than 5 ppm, and then for only a maximum of 2% of the total biomass (e.g., a pelagic species, herring). For the "accident scenario" all species showed tainting, although the maximum percentage of the total biomass tainted did not exceed 30%.

The maximum levels of tainting were reached between 11 and 23 days after the start of the spill (accident scenario). The pelagic species (i.e., herring) was contaminated most quickly (maximum in 11 days) and depurated rapidly from a maximum of 28% of the biomass tainted to less than 11% in 19 days. The slowest uptake was in the benthic invertebrates (i.e., sessile epifauna), with a maximum (less than 28% of the total biomass tainted) reached in approximately 23 days. Depuration (for the benthic invertebrates) is slow and from the data in Figure 20 would appear to be long-lasting.

Table 11.--Species biomass in study areas as percent of total biomass in eastern Bering Sea.[1/]

Species	Species biomass as percent of total biomass (kg) in Eastern Bering Sea		
	Pt. Moller	Pt. Heiden	Cape Newenham
Herring juveniles	.505	.187	.556
Herring adults	.505	.187	.556
Pollock juvenile	.471	.295	.414
Pollock adults	.471	.295	.414
Pacific cod juveniles	.577	.379	.418
Halibut juveniles	1.220	.551	.401
Yellowfin sole juveniles	.902	.602	.888
Other flatfish juveniles	1.141	.838	.939
Yellowfin sole adults	.900	.601	.888
Other flatfish adults	1.141	.838	.939
Pacific cod adults	.577	.309	.456
King and Bairdi crab juveniles	.806	.269	.524
King and Bairdi crab adults	.804	.268	.524
Mobile epifauna	.416	.348	.424
Sessile epifauna	.416	.348	.424
Infauna	.604	.433	.607

1/ Total biomass in eastern Bering Sea taken from DYNUMES model (Laevastu and Larkins 1981).

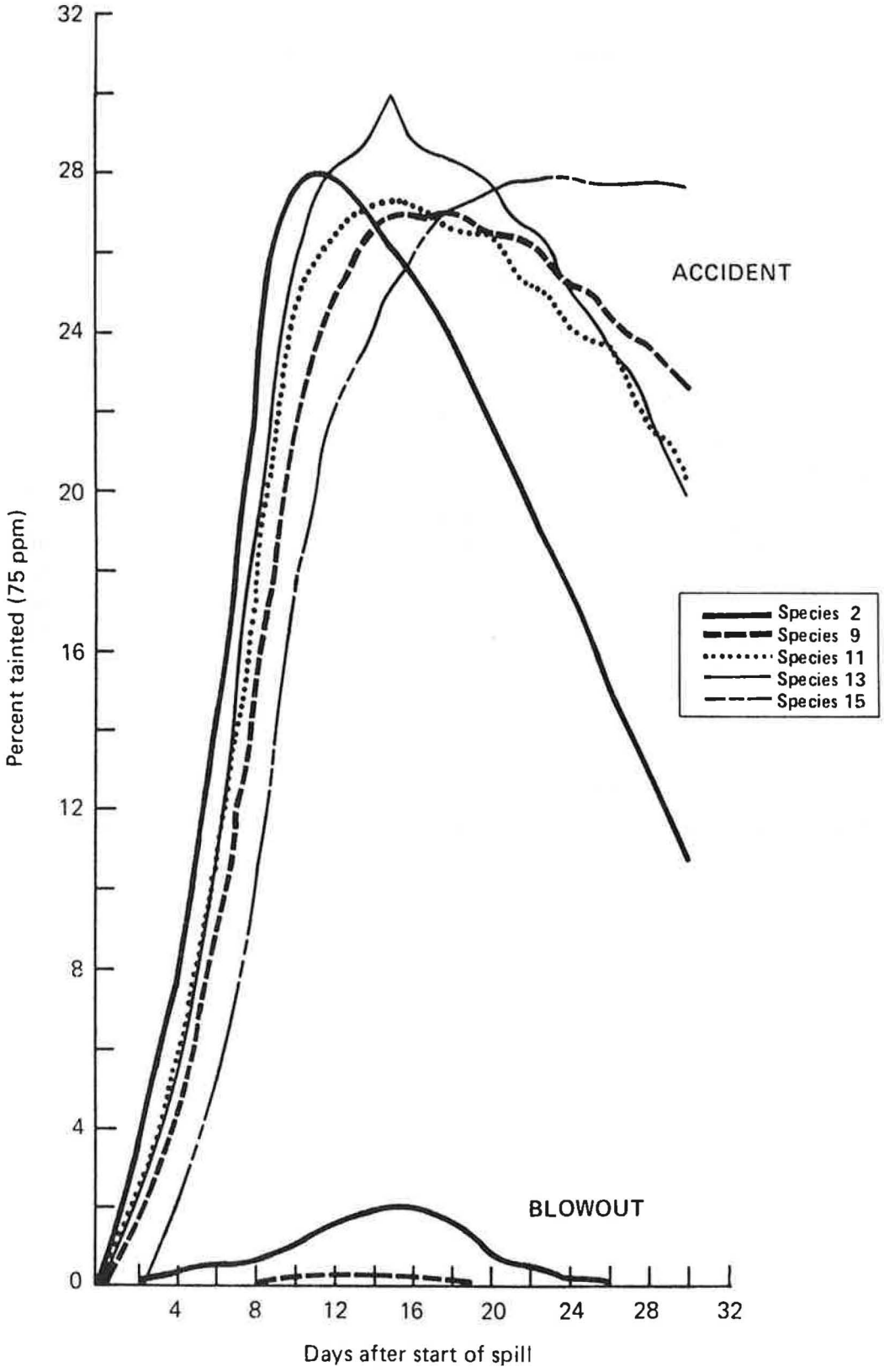


Figure 20.--Percent of biomass tainted (internal concentration >5ppm) for selected marine species at Pt. Heiden. Results from BIOS model for both "blowout" and "accident" scenarios.

