

Ecological Effects of Produced Water Discharges from Offshore Oil and Gas Production Platforms

**Health and Environmental Sciences
Departmental Report No. DR 94**

PREPARED UNDER CONTRACT BY:

BRIAN S. MIDDLEDITCH
UNIVERSITY OF HOUSTON
HOUSTON, TEXAS

MARCH 1984

**American
Petroleum
Institute**



AVA **Documents**
Document Sharing Hub

FOREWORD

API PUBLICATIONS NECESSARILY ADDRESS PROBLEMS OF A GENERAL NATURE. WITH RESPECT TO PARTICULAR CIRCUMSTANCES, LOCAL, STATE, AND FEDERAL LAWS AND REGULATIONS SHOULD BE REVIEWED.

API IS NOT UNDERTAKING TO MEET THE DUTIES OF EMPLOYERS, MANUFACTURERS, OR SUPPLIERS TO WARN AND PROPERLY TRAIN AND EQUIP THEIR EMPLOYEES, AND OTHERS EXPOSED, CONCERNING HEALTH AND SAFETY RISKS AND PRECAUTIONS, NOR UNDERTAKING THEIR OBLIGATIONS UNDER LOCAL, STATE, OR FEDERAL LAWS.

NOTHING CONTAINED IN ANY API PUBLICATION IS TO BE CONSTRUED AS GRANTING ANY RIGHT, BY IMPLICATION OR OTHERWISE, FOR THE MANUFACTURE, SALE, OR USE OF ANY METHOD, APPARATUS, OR PRODUCT COVERED BY LETTERS PATENT. NEITHER SHOULD ANYTHING CONTAINED IN THE PUBLICATION BE CONSTRUED AS INSURING ANYONE AGAINST LIABILITY FOR INFRINGEMENT OF LETTERS PATENT.

CONTENTS

Contents	i
Tables	vi
Acknowledgements	ix
Executive Summary	xi
1 INTRODUCTION	1
1.1 Background	1
1.2 Scope	2
1.3 Ecological Effects	2
2 COMPOSITION OF PRODUCED WATERS	5
2.1 Summary	5
2.2 Introduction	5
2.3 Hydrocarbons	6
2.3.1 Paraffinic	6
2.3.2 Aromatic	6
2.4 Heavy Metals	8
2.5 Other Ions	10
2.6 Conventional Pollutants	11
2.7 Added Chemicals	12
2.7.1 Biocides	12
2.7.2 Coagulants	15
2.7.3 Corrosion Inhibitors	15
2.7.4 Cleaners	15
2.7.5 Emulsion Breakers and Dispersants	16
2.7.6 Paraffin Control Agents	16
2.7.7 Reverse Emulsion Breakers	16
2.7.8 Scale Inhibitors	16
2.8 Other Substances	16
2.9 Significance	17
2.9.1 Petroleum Hydrocarbons	17
2.9.2 Polynuclear Aromatic Hydrocarbons	20
2.9.3 Heavy Metals	20
3 FATES OF CONTAMINANTS	23
3.1 Summary	23
3.2 Introduction	23
3.3 Physical Fates	24
3.3.1 Evaporation	24
3.3.2 Dispersion Within the Water Column	24
3.3.3 Transport to the Sediments	25
3.3.4 Sediment Resuspension	26
3.4 Chemical Fates	26
3.4.1 Oxidation	26
3.4.2 Hydrolysis	27



Documents

Document Sharing Hub

CONTENTS

3.4.3 Weathering	27
3.5 Biological Fates	27
3.5.1 Bacterial Degradation	27
3.5.2 Macroorganisms	28
3.5.2a Bioaccumulation	29
3.5.2b Biomagnification	36
3.5.2c Excretion/Depuration	39
3.5.2d Metabolism	40
3.6 Significance	40
3.6.1 Mechanisms of Dispersion	41
3.6.2 Maximum Concentrations of Contaminants	42
3.6.3 Coastal Ecosystems	43
3.6.4 Arctic Ecosystems	43
3.6.5 Alternative Disposal Practises	44
4 TOXICITY OF CONTAMINANTS	47
4.1 Summary	47
4.2 Introduction	47
4.3 Hydrocarbons	47
4.3.1 Paraffinic	47
4.3.2 Aromatic	48
4.4 Heavy Metals	48
4.5 Added Chemicals	52
4.6 Other Substances	53
4.7 Produced Water Bioassays	53
4.8 Petroleum Bioassays	54
4.9 Discussion	55
4.9.1 Bioassays	55
4.9.2 Heavy Metal Toxicity	56
4.9.2a Arsenic	56
4.9.2b Cadmium	56
4.9.2c Chromium	56
4.9.2d Cobalt	56
4.9.2e Copper	56
4.9.2f Iron	56
4.9.2g Lead	57
4.9.2h Manganese	57
4.9.2i Mercury	57
4.9.2j Nickel	57
4.9.2k Silver	57
4.9.2l Zinc	57
4.9.3 Contaminants in Sediments	57
5 WATER QUALITY CRITERIA	59
5.1 Summary	59
5.2 Introduction	60
5.2.1 1976 Water Quality Criteria	60
5.2.2 1980 Water Quality Criteria	61
5.3 Discussion	64
5.3.1 Acenaphthene	65
5.3.1a 1976 Criterion	65
5.3.1b 1980 Criterion	65



Documents

Document Sharing Hub

5.3.1c Discussion	65
5.3.1d Conclusion	65
5.3.2 Acrolein	65
5.3.2a 1976 Criterion	65
5.3.2b 1980 Criterion	65
5.3.2c Discussion	66
5.3.2d Conclusion	66
5.3.3 Antimony	66
5.3.3a 1976 Criterion	66
5.3.3b 1980 Criterion	66
5.3.3c Discussion	66
5.3.3d Conclusion	66
5.3.4 Arsenic	67
5.3.4a 1976 Criterion	67
5.3.4b 1980 Criterion	67
5.3.4c Discussion	67
5.3.4d Conclusion	67
5.3.5 Barium	68
5.3.5a 1976 Criterion	68
5.3.5b 1980 Criterion	68
5.3.5c Discussion	68
5.3.5d Conclusion	68
5.3.6 Benzene	68
5.3.6a 1976 Criterion	68
5.3.6b 1980 Criterion	68
5.3.6c Discussion	68
5.3.6d Conclusion	69
5.3.7 Beryllium	69
5.3.7a 1976 Criterion	69
5.3.7b 1980 Criterion	69
5.3.7c Discussion	70
5.3.7d Conclusion	70
5.3.8 Cadmium	70
5.3.8a 1976 Criterion	70
5.3.8b 1980 Criterion	70
5.3.8c Discussion	70
5.3.8d Conclusion	71
5.3.9 Chlorine	71
5.3.9a 1976 Criterion	71
5.3.9b 1980 Criterion	71
5.3.9c Discussion	71
5.3.9d Conclusion	71
5.3.10 Chromium	71
5.3.10a 1976 Criterion	71
5.3.10b 1980 Criterion	71
5.3.10c Discussion	71
5.3.10d Conclusion	72
5.3.11 Copper	72
5.3.11a 1976 Criterion	72
5.3.11b 1980 Criterion	72
5.3.11c Discussion	72
5.3.11d Conclusion	72

CONTENTS

5.3.12	2,4-Dimethylphenol	73
5.3.12a	1976 Criterion	73
5.3.12b	1980 Criterion	73
5.3.12c	Discussion	73
5.3.12d	Conclusion	73
5.3.13	Ethylbenzene	73
5.3.13a	1976 Criterion	73
5.3.13b	1980 Criterion	73
5.3.13c	Discussion	73
5.3.13d	Conclusion	74
5.3.14	Fluoranthene	74
5.3.14a	1976 Criterion	74
5.3.14b	1980 Criterion	74
5.3.14c	Discussion	74
5.3.14d	Conclusion	74
5.3.15	Gases, Total Dissolved	74
5.3.15a	1976 Criterion	74
5.3.15b	1980 Criterion	74
5.3.15c	Discussion	74
5.3.15d	Conclusion	75
5.3.16	Iron	75
5.3.16a	1976 Criterion	75
5.3.16b	1980 Criterion	75
5.3.16c	Discussion	75
5.3.16d	Conclusion	75
5.3.17	Lead	75
5.3.17a	1976 Criterion	75
5.3.17b	1980 Criterion	75
5.3.17c	Discussion	75
5.3.17d	Conclusion	76
5.3.18	Manganese	76
5.3.18a	1976 Criterion	76
5.3.18b	1980 Criterion	76
5.3.18c	Discussion	76
5.3.18d	Conclusion	76
5.3.19	Mercury	76
5.3.19a	1976 Criterion	76
5.3.19b	1980 Criterion	76
5.3.19c	Discussion	76
5.3.19d	Conclusion	77
5.3.20	Naphthalene	77
5.3.20a	1976 Criterion	77
5.3.20b	1980 Criterion	77
5.3.20c	Discussion	77
5.3.20d	Conclusion	77
5.3.21	Nickel	77
5.3.21a	1976 Criterion	77
5.3.21b	1980 Criterion	77
5.3.21c	Discussion	78
5.3.21d	Conclusion	78
5.3.22	Oil and Grease	78
5.3.22a	1976 Criterion	78

5.3.22b	1980 Criterion	78
5.3.22c	Discussion	78
5.3.22d	Conclusion	79
5.3.23	pH	79
5.3.23a	1976 Criterion	79
5.3.23b	1980 Criterion	79
5.3.23c	Discussion	79
5.3.23d	Conclusion	79
5.3.24	Phenol	79
5.3.24a	1976 Criterion	79
5.3.24b	1980 Criterion	79
5.3.24c	Discussion	79
5.3.24d	Conclusion	80
5.3.25	Polynuclear Aromatic Hydrocarbons	80
5.3.25a	1976 Criterion	80
5.3.25b	1980 Criterion	80
5.3.25c	Discussion	80
5.3.25d	Conclusion	81
5.3.26	Selenium	81
5.3.26a	1976 Criterion	81
5.3.26b	1980 Criterion	81
5.3.26c	Discussion	81
5.3.26d	Conclusion	82
5.3.27	Silver	82
5.3.27a	1976 Criterion	82
5.3.27b	1980 Criterion	82
5.3.27c	Discussion	82
5.3.27d	Conclusion	82
5.3.28	Sulfide	83
5.3.28a	1976 Criterion	83
5.3.28b	1980 Criterion	83
5.3.28c	Discussion	83
5.3.28d	Conclusion	83
5.3.29	Thallium	83
5.3.29a	1976 Criterion	83
5.3.29b	1980 Criterion	83
5.3.29c	Discussion	83
5.3.29d	Conclusion	83
5.3.30	Toluene	84
5.3.30a	1976 Criterion	84
5.3.30b	1980 Criterion	84
5.3.30c	Discussion	84
5.3.30d	Conclusion	84
5.3.31	Zinc	84
5.3.31a	1976 Criterion	84
5.3.31b	1980 Criterion	84
5.3.31c	Discussion	85
5.3.31d	Conclusion	85

6 SUBLETHAL EFFECTS OF CONTAMINANTS

6.1 Summary

6.2 Introduction



CONTENTS

6.3 Plankton	87
6.4 Algae	88
6.5 Fouling Organisms	89
6.6 Fish and Benthic Organisms	89
6.7 Man	90
6.8 Sublethal Effects of Petroleum Products	90
6.8.1 Bacteria	90
6.8.2 Algae	91
6.8.3 Fouling Organisms	91
6.8.4 Benthic Organisms	91
6.8.5 Fish	92
6.8.6 Mammals	93
6.9 Significance	93
6.9.1 Cadmium	94
6.9.2 Chromium	94
6.9.3 Copper	94
6.9.4 Lead	94
6.9.5 Mercury	94
6.9.6 Zinc	94
7 ECOSYSTEM EFFECTS	97
7.1 Summary	97
7.2 Introduction	97
7.3 Biofouling Community	97
7.4 Benthic Community	98
7.5 Pelagic Community	98
7.6 Economic Impacts	99
7.7 Significance	101
8 CONCLUSIONS AND RECOMMENDATIONS	103
9 APPENDIX: AREAL STUDIES	105
9.1 Offshore Ecology Investigation	105
9.2 Central Gulf Platform Study	111
9.3 Buccaneer Gas and Oil Field Study	115
10 LITERATURE CITED	125

TABLES

TABLE 1. Mean concentrations (ppm) of aromatic hydrocarbons in produced waters from the Gulf of Mexico	7
TABLE 2. Mean concentrations (ppm) of heavy metals in produced waters from the Gulf of Mexico	9
TABLE 3. Chemicals added to the produced water on platforms surveyed by JACKSON et al. (1981), with additional information provided by the manufacturers of the chemicals	13
TABLE 4. Input of petroleum hydrocarbons into the marine environment. Draft of a tabulation prepared by the National Academy of Sciences, as reported by RUDD (1982)	18
TABLE 5. Estimated input (tons/year) of benzo[a]pyrene into the environment. Adapted from BROWN and WEISS (1978) and BROWN et al. (1980). In comparison, world-wide offshore production activities contribute 0.1 tons/year (see text)	21
TABLE 6. Levels of heavy metals reported in marine organisms. This table represents a summary of data reviewed by REISH et al. (1976, 1977, 1978, 1979, 1980, 1981, 1982), and the reader is referred to those reviews for citations of the original cited literature	31
TABLE 7. Mean concentrations (ppm) of heavy metals in biota associated with Platform 296-B of the Buccaneer Field	37
TABLE 8. Toxicities of heavy metals toward marine organisms. This table represents a summary of data reviewed by REISH et al. (1976, 1977, 1978, 1979, 1981, 1982) and ENVIRONMENTAL PROTECTION AGENCY (1976), and the reader is referred to those reviews for citations of the original literature	49
TABLE 9. Sublethal effects of petroleum and its constituents. This Table represents a summary of data reviewed by REISH et al. (1977, 1978, 1979, 1981, 1982), and the reader is referred to those reviews for citations of the original literature. Concentrations are expressed in ppm.	59

ACKNOWLEDGEMENTS

The preparation of this review was sponsored by the American Petroleum Institute, Environmental Affairs Department. D. Caudle (Conoco), H. Clotworthy (Texaco), C.B. Koons (Exxon), C.D. McAuliffe (Chevron), J.E. O'Reilly (Exxon), and F.T. Weiss (Shell) were members of the committee established to monitor this program and J.R. Gould provided API technical and administrative support. They each provided constructive criticism of drafts of the review and invaluable assistance in locating and obtaining copies of some of the articles cited.

Additional information and advice were generously provided by S.G. Appan (Gulf Universities Research Consortium), C.A. Bedinger, Jr. (Southwest Research Institute), C.W. Caillouet (National Marine Fisheries Service), B.J. Gallaway (LGL Ecological Research Associates), J.L. Gumnick (Gulf Universities Research Consortium), E.S. Littmann (Nalco Chemical Corporation), and S. Toscano (Tretolite Division of Petrolite Corporation).

EXECUTIVE SUMMARY

The literature pertaining to the composition of produced waters and the fates and effects of these effluents in the marine environment has been reviewed. Discussions of lethal and sub-lethal effects have been complemented by considerations of data relating to crude oils, petroleum products, and individual constituents.

Two distinct strategies have been employed in attempts at discerning the ecological effects of produced water discharges: predictive and observational.

The predictive approach involves determining the composition of the effluents and considering the toxicities of individual components in an attempt to deduce the overall toxicity of the effluent. Its advantage is that it is not site-specific, but our current level of knowledge concerning the factors which control the dispersion and degradation of contaminants is barely sufficient to permit us to derive assessments with any great degree of reliability. Data which have accumulated during the course of laboratory bioassays and analyses of produced water samples support the following conclusions:

(1) There is little basis for concern with hydrocarbons at concentrations found in undiluted produced waters. Levels of most toxic substances in undiluted produced water are below their individual 96-hour LC₅₀ concentrations. Thus, toxic levels of hydrocarbons should not be encountered in the water column beyond the immediate vicinity of the mixing zone.

(2) All of the Environmental Protection Agency's 1976 and 1980 'Water Quality Criteria' are met by the receiving waters beyond the mixing zones surrounding produced water outfalls.

(3) Concentrations of individual constituents of produced waters found to be responsible for sublethal effects during laboratory experiments are unlikely to be encountered in the vicinity of offshore production platforms beyond the mixing zones surrounding the outfall pipes.

(4) It is suspected that the small degree of toxicity of produced waters can largely be attributed to the biocides added to it on the production platform, but more detailed studies are required to test this hypothesis.

(5) The input to the oceans of hydrocarbons from produced waters is very low in comparison with other sources, even in regions

EXECUTIVE SUMMARY

such as the Louisiana continental shelf of the Gulf of Mexico (because the Mississippi River is, coincidentally, a major contributor of environmental hydrocarbons).

(6) Likewise, the quantities of heavy metals in produced waters are small in comparison with riverine inputs to the oceans.

(7) The quantity of benzo[a]pyrene discharged from offshore production platforms is extremely low in comparison with other sources of this carcinogen.

(8) There is every indication that contaminants from the produced water are diluted and dispersed rapidly in the vicinity of offshore platforms. It is reasonable to assume that dispersion will be low under quiescent hydrological and meteorological conditions and that sedimentation will be more efficient in shallower waters, but there is a paucity of experimental data to test this hypothesis.

The observational approach should provide direct and unequivocal information relating to 'real-world' effects, but conclusions are site-specific and it is virtually impossible in many instances to distinguish among effects attributable to produced water discharges, other contaminants with anthropogenic sources, and natural ecosystem perturbations. Field studies have shown that:

(1) Visible damage to the biofouling community is restricted to a vertical difference of about 1 meter and a horizontal distance of less than 10 meters from the point of entry of produced waters into surface waters.

(2) There is no unequivocal evidence for effects of produced waters upon pelagic communities, and suggestions that petroleum production activities are responsible for reduced shrimp and red snapper catches are not sustained upon critical examination of the data.

(3) There is no evidence for permanent sedimentary contamination in the region of oil fields in the Gulf of Mexico due to produced waters.

(4) Benthic communities may be suppressed in the immediate vicinity of production platforms in shallow coastal waters, but not around offshore platforms in deeper waters.

(5) Ecological damage attributed to oil spills is very different in nature to the effects of chronic, low-level discharges of produced waters.

EXECUTIVE SUMMARY

At the current time it is necessary to combine both the predictive approach and the observational approach in formulating conclusions relating to ecological effects of effluents from production platforms. We can conclude with a high degree of confidence that current practises for the disposal of produced waters are ecologically sound. It is possible, however, that refined analyses of extant data will reveal effects which are masked by natural ecosystem perturbations. It would be desirable for future studies to focus upon direct measurements of toxic effects in the field.

1 INTRODUCTION

1.1 BACKGROUND

Subterranean oil and gas reservoirs are frequently associated with accumulations of brine. This 'formation water' is generally separated from the oil and gas on a production platform and discharged into the sea. The 'produced water' effluent contains some petroleum components, along with any chemicals which might have been added to the product stream on the production platform. This report summarizes our current knowledge of the composition of produced waters and their effects upon the marine environment. It does not address other potential impacts of offshore production activities.

The acute effects of oil spills at sea are readily apparent and well documented (NELSON-SMITH, 1973; CANONNE, 1976; WOLFE, 1977; PETRAKIS and WEISS, 1980). The chronic effects of continual discharge of produced waters, however, are somewhat enigmatic since the amounts of oil in effluents from production platforms are usually sufficiently low that no sheen appears at the air/sea interface. Accordingly, Koons and co-workers failed to find any documented evidence of ecological effects resulting from the discharge of produced waters from offshore platforms (KOONS et al., 1975, 1976, 1977; WEISS et al., 1977). Similarly, GALLAWAY (1981) recently concluded (after participating in two major studies in the Gulf of Mexico: the Buccaneer Gas and Oil Field Study and the Central Gulf Platform Study) that effects of any aspects of oil production were very limited. A comprehensive review of offshore oil and gas activities by MENZIE (1982) also concluded that most effects were minor and localized.