As demonstrated previously in the results from the sensitivity analysis (Figures 6 to 13), the percentage of a species' biomass that is tainted appears to be a function of the relative pelagic or demersal nature of the species. In addition, all species, with the exception of benthic invertebrates (i.e., sessile epifauna), depurate rather rapidly within 24 days following the spill, and after 30 days have a maximum percentage biomass tainted of less than 23%.

4. DISCUSSION AND CONCLUSIONS

The submodel FEDOIL proved most sensitive to changes in the depuration rate (k_2), with the absolute value of the relative sensitivity values, $|R_i|$ dependent on the pelagic or demersal nature of the species and the level of external concentration. Since the depuration rate directly determines the amount and retention time of hydrocarbons accumulated (and also indirectly through Equation 5, i.e., an increase (decrease) in the depuration rate k_2 causes a concomitant increase (decrease) in the uptake rate k_1), the relative magnitude of each species group's maximum internal concentration level (i.e., tainting) depends primarily on the submodel's definition of the uptake and depuration processes.

Although all sensitivity values, R_i, were related to the relative pelagic or demersal nature of the species, only changes in the depuration rate showed any direct correlation between relative sensitivity values and the level of external concentration. For example, the relative sensitivity of submodel output to changes in the bioconcentration factors (BCFPEL, BCFDEM) is constant over external concentration values. This suggests that although the external concentration data do determine the type of uptake and depuration curve generated by the model (see Figures 6 and 10), for an individual curve, the bioconcentration values only affect the absolute values of the internal concentration. The actual shape of a specific curve (see Figure 6) is determined almost solely by the depuration rate value, and the larger the rate constant, the sooner any percentage of the asymptotic value (under constant external concentration; see Figure 6) or maximum value (under time-dependent external concentration; see Figure 10) of the submodel is reached. These results not only indicate general model sensitivity but they also highlight how the model structure affects model behavior. As

discussed in Livingston (1980), to evaluate a simulation model as a whole, its structure and behavior should be appraised on the basis of generality, resolution, realism, and precision (Orth 1979).

Generality refers to the applicability of the model to other areas and species communities. The submodel FEDOIL was developed from existing and well accepted approaches that have been used to simulate the uptake and depuration processes. The submodel should be fairly transferable to other marine areas but for each area it would require a careful analysis of the external hydrocarbon concentrations in order to define the hydrocarbon specific bioconcentration factors to be used.

Resolution is defined by the number of characteristics of the real system that are included in the model. The submodel FEDOIL has a low resolution. It does not address multi-species predator-prey behavior, size specific effects of uptake and depuration, temperature effects, or hydrocarbon specific bioconcentration rates. Most of these processes are poorly understood and, in almost all cases, are difficult if not impossible to simulate due to lack of available data. As Livingston (1980) points out, higher resolution does not necessarily produce more accurate results. Higher resolution is clearly needed in this study but full utilization of this model, or any other, as an effective and predictive management tool "will only become possible when laboratory (and field) techniques to measure the critical parameters are formulated" (Hamelink 1977).

Realism is the closeness of the model's equations to the actual biological processes. As discussed previously, the submodel FEDOIL is almost by definition a simplification; no attempt has been made to accurately describe the specific biological processes of uptake and depuration. The model is thus useful as a

conservative and qualitative measure of bioconcentration potential but must await the results of further laboratory studies before it can attempt to simulate the actual biological processes involved; in particular, the disposition of accumulated hydrocarbons.

Precision is the degree of correspondence of model outputs to observed values. There are few specific data values with which to compare submodel results. In a qualitative sense, however, the low levels of contamination and tainting and the relative differences among species in internal concentration levels and retention times of accumulated hydrocarbons are in general agreement with the findings from actual oil spill events (see Laevastu and Fukuhara 1984a, 1984b, for reviews).

Thus the submodel FEDOIL is a general qualitative estimator of internal hydrocarbon concentration potential that has some limited value in assessing the impact of oil spill scenarios on marine species in the eastern Bering Sea. Although its sensitivity to changes in input parameters suggests the model is somewhat robust with respect to the error associated with those parameters, the low resolution of the submodel severely limits its present use as a predictive management tool.

When viewed in conjunction with the full BIOS model, the results from this study indicate that distinct but very limited tainting and mortality effects will result from the accident scenario in the Port Heiden area. Almost no direct effects will occur under the external concentration conditions of the blowout scenario. Although sub-lethal toxic effects could result from either scenario, they are almost impossible to assess quantitatively. Considered in light of available total biomass estimates for the associated stocks in the

eastern Bering Sea, only a small percentage (i.e., less than 2%) of the total species biomasses would be affected directly by the oil spill scenarios analyzed in this study. (This is exclusive of mortality and resultant year class effects, which are considered in detail in the final report.) Finally, the potential impacts from the accident scenario appear to be most pronounced and will be longest lasting in demersal species.

In closing, the limited and qualitative results of this study support the findings of earlier workers who concluded that "relatively little generic information has been generated that can be applied to understanding processes or the dynamics governing petroleum-related perturbations in marine organisms and ecosystems" (Malins and Hodgins 1981). A more detailed quantitative analysis must await the results of future laboratory and field experiments.

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