During the past decade, advances in the field of analytical chemistry have allowed us to discern the individual toxic constituents of produced waters, and there have been several intensive studies of their effects upon the environment. In most instances, however, the data resulting from such studies have merely been catalogued, with no attempt made to provide a critical assessment. Any evaluation of data from the various studies is complicated by the complexity and difficulty encountered in analyzing high brine content waters for toxic pollutants which occur in such small concentrations. It is extremely difficult to achieve repeatability of pollutant concentration determinations, not only between laboratories, but also in the same laboratory.

INTRODUCTION

1.2 SCOPE

Oil production in coastal waters dates from the 1890's, when wells were drilled from wharves extending into the Santa Barbara Channel. By the 1920's, floating platforms were being used in the marshlands, bayous, and lakes bordering the Gulf of Mexico, and in Lake Maracaibo, Venezuela. The first successful offshore well, twelve miles off the Louisiana coast, was drilled during 1947 (MANNERS, 1982).

Offshore oil now accounts for more than 24% of the world's total production. Saudi Arabia is, by far, the leading producer of offshore oil, accounting for 22.0% of the total offshore oil in 1981. Other major producers of offshore oil include the United Kingdom (13.2%), Mexico (8.1%), and - in fourth place - the United States (7.8%). Another 32 countries account for the remaining 48.9% of offshore production (ANONYMOUS, 1982a).

The distribution of research effort directed toward discovering and mitigating the ecological effects of offshore activities is significantly different. Almost all of the research in this field has been conducted in the Gulf of Mexico, off the coasts of Louisiana and Texas.

1.3 ECOLOGICAL EFFECTS

Two distinct strategies have been employed in attempts at discerning the ecological effects of produced water discharges: predictive and observational.

The predictive approach involves determining the composition of the effluents and considering the toxicities of individual components in an attempt to deduce the overall toxicity of the effluent. Such studies may be supplemented by information gleaned from bioassay experiments with samples of the effluents. Toxicity data are then related to the distribution of the contaminants in the environment, and predictions of ecological effects can be made. The advantage of this approach is that it is not site-specific. It should be possible to make predictions of environmental impact with a knowledge of the composition of the effluents along with hydrographic and meteorological data. Unfortunately, our current level of knowledge concerning the factors which control the dispersion and degradation of contaminants is barely sufficient to permit us to derive assessments with any great degree of reliability. Moreover, we have only limited information on the toxicities of either the effluents or their individual constituents.

No understanding of the mechanisms by which impacts are exerted is needed if one uses the observational Assessments are based upon actual measurements of impacts. This

approach should provide direct and unequivocal information relating to 'real-world' effects. The major disadvantages are that conclusions are site-specific and that it is virtually impossible in many instances to distinguish between effects attributable to produced water discharges, other anthropogenic sources, and natural ecosystem perturbations.

At the current time it is necessary to combine both approaches in formulating conclusions relating to ecological effects of effluents from production platforms. In this report, each approach is considered in turn and conclusions are based upon an overall assessment of the extant data.

2 COMPOSITION OF PRODUCED WATERS

2.1 SUMMARY

Produced waters contain as much as 50 ppm of petroleum components. Detailed analyses have been performed on relatively few effluent samples but, generally, the volatile and liquid hydrocarbons (especially benzene, toluene, ethylbenzene, and the xylenes) are present in higher concentrations than the heavier components. The input to the oceans of petroleum from produced waters is very low in comparison with other sources, even in regions such as the Louisiana continental shelf of the Gulf of Mexico (because the Mississippi River is, coincidentally, a major contributor of petroleum hydrocarbons). The quantity of polynuclear aromatic compounds (PNA's), including benzo[a]pyrene, discharged from offshore production platforms is extremely low in comparison with other sources of these materials. Levels of heavy metals in produced waters are generally not much higher than those found in seawater. Produced waters can also contain biocides and other water-treatment chemicals in relatively low concentration.

2.2 INTRODUCTION

It is convenient to consider produced waters as petroleum-containing effluents. They do indeed contain droplets of oily material, and petroleum components are also found in solution. The use of modern chemical techniques has, however, revealed that the petroleum components in produced waters are markedly different from those found in the associated crude oil. Moreover, formation water is treated on the platform to reduce its petroleum content (BERRY and ENGEL, 1969; WYER et al., 1975; ANONYMOUS, 1977), and a variety of chemicals may be added to the product stream during the process. Thus, the petroleum components in the discharged produced water may be different in composition from the petroleum components found in the formation water and significantly different from that of the associated crude oil.

Any reasonable prediction of the effects of produced water discharges leans very heavily upon reliable estimates of the composition of these effluents. Most investigators have emphasized the hydrocarbon and/or heavy metal content of the effluents, but additional information is becoming available on other constituents.

2.3 HYDROCARBONS

The heavier saturated hydrocarbons (alkanes and cycloalkanes from C_{10} through C_{40}) can be determined with relative ease by gas chromatography, so it follows that there are ample data for these hydrocarbons. The lighter saturated hydrocarbons, by virtue of their volatility, present greater problems for the analyst but they are still amenable to analysis by gas chromatography. For the aromatic hydrocarbons, however, the use of mass spectrometry is desirable to obtain unambiguous identifications of all but the simplest of these hydrocarbons. Accordingly, the data on the lighter saturates and the aromatic hydrocarbons are somewhat less abundant.

2.3.1 Paraffinic

At the Buccaneer Field, methane concentrations in produced water were 0.63-3.2 ppm, C_2 - C_5 saturate concentrations were 0.64-3.7 ppm, and C_5 - C_{14} saturate concentrations were 0.42-5.1 ppm (WIESENBURG et al., 1981, 1982). The mean concentration of the heavier saturates (C_{12} - C_{38}) was 3.4 ppm, and concentrations as high as 12 ppm were sometimes observed (MIDDLEITCH, 1981b).

The mode of sample collection and storage can have a significant effect upon the accuracy of quantitative analyses, particularly with the lighter hydrocarbons (BROOKS et al., 1977).

The use of isotope-labeled internal standards (MIDDLEITCH and BASILE, 1976) has improved the precision of analyses of the heavier alkanes. The accuracy of such analyses may still be compromised by adsorption of hydrocarbons onto the internal surfaces of sampling containers, but this effect can be minimized if the initial solvent extraction is conducted in the sampling container itself.

Participants in the Buccaneer study were well aware of these potential pitfalls and took steps to counter them. It seems probable, therefore, that the data obtained for paraffinic hydrocarbons during this study are reliable (MIDDLEITCH and BASILE, 1976; BROOKS et al., 1977).

2.3.2 Aromatic

Data for aromatic hydrocarbons obtained in three studies are summarized in TABLE 1. Given the high degree of variability in hydrocarbon concentrations with time at any single platform, the mean concentrations of benzene and toluene determined during the three studies are comparable.

TABLE 1. Mean concentrations (ppm) of aromatic hydrocarbons in produced waters from the Gulf of Mexico.

Study	Buccaneer	Buccaneer	Lysyj	Radian
Reference	A	B	C	D
Benzene	9.5		0.84	3.5
Toluene	4.6		2.1	2.4
m/p-Xylenes	1.0			
o-Xylene	0.99			
Naphthalene			0.03	0.15
Anthracene			0.01	
Methylnaphthalenes		0.043		
Benzo[a]pyrene		0.0012		

References: A, BROOKS et al. (1980b); B, MIDDLEITCH (1981b); C, LYSYJ (1981); D, RADIAN CORPORATION (1982)

Quantitative data for light aromatic hydrocarbons in four samples of produced water from Platform 296-B of the Buccaneer Field are available. Benzene, toluene, ethylbenzene, and the xylenes (collectively known as 'BTX') were found in concentrations of 10-31 ppm. Of this total, benzene accounted for 5.6-18 ppm (mean, 9.5 ppm), toluene accounted for 2.6-8.5 ppm (mean, 4.6 ppm), ethylbenzene accounted for 0.22-1.1 ppm (mean, 0.53 ppm), and the xylenes accounted for 0.98-3.7 ppm (mean, 2.7 ppm) (WIESENBERG et al., 1981, 1982). Many additional light aromatic hydrocarbons were also identified (MIDDLEITCH, 1981b, 1982).

At five platforms in the Gulf of Mexico, LYSYJ (1981) found that concentrations of benzene ranged from 0.17 to 1.9 ppm (mean, 0.84 ppm), toluene ranged from 0.77 to 3.3 ppm (mean, 2.07 ppm), and ethylbenzene ranged from 0.042 to 0.20 ppm (mean, 0.10 ppm). Naphthalene was found at concentrations of 0.012 to 0.044 ppm at three of the five platforms, while anthracene and/or phenanthrene were found at a concentration of 0.015 ppm at only one of the platforms. The detection limit of the technique used was 0.01 ppm.

COMPOSITION OF PRODUCED WATERS

More recently, RADIAN CORPORATION (1982) examined produced waters from six platforms in the Gulf of Mexico. Concentrations of aromatic hydrocarbons were: benzene, 0.17-16 ppm (mean, 3.5 ppm); toluene, 0.15-8.6 ppm (mean, 2.4 ppm); ethylbenzene, 0.027-0.56 ppm (mean, 0.23 ppm); and naphthalene, 0.017-0.44 ppm (mean, 0.15 ppm).

A matter of particular concern among ecologists has been the aromatic hydrocarbon content of produced waters. A widely-studied polynuclear aromatic hydrocarbon is benzo[a]pyrene (BROWN and WEISS, 1978; BROWN et al., 1980). Benzo[a]pyrene, a known carcinogen, was not detected during the study of produced waters conducted by RADIAN CORPORATION (1982). The detection limit was not specifically mentioned in the report, but it was probably 10 ppb [some aromatic hydrocarbons are reported as being 'detected' at concentrations below 10 ppb, but actual concentrations are given only when they are greater than this value]. Data from the Buccaneer Gas study indicate that produced waters have a mean benzo[a]pyrene content of 1.2 ppb (MIDDLEITCH, 1981b). These values may appear to be rather high if one considers that a typical crude oil contains 2 ppm of benzo[a]pyrene (WARNER, 1978) and that produced waters contain a maximum of 50 ppm of oil; on this basis, the produced water should contain no more than 0.1 ppb of benzo[a]pyrene. One possible explanation for the higher values actually found is that the produced water is not a homogeneous material: it likely contains minute droplets of oil, so one sample containing a disproportionate amount of oil droplets could exhibit an elevated concentration of hydrocarbons.

Attention has also focused on the two-ring aromatic hydrocarbons - naphthalene and the alkylnaphthalenes - since they are relatively water-soluble and moderately toxic (ARMSTRONG et al., 1977). During the Buccaneer study, the mean concentration of methylnaphthalenes measured in produced waters was 43 ppb, and a maximum concentration of 170 ppb was encountered (MIDDLEITCH, 1981b).

2.4 HEAVY METALS

Reported concentrations of heavy metals in produced water samples collected during three major studies are summarized in TABLE 2. The data reported by TILLERY (1980a,b) are somewhat confusing. Typographical errors have resulted in the interchangeable use of the terms ppb and ppm. It is believed that the data presented in TABLE 2 are correct, although many of the values are very much lower than detection limits reported by other laboratories. In a study not included in TABLE 2, JACKSON et al. (1981) found that mean barium and iron levels were 360 and 11 ppm, respectively, in ten produced water samples from platforms off the Louisiana coast.

COMPOSITION OF PRODUCED WATERS

TABLE 2. Mean concentrations (ppm) of heavy metals in produced waters from the Gulf of Mexico.

Study	Buccaneer	Buccaneer	Buccaneer	Lysyj	Radian
Reference	A	B	C	D	E
Antimony		0.000061		ND	
Arsenic		0.00032		ND	
Barium	3.5	0.0064	1.3		
Beryllium		0.00025		0.0016	
Cadmium	ND	0.001	0.000057	0.029	0.004
Chromium	ND	0.00092	0.00083	0.26	0.014
Cobalt	ND		ND		
Copper	ND	0.0016	0.00055	0.075	ND
Iron	10	2.9	0.26		
Lead	0.5	0.00078	0.0012	0.6	0.30
Manganese	ND	0.0043	0.00084		
Mercury	ND	0.00016	0.00019	0.00008	
Nickel	0.5	0.00073	0.00035	0.96	0.09
Silver		0.000028		0.066	ND
Strontium	34	0.230	71		
Thallium		0.00033		ND	
Zinc	ND	0.61	0.015	0.28	0.098

ND = Not detected. Detection limits vary according to metal and are also different in each report. Absence of an entry for a metal indicates that no determination was performed. Some data in columns B and C may be low by a factor of 1000 (see text).

References: A, ANDERSON et al. (1979a); B, TILLERY (1980b); C, TILLERY (1980a); D, LYSYJ (1981); E, RADIAN CORPORATION (1982).

COMPOSITION OF PRODUCED WATERS

In contrast to the aromatic hydrocarbons, there is a very wide spread in values obtained for some of the heavy metals. This divergence may be due in part to differences in the methodology employed by the investigators.

The reliability of heavy metal analyses is a problem which cannot be ignored. There are very large differences between concentrations of some metals from study to study. It is unlikely that these differences are entirely real, and they must be interpreted in the context of the completeness and reliability of the data presented. The very large discrepancy between the levels of some metals reported in produced water from Platform 296-B of the Buccaneer Field deserves comment (ANDERSON et al., 1979a; TILLERY, 1980a,b). All three of these reports were reviewed by scientists associated with the National Oceanic and Atmospheric Administration and the Environmental Protection Agency before publication, so they met the criteria for peer review. With the information provided in their reports, it is impossible to judge whether Anderson and co-workers or Tillery have erred in their determinations; it is not impossible that they have both reported valid data (if there are large temporal changes in iron concentrations).

Issues such as this can only be resolved if the analysts have an adequate and well documented quality control/quality assurance program. That is, the analyses should not only be conducted in a reliable manner, but they should also be demonstrated as being reliable. The RADIAN CORPORATION (1982) study is the only one which meets these criteria. Their documentation of analyses of blanks, standards, and recoveries is now standard in the industry, and they have also employed the 'method of standard additions' to ensure that the validity of the data would not be compromised by the influence of unexpected interferences. Thus, it can be concluded that the Radian data represent the current state-of-the-art and can be used with confidence. The data reported by ANDERSON et al. (1979a) and LYSYJ (1981) are generally very similar to those of RADIAN CORPORATION (1982).

2.5 OTHER IONS

JACKSON et al. (1981) reported mean ionic concentrations in produced water samples from ten platforms off Louisiana as: sodium, 57,000 ppm; potassium, 377 ppm; magnesium, 807 ppm; chloride, 75,000 ppm; sulfate, 79 ppm; alkalinity (as bicarbonate), 329 ppm; and sulfide (as hydrogen sulfide), 0.40 ppm. The ranges of concentrations reported were extremely wide, reflecting differences in salinities of the various produced waters.

2.6 CONVENTIONAL POLLUTANTS

While convenient and more effective methods were developing for the determination of individual hydrocarbons in produced water, earlier investigators used gravimetric or spectrophotometric (infrared or ultraviolet) methods to determine 'total oil' or 'oil and grease.' These methods continue to be used by platform operators to monitor the effectiveness of produced water treatment. The amounts of oil in produced water are highly variable. Thus, THOMPSON et al. (1972) reported values of 9.3 ± 6.1 ppm (mean $\pm$ standard deviation) for one platform, 2.3 ± 2.09 ppm for another platform in the same field, and 4.92 ± 3.61 ppm for an associated onshore facility. In their study of produced waters from ten platforms, JACKSON et al. (1981) measured total oil contents of 7.6-77 ppm (mean, 39 ppm).

THOMPSON et al. (1972) reported produced water pH values of 6.50 ± 0.28 and 6.12 ± 0.23 for two production platforms, and 6.44 ± 0.26 for an associated onshore facility. Seawater normally has a pH of 7.5-8.4. In isolated basins where H_2S is produced the pH may approach 7.0 or fall in the acid range.

Solids in the produced water can be classified according to whether they remain in suspension on standing ('total suspended solids') or whether they settle. Some investigators further fractionated the suspended solids, providing separate estimates of 'volatile' and 'fixed' suspended matter. These values vary greatly with time. THOMPSON et al. (1972) reported 76 ± 81 ppm for settleable matter and 190 ± 110 for total suspended matter (140 ± 87 ppm fixed, 45 ± 55 ppm volatile) in produced water from one platform, and similarly wide ranges for another platform in the same field and at an associated onshore facility.

The specific gravity of produced water from two platforms off the Texas coast was 1.032-1.094, compared with 1.025 for seawater (THOMPSON et al., 1972).

The total hardness of produced water from two platforms off the Texas coast was 6,500-12,000 ppm, compared with 1,700 ppm for seawater (THOMPSON et al., 1972).

The salinity of produced water from two platforms off the Texas coast was much higher than ambient levels. Sodium concentrations were 14,000-41,000 ppm and chloride concentrations were 28,000-73,000 ppm (THOMPSON et al., 1972). At ten platforms off the Louisiana coast, sodium concentrations were 38,000-97,000 ppm and chloride concentrations were 37,000-110,000 ppm (JACKSON et al. (1981). Normal values for seawater are 11,000 ppm and 19,000 ppm, respectively, approximately the same as the salinities of produced waters from the Buccaneer Field (DANEK and TOMLINSON, 1981).

2.7 ADDED CHEMICALS

Many different chemicals may be used on production platforms as biocides, coagulants, corrosion inhibitors, cleaners, dispersants, emulsion breakers, paraffin control agents, reverse emulsion breakers, and scale inhibitors. Detergents used to clean the platforms will also be found in produced water. The use of chemicals varies from one platform to another, and it is unusual for more than a few of the many available chemicals to be employed on any one platform. JACKSON et al. (1981) has provided information on the chemicals used on ten Louisiana production platforms: TABLE 3 lists the individual chemicals mentioned in that report, along with information on their compositions obtained from the suppliers. Most of the chemicals are proprietary in nature and many are not composed of individual chemicals with defined structures, so only an indication of their identities or functions can be given.

Much of the information in this section of the review was provided by interviews with chemical suppliers.

2.7.1 Biocides

Sulfate reducing bacteria (such as Desulfoxybriro) can convert sulfate ions to sulfide ions, which will corrode metal pipes and storage vessels. Sulfate ions, in turn, are produced from elemental sulfur by the action of sulfur oxidizing bacteria. One method of minimizing this effect is to reduce the bacterial populations by adding biocides to the product stream. These substances, or their degradation products will, therefore, be discharged in the produced water. Two biocides were used in the Buccaneer Field during the first two years of the study performed by MIDDLEITCH (1981c): K-31 (glutaraldehyde) and KC-14 (alkyl-dimethylbenzyl chloride), both supplied by Champion Chemical Co. A surfactant (Surfatron DQ44) was also employed. The weekly alternation in application of the two biocides was only partially successful in reducing the bacterial populations, so Shell Oil Co. began using Magnacide B (acrolein) during the third year of the study. Acrolein is a highly volatile, toxic, and reactive substance, and residual acrolein in produced water was scavenged by treatment with Magnatreat OS-L (sodium bisulfite) prior to discharge. Acrolein was never detected in produced water samples during this study (MIDDLEITCH, 1981c; ROSE and WARD, 1981).

Other traditional biocides include fatty amines and quaternary ammonium compounds. More modern biocides, which hydrolyze easily and have relatively low fish toxicities, include 2,2-dibromo-3-nitrilopropionamide and chlorinated isothiazolines.

TABLE 3. Chemicals added to the produced water on platforms surveyed by JACKSON et al. (1981), with additional information provided by the manufacturers of the chemicals.

CHAMPION DQ61. Biocide.

DOW CORNING 200. Foam inhibitor. Silicone polymer.

EXXON VARSOL. Hydrocarbon solvent.

GREAT SOUTHERN VALVE AND CHEMICAL GS1011. Heavy duty degreaser.

M-CHEM DW-9 RIG WASH. Soap.

METHANOL. Dewatering agent.

NALCO 8AF542. A blend of aluminum salt/polyamides-polyamines in an aqueous solution.

NALCO VISCO 914. Paraffin control agent. Oxyalkylated surfactants in terpene and aromatic solvent.

NALCO VISCO 970. Gas system corrosion inhibitor. A blend of fatty acid amide salts in a hydrocarbon solvent.

NALCO KOAGULAN 3349. Flotation aid. Oxygenated polyamines and inorganic salts.

NALCO VISCO 4400. Demulsifier. A blend of oxyalkylates.

TRETOLITE BR-4050 BROUSSARD. Demulsifier. A solution of polyglycol, oxyalkylated phenol formaldehyde resins, oxyalkylated phenols, and aryl sulfonates in aromatic hydrocarbons and fatty alcohols (C₆-C₈).

TRETOLITE VEZ D-91. Antifoamer. A solution of silicon compounds in aromatic hydrocarbons.

TRETOLITE F-17. A solution of aryl sulfonates in aromatic hydrocarbons.

TRETOLITE TOL-FLOTE FR-81. Flotation aid. A solution of polyacrylamides in water and methanol.

TRETOLITE TOL-FLOTE FR-87. Flotation aid. A solution of salts of quaternized amines, an acrylic polymer, a carboxylic acid, and salt in water and methanol.

(continued)

COMPOSITION OF PRODUCED WATERS

TABLE 3 (continued)

TRETOLITE TOL-FLOTE FR-88. Flotation aid. A solution of quaternized amines in water.

TRETOLITE TOL-FLOTE FR-98D. Flotation aid. A solution of an acrylic-type polymer, salts of oxyalkylated amines, and salt in water and methanol.

TRETOLITE JW-8206. Flotation aid. A solution of salts of condensed alkanolamines, quaternized amines, and zinc chloride in water and methanol.

TRETOLITE RN-3003. Demulsifier. A solution of oxyalkylated phenol formaldehyde resins in aromatic hydrocarbons.

TRETOLITE RP-34. Demulsifier. A solution of oxyalkylated phenol formaldehyde resins, polyglycols, and acylated polyglycols in aromatic hydrocarbons and methanol.

TRETOLITE RP-79. Demulsifier. A solution of polyglycols in aromatic hydrocarbons.

TRETOLITE RP-101. Demulsifier. A solution of polyglycols, oxyalkylated phenol formaldehyde resins, and oxyalkylated phenols in aromatic hydrocarbons and fatty alcohols.

TRETOLITE RP-2256. Demulsifier. A solution of oxyalkylated phenol formaldehyde resins in aromatic hydrocarbons.

TRETOLITE RP-2327. Demulsifier. A solution of oxyalkylated phenol formaldehyde resins, aryl sulfonates, and oxyalkylated alkanolamines in aromatic hydrocarbons and isopropanol.

TRETOLITE SCALE PREVENTIVE SP-36. Scale inhibitor. A dry powder of sulfamic acid coated with a quaternized amine and an oxyalkylated phenol.

TRETOLITE SCALE PREVENTIVE SP-175. Scale inhibitor. A solution of polyphosphate esters of oxyalkylated polyols and alkanolamines in water and methanol.

TRETOLITE SCALE PREVENTIVE SP-246. Scale inhibitor. A solution of an organic phosphonate in water.

TRETOLITE FLUDEX WF-123. Scale inhibitor. A solution of salts of acylated amines and organic phosphonates in water and methanol.

(continued)

TABLE 3 (continued)

TRETOLITE FLUDEX WF-75S. Multi-purpose water treatment additive. A solid stick containing polyglycols, quaternized amines, fatty amines, and oxyalkylated phenol formaldehyde resins.

TRETOLITE X-CIDE XC-102. Biocide. An aqueous solution of glutaraldehyde.

TRETOLITE X-CIDE XC-370. Biocide. A solution of oxydiethylene-bis(alkyl dimethyl ammonium chloride) in water and methanol.

TIDE. Detergent.

Most biocides are used in concentrations no higher than 20 ppm, and the concentrations in the effluents are usually a few ppm at most.

2.7.2 Coagulants

These include cationic and anionic substances and quaternary ammonium compounds. Some coagulants contain zinc chloride in concentrations of 5-30%. Excessive concentrations of coagulants have an opposite effect from that intended, so treatment with 1-5 ppm is attempted initially, and the concentration may be raised later if the treatment proves to be ineffective. Treatment at the rate of 20 ppm with a formulation containing 30% zinc chloride will lead to discharge of 7 ppm of zinc chloride in the effluent.

2.7.3 Corrosion Inhibitors

Corrosion inhibitors may contain fatty amines, fatty acid amides, quaternary ammonium compounds, and fatty amine salts. Almost all are cationic in nature. The amines are relatively toxic toward fish, and the surface active agents tend to coat the gills of fish. However, most of the residual corrosion inhibitor is contained in the oil, with much less than 1 ppm remaining in the effluent.

2.7.4 Cleaners

Detergents used for washing the platforms collect in the separator tanks (so that residual oil can be removed) and will be included in the produced water. Concentrations of these detergents would usually be low.

COMPOSITION OF PRODUCED WATERS

2.7.5 Emulsion Breakers and Dispersants

Emulsion breakers may be nonionic or anionic polymers and include sulfonates and other esters as well as alkylene oxides. Most are oil-soluble, but some are partially soluble in water. The alkylene oxides are more soluble in oil at the elevated temperatures which normally prevail. Low concentrations of ethoxylates and low-molecular-weight acrylates might be employed as dispersants.

2.7.6 Paraffin Control Agents

The heavier paraffins can precipitate from the product stream at ambient temperatures. Most control agents are fatty esters, which are oil-soluble. Phenol adducts are also employed.

2.7.7 Reverse Emulsion Breakers

See coagulants.

2.7.8 Scale Inhibitors

Scale inhibitors include phosphonates, phosphate esters, inorganic phosphates, and acrylic polymers. Typical concentrations in effluents are 5-10 ppm. These substances are biodegradable and, accordingly, will elevate the BOD of the produced water.

2.8 OTHER SUBSTANCES

Elemental sulfur was a major component of the produced waters from the Buccaneer Field. The mean concentration was 460 ppm (MIDDLEITCH, 1981b).

Radionuclides have been reported in formation waters at concentrations several orders of magnitude above ambient. Of particular concern are radium-224, radium-226, and radium-228 (ANONYMOUS, 1978a, 1981). Reported levels in produced waters from Arkansas and Oklahoma are: radium-224, 100-1100 pCi/L; radium-226, 1-1600 pCi/L; and radium-228, 0-400 pCi/L. All three isotopes of radium are (in a geological context) relatively short-lived and, while they are isotopes of the same element, are actually entirely separate entities with completely different sources. Radium-226 has a half-life of 1,620 years and is a fission product of uranium-238 (half-life, 4.51×10^9 years), while radium-228 has a half-life of 6.7 years and is a fission product of thorium-232 (half-life, 1.39×10^{10} years). The radium-228 decays to form, in turn, actinium-228 (half-life, 6.13

hours), thorium-228 (half-life, 1.90 years), and radium-224 (half-life, 3.64 days) (BELL and LOTT, 1963). Thus, one would expect to encounter the radium isotopes in formation waters in regions where uranium-238 and/or thorium-232 are abundant.

The cause for concern over the radium isotopes is that background radiation levels of open ocean surface waters are only 0.05 pCi/L, several orders of magnitude lower than those attributed to produced waters. However, recent measurements of produced waters (including some from the same wells sampled in the reports described above) have failed to confirm the high levels of radium isotopes reported previously (CLOTWORTHY, personal communication: measurements conducted for Texaco, 1979).

2.9 SIGNIFICANCE

A reasonable perspective of the significance of produced water discharges can be obtained by considering other sources of marine contaminants. Petroleum hydrocarbons are addressed first, and this discussion is followed by consideration of carcinogens and trace metals.

2.9.1 Petroleum Hydrocarbons

The most widely cited comparison of inputs of petroleum hydrocarbons into the marine environment is contained in the proceedings of a 1973 workshop conducted by the NATIONAL ACADEMY OF SCIENCES (1975). That organization has recently revised its estimates of the magnitudes of the various sources of hydrocarbons, but has not yet published its findings. A draft has, however, been included in a recent review by RUDD (1982), and it is reproduced here as TABLE 4.

Almost half of the 3.2 million tons per year of oil entering the sea is attributed to tanker operations, while offshore production accounts for 1.6% of the total. RUDD (1982) did not indicate how much of the 1.6% derived from produced water discharges and how much was from spills. The earlier estimates presented by the NATIONAL ACADEMY OF SCIENCES (1975) indicated that offshore production accounted for 0.08 million tons per year, or 1.3% of the total oil input of 6.11 million tons per year.

These estimates were challenged by MILEYKOVSKIY (1979), who suggested that the annual input of oil into the sea was probably 13-14 million tons, and maybe as high as 25 million tons. His estimate is based upon a reappraisal of spillages during transportation and aerial transport of hydrocarbons. If his estimates are correct, the proportion attributable to offshore

COMPOSITION OF PRODUCED WATERS

TABLE 4. Input of petroleum hydrocarbons into the marine environment. Draft of a tabulation prepared by the National Academy of Sciences, as reported by RUDD (1982).

Source	Input rate, million metric tons/year	
	Best estimate	Probable range
Natural sources		
Marine seeps	0.2	0.02-2.0
Sediment erosion	0.05	0.005-0.5
Offshore production	0.05	0.04-0.07
Transportation		
Tanker operations	0.7	0.4-1.5
Drydocking	0.03	0.02-0.05
Marine terminals	0.02	0.01-0.03
Bilge and fuel oils	0.3	0.2-0.6
Tanker accidents	0.4	0.3-0.4
Non-tanker accidents	0.02	0.02-0.04
Atmosphere	0.3*	0.05-0.5
Municipal and industrial wastes and run-off		
Refineries	0.15	0.1-0.6
Municipal wastes	0.7	0.4-1.5
Non-refining industrial wastes	0.2	0.1-0.3
Urban run-off	0.03	0.01-0.2
River run-off	0.04	0.01-0.5
Ocean dumping	0.02	0.005-0.02
Total	3.2	1.6-8.8

*RUDD (1982) states that a value of 0.3 was used for the atmospheric inputs in the calculations, although the NAS Atmospheric Panel did not wish to give a best estimate for this input.

The relative significance of produced water discharges should, perhaps, be considered in comparison with the other sources of oil in that same region. The most intensively developed offshore region is the continental shelf of the Gulf of Mexico off the shores of Louisiana. Coincidentally, these waters are adjacent to the mouth of the Mississippi River.

COMPOSITION OF PRODUCED WATERS

SHARP (1979) has estimated that the Mississippi River contributes 2.8 million bbl/year of hydrocarbons to the waters of the Gulf of Mexico [he noted that the average flow of the river is 500,000 cfs, and based his calculations upon a hydrocarbon content of 1 ppm, a value which he suggested to be lower than the actual concentration]. This corresponds to an annual flow of some 0.4 million metric tons, eight times the total world-wide annual discharge of hydrocarbons attributed to offshore production (RUDD, 1982), and likely two orders of magnitude higher than discharges from offshore production into the Gulf of Mexico.

A report (ANONYMOUS, 1982b; based upon a presentation by E.S. Van Vleet, "Oil contamination of the Gulf of Mexico," at "Gulf of Mexico - Trends for the 80's," July 23-25, 1982, Tulane University, New Orleans, Louisiana) claimed that ballast discharges from tankers were responsible for the major portion of oil pollution in the Gulf of Mexico and that "offshore oil drilling along the Louisiana coast had not contributed significantly."

It can be concluded, therefore, that production activities in the Gulf of Mexico off Louisiana do not result in disproportionately high levels of hydrocarbon input into the sea.

Some information is also available concerning the sources of hydrocarbons entering the sea off the coast of southern California. There are currently no produced water discharges in this region. Unlike the Gulf of Mexico, there are no major rivers draining into the Pacific Ocean off southern California, although natural seeps are more in evidence.

The hydrocarbons found in municipal wastewater effluents discharged into the Pacific Ocean off the southern California coast are primarily of petroleum origin, and most closely resemble the profiles characteristic of lubricating oils (EGANHOUSE and KAPLAN, 1982b). The total quantity of these discharges was found to be relatively high (17,000 metric tons per annum), corresponding to 5.8% of the 1973 estimate by the NATIONAL ACADEMY OF SCIENCES (1975) worldwide input of wastewater-borne petroleum to the ocean (EGANHOUSE and KAPLAN, 1982a). The 1983 National Academy of Sciences estimate for hydrocarbons in municipal wastes has, accordingly, been increased from 0.3 to 0.7 million tons per year (RUDD, 1982). Wastewater effluents in this region alone account for 34% of the worldwide total input of hydrocarbons from offshore production.

In the northeastern United States, municipal wastes also contribute significant quantities of hydrocarbons to the ocean. A major portion of the oil in water and biota from Jamaica Bay, New York was attributed by TANACREDI (1977) to disposal of used lubricating oils. He noted that only 40% of the estimated 0.25 metric tons per year of lubricating oils used in the metropolitan

New York area is recycled, so that as much as 0.15 metric tons per year may be dumped into sewers. Placed in perspective, this is equivalent to three times the annual worldwide input of hydrocarbons from offshore production. Not all of the oil from the sewers will be discharged in the wastewater effluent. Some will remain in sewage sludges separated in the treatment plants. KOONS and THOMAS (1979) have, however, determined that sewage sludges and dredging spoils are indeed a major source of hydrocarbons found in sediments from the New York Bight, with levels of hydrocarbons as high as 0.65%.

2.9.2 Polynuclear Aromatic Hydrocarbons

A major cause for concern in some circles has been the presence of polynuclear aromatic hydrocarbons, such as benzo[a]pyrene, in produced waters. As discussed above, one would expect to find approximately 0.1 ppb of this carcinogen in produced water effluents, corresponding to a worldwide annual discharge of 0.1 metric tons during offshore production operations [2 ppm in the 0.05 metric tons of oil discharged (RUDD, 1982)]. The total amount of benzo[a]pyrene in the 3.2 million metric tons of petroleum entering the sea each year would be 6.4 tons. These amounts are extremely small in comparison with the total quantity of benzo[a]pyrene entering the environment, estimated at more than 5,000 tons per year by BROWN and WEISS (1978) and BROWN et al. (1980). The various sources are summarized in TABLE 5.

2.9.3 Heavy Metals

The discussion (above) pertaining to petroleum hydrocarbons is also generally applicable to the heavy metals. Thus, if the mean concentration of 0.30 ppm for lead obtained by RADIAN CORPORATION (1982) were representative of all produced water effluents the annual total worldwide discharge of this metal would be 300 tons. The annual worldwide discharge rates of the other heavy metals detected by Radian Corporation would be: cadmium, 3.5 tons; chromium, 14 tons; nickel, 90 tons; and zinc, 98 tons. These amounts are small in comparison with the estimated 1400 tons of metals annually contained in waste discharges from Los Angeles City and County alone (BASCOM, 1983).

Some comparisons can also be made with the ambient levels of heavy metals in seawater (SVERDRUP et al., 1946). Seawater contains 0.004-0.005 ppm of lead, so that the levels found in produced water effluents are 60-75 times those of seawater. Similarly, levels of nickel in produced waters are 120-900 times the 0.0001-0.0005 ppm found in seawater, while levels of zinc in produced waters are only 7-20 times the 0.005-0.014 ppm found in seawater.

COMPOSITION OF PRODUCED WATERS

TABLE 5. Estimated input (tons/year) of benzo[a]pyrene into the environment. Adapted from BROWN and WEISS (1978) and BROWN et al. (1980). In comparison, worldwide offshore production activities contribute 0.1 tons/year (see text).

Source	Worldwide (excluding U.S.A.)	U.S.A.
Coke production	840	190
Catalytic cracking	6	6
Coal refuse fires	340	340
Open burning (agricultural & forest fires)	420	248
Heat and power generation	2130	475
Motor vehicles	23	22
Oil spills and seeps	5*	-
Petroleum refinery effluents	0.4	0.1
Municipal sewage effluents	-	1.5
Total, tons/year	3764.4	1282.6

*Including U.S.A.

3 FATES OF CONTAMINANTS

3.1 SUMMARY

There is every indication that contaminants from the produced water are diluted and dispersed rapidly and efficiently. Concentrations of hydrocarbons in the mixing zone of the receiving water rarely exceed 30 ppb, while elevated levels of heavy metals in the water column are generally not observed. Transient accumulations of hydrocarbons in surficial sediments may reach 15 ppm, but they are dispersed during periodic resuspension of the surficial sediments. Temporary elevations of heavy metals have also been observed (maxima are: cobalt, 2 ppm; chromium, 2 ppm; copper, 7 ppm; mercury, 0.04 ppm; manganese, 155 ppm; lead, 45 ppm; zinc, 522 ppm), but it is not possible to distinguish among the various sources of heavy metal contamination, which also derives from leaded gasoline and corrosion of platforms, sacrificial electrodes, and debris. There is no evidence for permanent sedimentary contamination in the region of oil fields in the Gulf of Mexico due to produced waters.

Little is known about the mechanisms and rates of the processes responsible for the distribution of contaminants from produced water discharges, or the ultimate fates of these contaminants. It is reasonable to assume that dispersion will be low under quiescent hydrological and meteorological conditions and that sedimentation will be more efficient in shallower waters. In the case of hydrocarbons, evaporation is expected to be reduced in magnitude in colder waters, but it has been suggested that increased turbulence in rougher northern seas counteracts this effect.

There is evidence that disposal of produced waters via pipes terminating above the air/sea interface is less detrimental to the environment than subsurface disposal, although no direct experimental comparisons have been made.

3.2 INTRODUCTION

The various fates of oil components from oil spills have been discussed in a well-documented review by McAULIFFE (1977a). It is likely that many of these fates are shared by produced water components discharged from production platforms.

FATES OF CONTAMINANTS

3.3 PHYSICAL FATES

The processes of mixing and transport of pollutants have defied attempts by modelers to provide accurate predictions of the fates of oil in the sea, except under carefully controlled conditions (DITMARS, 1976). Thus, most of our knowledge concerning the dispersion of hydrocarbons has been based upon individual observations. An accumulation of such knowledge has enabled us to make some broad generalizations, and the major aspects are summarized here.

3.3.1 Evaporation

Studies of the fates of No. 2 fuel oil during controlled ecosystem experiments have indicated that evaporation was the dominant mode of loss of the hydrocarbons (GEARING et al., 1979). Moreover, loss rates of light hydrocarbons from small spills are in accordance with their individual vapor pressures, and these substances can be dissipated entirely within four to eight hours (McAULIFFE, 1977b). When produced water is discharged from a pipe located above the air/sea interface it is reasonable to expect that a substantial proportion of the more volatile hydrocarbons will be lost rapidly through evaporation.

3.3.2 Dispersion Within the Water Column

The rates of loss of both benzene and cyclohexane from small oil spills are about equal, even though they have very different solubilities in water. This finding indicates that loss by solution (into the water column) is minor, compared with evaporation (McAULIFFE, 1977b).

There is very clear evidence that both petroleum-derived and biogenic hydrocarbons accumulate in a surface microlayer at the air/sea interface. MARTY and SALIOT (1976) found that the concentration of alkanes in this microlayer (as high as 1.2 ppm) was 50 times higher than in the underlying water column. These authors reported that n-alkanes were among the most abundant hydrocarbons in the areas which they studied (English Channel, Mediterranean Sea, and Atlantic Ocean off West Africa), whereas there were reports of a predominance of branched and cyclic paraffins in the surface microlayer (and n-alkanes in the underlying water column) in the Gulf of Mexico off Louisiana (LEDET and LASETER, 1974b; LASETER and LEDET, 1979).

The composition of the substances collected at the air/sea interface depends to a large degree on the sampling method used. These differences are apparently due to the thickness of the layer sampled. A Garrett sampler (stainless steel mesh screen) samples a layer with an average thickness of 0.44 mm, while a

Harvey sampler (rotating PVC drum) samples a layer 0.05-0.08 mm thick (DAUMAS et al., 1976). MARTY and SALIOT (1976) employed a Garrett sampler in the study described above, whereas LEDET and LASETER (1974b) used a Teflon disc (MIGET et al., 1974), which they found to be superior to the Garrett sampler for the recovery of the lighter hydrocarbons (LEDET and LASETER, 1974a).

Rhodamine dyes are frequently used to simulate the potential movement of oil in the sea since they are nontoxic, readily available, and contrast strongly with the color of coastal waters (KLEMAS et al., 1974; ARMSTRONG and HAMILTON, 1979; WORKMAN and JONES, 1979). When a rhodamine dye was added to produced water at the discharge point of a production platform in the Buccaneer Field, however, no correlation was found between dye and hydrocarbon concentration in the dye plume at the air/sea interface (MIDDLEITCH, 1981b).

The presence of naphthalenes, phenanthrenes, and dibenzothiophenes in seawater provides a good indication of the presence of petroleum. From such analyses of samples from throughout the North Sea, it was determined that petroleum concentrations were uniformly low, even in the region of active oil fields (GRAHL-NIELSEN et al., 1979).

3.3.3 Transport to the Sediments

Very little information is available on the rates of settling of contaminants. Mechanisms which have been implicated in this process include simple attachment of the contaminant to particulates in the water column (or in the produced water prior to discharge) and their incorporation into fecal pellets of zooplankton.

Dispersion models can be used to estimate the settling rates of particulates. Such models are usually based upon the assumption that Stokes' law applies under field conditions, and this has lead to predictions that particulates the size of fine sand (120 microns) have a settling velocity of approximately 1 cm/sec (SMEDES et al., 1981). In the Buccaneer Field, this would result in a settling time of 34 min (to a depth of 20 m) within a distance of 300 m from the platform (in an average current of 15 cm/sec) (ARMSTRONG, 1981).

These predictions are difficult to test but, in a detailed study of the sedimentation of particulate matter during a phytoplankton bloom in the Baltic Sea, it was determined that species as small in size as Skeletonema costatum can sink to depths of 65 m within a few days, and that this movement was not impeded by either a weak thermocline or a strong halocline (SMETACEK et al., 1978).

FATES OF CONTAMINANTS

Sediments collected at depths of 520-4600 m in the Gulf of Mexico frequently contained plant material of terrestrial origin, demonstrating that the deep benthos represents a sink for materials transported from coastal regions. Many of these sediments also contained petroleum hydrocarbons, but they were generally attributed to natural seeps (PEQUEGNAT and JEFFREY, 1979).

3.3.4 Sediment Resuspension

Resuspension of sediments undoubtedly contributes to the redistribution of contaminants in dynamic environments, and this process is dependent upon current speeds, sediment type, and turbulence (BROOKS et al., 1981). There is no doubt that discharge of produced waters from platforms in shallow bays can lead to accumulation of contaminants in the surrounding sediments (ARMSTRONG et al., 1977). In contrast, it has been observed that petroleum hydrocarbons were rapidly released from intentionally oiled sediments at Port Valdez, Alaska, and the ease of loss of the hydrocarbons was attributed to an absence of strong wave action which might have buried the oil (SHAW et al., 1977). Thus there is no unequivocal evidence that quiescent conditions favor the incorporation and retention of hydrocarbons in sediments. In offshore waters, however, there is ample evidence that turbulence, wave action, and currents tend to resuspend sediments and disperse discharged contaminants efficiently (BURCHFIELD et al., 1974, 1979; GRIFFIN, 1978, 1979; GRIFFIN and RIPPY, 1974; RIPPY, 1974; ANDERSON et al., 1981a; BROOKS et al., 1981; BEHRENS, 1981; DANEK and TOMLINSON, 1981). Large day-to-day changes in hydrocarbon concentrations suggest a significant degree of sediment resuspension (MIDDLEDITCH, 1981b), but this could be due to patchy distribution.

In summary, low levels of resuspension lead to less widespread dispersion and therefore increased exposure levels to fewer benthic organisms. Higher levels of resuspension will lead to eventual wider dispersion and therefore reduced exposure concentrations to more benthic organisms. Under the latter conditions, any accumulations of contaminants in surficial sediments in the vicinity of production platforms will be transient in nature.

3.4 CHEMICAL FATES

3.4.1 Oxidation

Oxidation of oil components is generally considered a route by which hydrocarbons are detoxified. However, photooxidation of a No. 2 fuel oil results in increased toxicity to baker's yeast. The toxic products are water-soluble and have not been fully



Documents

Document Sharing Hub

characterized, but appear to include peroxides and acidic materials (LARSON et al., 1977). If such oxidation products are produced from produced water constituents it is anticipated that they would undergo rapid dilution as they are produced, thereby reducing or eliminating toxic effects as shown in the laboratory.

Oxidation of hydrocarbons has been suggested as a possible reason for an increase in dissolved nonvolatile organic matter during produced water treatment (LYSYJ et al., 1981b), but there is no indication that the substances produced are toxic.

3.4.2 Hydrolysis

This is a major route by which residues of the biocide acrolein are degraded, and may also be significant for other added chemicals.

3.4.3 Weathering

The phenomenon known as 'weathering' is a culmination of all of the various effects (chemical and biological) known to degrade oil. The result can be quite pronounced, and is sometimes not easily interpreted.

3.5 BIOLOGICAL FATES

3.5.1 Bacterial Degradation

The microbial degradation of aromatic petroleum hydrocarbons has been reviewed by GIBSON (1977). He suggests that many of the polynuclear aromatic hydrocarbons, particularly those containing sulfur, that are present in crude oil are poor candidates for biodegradation.

Six individual radiolabeled polynuclear aromatic hydrocarbons were incubated with river water and sediments collected in the vicinity of a coal-coking treated wastewater discharge in order to assess the degree of ambient microbial degradation. Mean turnover times in sediments for naphthalene, anthracene, and benz[a]anthracene were 13, 62, and 300 hours, respectively. No unequivocal evidence for transformation of benzo[a]pyrene or dibenz[a,h]anthracene was obtained. Only naphthalene and anthracene transformations were observed in water samples, with rates 5- and 20-fold lower than in sediments. The study also provided an indication that continuous inputs of polynuclear aromatic hydrocarbons result in an increased ability within a microbial community to utilize certain polynuclear aromatic hydrocarbons. Since transformation rates remained elevated for more than one year after removal of the source of polynuclear aromatic hydro-

carbons, it is evident that microbial communities may shift only slowly in response to changes in polynuclear aromatic hydrocarbon concentrations (HERBES, 1981).

Populations of bacteria tend to increase when supplies of the appropriate nutrients are abundant. Accordingly, hydrocarbon-degrading bacteria are most abundant in areas, such as those which receive refinery effluents (TAGGER et al., 1979), where hydrocarbon levels are high. As a result of this relationship, the extent of contamination can often be discerned by studying the distribution and abundance of bacteria and, moreover, adequate numbers of bacteria are available for hydrocarbon degradation in regions which experience chronic exposure.

Hydrocarbon-degrading bacteria are widely distributed in the Beaufort and Chukchi Seas, but it has been found that their populations are lower in ice than in water or sediment. Degradation rates of all classes of hydrocarbons studied were low, and were limited by temperature and concentrations of available nitrogen and phosphorus (ATLAS, 1977). Specific degradation rates have been reported by ARHELGER et al. (1977).

The importance of the availability of nitrogen and phosphorus as nutrients for hydrocarbon-degrading bacteria has been a matter of some discussion. Laboratory experiments have indicated that hydrocarbon degradation is severely limited in the absence of appropriate amounts of nitrogen and phosphorus (BRIDIE and BOS, 1971). Similar findings have resulted from studies of accidentally or deliberately spilled oil in cold climates (ATLAS, 1981). Field experiments have, however, demonstrated that degradation does indeed take place efficiently, at least in temperate climates (GILBERT and HIGGINS, 1978). Moreover, cycloalkanes and aromatic hydrocarbons are found to be degraded more rapidly in the water column than in the sediments (WALKER et al., 1975). ATLAS (1981) has concluded that the availability of nitrogen and phosphorus is critical when oil spills are considered, but not for the degradation of dispersed oil. He specifically states that, "Investigators considering the fate of low-level discharges of hydrocarbons (soluble hydrocarbons) have, thus, properly concluded that available nutrient concentrations are adequate to support hydrocarbon biodegradation."

3.5.2 Macroorganisms

LEE (1977) has reviewed the research which has been conducted upon the accumulation and turnover of petroleum hydrocarbons in marine organisms, and TEAL (1977) has reviewed the food chain transfer of these substances. While bioaccumulation (uptake) of hydrocarbons has been amply documented, there is no unequivocal evidence for biomagnification (increase in concentration during passage through the food web).



3.5.2a Bioaccumulation. Most of the research on bioaccumulation of hydrocarbons has been restricted to the polynuclear aromatic hydrocarbons (NEFF, 1979).

Mummichogs (*Fundulus heteroclitus*) exposed to naphthalene for four hours at concentrations of 2 or 0.02 ppm contained approximately double the ambient concentration of this compound. Particularly high concentrations were found in the spleens of fish exposed to concentrations of 2 ppm, probably due to an accumulation of dead erythrocytes containing naphthalene (DiMICHELE and TAYLOR, 1978). Fish exposed to naphthalene accumulated this compound in the liver and gall bladder. Naphthalene was not excreted in significant amounts within 24 hours (RICE et al., 1978). In controlled ecosystem studies, oysters accumulated naphthalenes from seawater contaminated with crude oil very rapidly, achieving tissue concentrations six to eight times higher than in the water within two days. The accumulation of heavier polynuclear aromatic hydrocarbons proceeded more slowly, with tissue concentrations generally lower than those of the seawater (LEE et al., 1978). The temperate clam (*Rangia cuneata*) and the boreal clam (*Protothaca staminea*) were both found to have increased uptakes of naphthalenes at reduced temperatures. This effect is apparently unrelated to preferential evaporation of naphthalenes at the higher temperatures, since concentrations of these compounds in the water were found not to vary with time (FUCIK and NEFF, 1977).

It is now well established that detritivores do not accumulate hydrocarbons efficiently from oiled sediments (ANDERSON et al., 1977, 1978). Benthic amphipods were able to take up naphthalenes from moving water several hundred times more efficiently than from oiled sediments (ANDERSON et al., 1979b).

How do the laboratory studies on the bioaccumulation of hydrocarbons compare with measurements made at sea? In examining specimens collected at sea, care must be taken to distinguish between petroleum hydrocarbons and those of different sources. The manner in which this can be achieved is illustrated by the painstaking investigations of PANCIROV and BROWN (1977) with fish and shellfish collected from various locations, mainly off the Atlantic coast of North America. They were particularly interested in the origin of benzo[a]pyrene. In specimens containing significant amounts of this carcinogen, the levels of pyrene and methylpyrene were also elevated. In each instance pyrene predominated over methylpyrene, indicating that these compounds derived from combustion. Thus, it was concluded that the benzo[a]pyrene also was of pyrolytic rather than petroleum origin.

In the region of the Buccaneer Field, measurements of hydrocarbon concentrations were made in barnacles and other components of the fouling community on the platforms, as well as in the water column. Documents
Document Sharing Hub

shrimp, and a variety of benthic biota. Petroleum hydrocarbons were found in concentrations as high as 4 ppm in the flesh of barnacles (*Balanus tintinnabulum*) collected from locations just below the air/sea interface at the production platforms. Higher concentrations (up to 16 ppm) were found in barnacles from a flare stack adjacent to one of the production platforms. The fouling mat contained significantly higher concentrations of petroleum hydrocarbons (mean, 120 ppm), and the presence of lighter hydrocarbons was indicative of relatively "fresh" (unweathered) oil. The crested blenny (*Hypleurochilus geminatus*), a small fish which feeds on and among the fouling community, had a mean alkane concentration of 6.8 ppm. The sheepshead (*Archosargus probatocephalus*), which feeds on barnacles, had a mean alkane concentration of 4.6 ppm in muscle tissue and 6.1 ppm in livers. Two fish which feed in the water column contained lower concentrations of alkanes: spadefish (*Chaetodipterus faber*), 0.6 ppm (muscle), 2.0 ppm (liver); and red snapper (*Lutjanus campechanus*), 1.1 ppm (muscle), 1.3 ppm (liver). Shrimp tend to be transients in the region of the Buccaneer Field, and the highest level of contaminants encountered (2.5 ppm of petroleum alkanes) was in a brown shrimp (*Penaeus aztecus*). There was no evidence for bioaccumulation of hydrocarbons (MIDDLEITCH, 1981b).

Some concern has been expressed over the possibility of bioaccumulation of heavy metals. Laboratory experiments have demonstrated that, for example, lead and cadmium can both be accumulated from water in several tissues of coho salmon (*Oncorhynchus kisutch*) and starry flounder (*Platichthys stellatus*). Depuration rates are much lower than for hydrocarbons, with more than 50% of the metal remaining after 37 days (MALINS et al., 1978). Also, apparently elevated levels of heavy metals have been measured in tissues of fish and other marine organisms: again, the reader is referred to the reviews by REISH et al. (1976, 1977, 1978, 1979, 1980, 1981, 1982). The range of concentrations of the heavy metals in marine organisms is indicated in TABLE 6. Those measurements were made on specimens from a diversity of locations (some exposed to contaminants; others not) so they merely provide an indication of the range of concentrations which have been encountered. Studies conducted to determine 'baseline' concentrations of contaminants have been performed in several regions, but the possible exposure of organisms to non-petroleum heavy metals is a problem which has not been adequately addressed. It should be noted that some of the heavy metals are essential components of many tissues and body fluids. Thus, human semen contains approximately 140 ppm of zinc (SEARCY, 1969) - a concentration 1,400-fold higher than the level found by RADIAN CORPORATION (1982) in produced waters.

TABLE 6. Levels of heavy metals reported in marine organisms. This Table represents a summary of data reviewed by REISH et al. (1976, 1977, 1978, 1979, 1980, 1981, 1982), and the reader is referred to those reviews for citations of the original cited literature.

Metal	Organisms	Reported concentrations (ppm)*
Aluminum	Algae	10-53
	Polychaetes	930-9600
	Bivalves	2.8-8200
	Gastropods	1,7-390
	Crustaceans	1.2-2
	Tunicates	0-940
	Fish	0.6-15
Antimony	Algae	0.067-2.6
	Plankton	0-6.8
	Bivalves	0.08-3.1
	Gastropods	0.08-2
	Cephalopods	0.84-0.92
	Crustaceans	0.06-3.3
	Tunicates	2.4-6.8
Arsenic	Fish	0.002-0.6
	Algae	0.17-190
	Polychaetes	1.1-87
	Coelenterates	53-59
	Bivalves	0.61-192
	Gastropods	2.3-98
	Crustaceans	0.07-80
Bismuth	Chaetognaths	7.5-7.7
	Echinoderms	1.4-16
	Fish	0.025-320
	Algae	0.46-1.1
	bivalves	0-0.88
	Gastropods	0.79-0.95
	Crustaceans	0.53-1.1
Cadmium	Tunicates	1.3-2.7
	Algae	0.0005-29
	Plankton	0.3-21
	Coelenterates	0.3-0.4
	Polychaetes	0.1-40
	Bivalves	0.005-600
	Gastropods	0.03-1120
(continued)	Cephalopods	0.02-1100
	Crustaceans	0.0015-1600

FATES OF CONTAMINANTS

TABLE 6 (continued)

	Chaetognaths	1.2-1.3
	Echinoderms	0.02-18
	Fish	0.001-930
	Birds	0.0002-480
	Mammals	0.1-570
Cerium	Algae	0.01-0.1
	Bivalves	0.007
	Gastropods	0.001
	Crustaceans	0.01
	Fish	0.006-0.04
Cesium	Algae	0.037-0.07
	Plankton	2.2-22
	Bivalves	0.005-0.067
	Gastropods	0.03
	Cephalopods	0.016-6.4
	Crustaceans	0.028-0.05
	Fish	0.06-130
	Mammals	16-45
Chromium	Algae	0.05-590
	Plankton	1.1-35
	Polychaetes	0.1-2.4
	Bivalves	0.01-290
	Gastropods	0.04-23
	Crustaceans	0.02-8
	Echinoderms	0.04-42
	Tunicates	0-0.95
	Fish	0.01-4.9
Cobalt	Algae	0.018-40
	Plankton	0-0.5
	Polychaetes	1.6-7.9
	Bivalves	0.02-160
	Gastropods	0.01-3.6
	Cephalopods	0.06-0.42
	Crustaceans	0.004-0.51
	Fish	0.002-1.0
	Mammals	0.5-72
Copper	Algae	0.1-230
	Plankton	5.9-130
	Protozoans	640
	Coelenterates	7.6-7.9
	Polychaetes	1.6-130,000
	Bivalves	0.004-2500
	Gastropods	0.02-1800

(continued)

TABLE 6 (continued)

	Cephalopods	16-25,000
	Crustaceans	0.01-600
	Chaetognaths	5.6-6.3
	Echinoderms	0.19-42
	Tunicates	0.3-100
	Fish	0.02-3700
	Birds	4-370
	Mammals	1.5-610
Europium	Bivalves	0-0.75
Germanium	Algae	0.003-0.03
	Crustaceans	0.002-0.28
	Fish	0.002
Gold	Bivalves	0-0.54
Iron	Algae	11-15,000
	Plankton	10,000
	Protozoans	1500
	Polychaetes	21-5600
	Bivalves	0.02-4000
	Gastropods	11-5900
	Cephalopods	1.3-850
	Crustaceans	0.62-2300
	Chaetognaths	32-33
	Echinoderms	190-2600
	Tunicates	16-2100
	Fish	0.3-60,000
	Birds	0.35-2900
	Mammals	130-82,000
Lanthanum	Polychaetes	0.8-4.1
	Bivalves	0.3-45
Lead	Algae	0.002-1200
	Plankton	11-81
	Protozoans	550
	Polychaetes	4.8-397
	Bivalves	0.01-3100
	Gastropods	0.05-96
	Cephalopods	0.1-26
	Crustaceans	0.0048-60
	Echinoderms	0.01-32
	Tunicates	0.12-1.6
	Fish	0.001-45
	Mammals	0.03-16

(continued)

FATES OF CONTAMINANTS

TABLE 6 (continued)

Manganese	Algae	0.73-2700
	Plankton	0.06-200
	Polychaetes	1-1100
	Bivalves	0.1-1200
	Gastropods	0.21-130
	Cephalopods	0.26-30
	Crustaceans	0.25-670
	Tunicates	0.65-3.7
	Fish	0.02-300
	Birds	0.0036
	Mammals	1.5-62
Mercury	Algae	0.0002-140
	Plankton	0.02-25
	Polychaetes	0.01-4.3
	Bivalves	0.005-570
	Gastropods	0.002-9.4
	Cephalopods	0.006-27
	Crustaceans	0.0001-57
	Bryozoans	0.09-0.1
	Tunicates	0.1
	Echinoderms	0.006-0.1
	Fish	0.00008-7500
	Birds	0.0009-62
	Mammals	0.01-1300
Molybdenum	Bivalves	0-23
Nickel	Algae	0.35-39
	Plankton	0.9-4.5
	Polychaetes	2.1-4.1
	Bivalves	0.05-170
	Gastropods	0.14-76
	Cephalopods	0.4-1.1
	Crustaceans	0.03-16
	Echinoderms	0.02-42
	Tunicates	0.13-1.2
	Fish	0.006-460
	Birds	1-5
Rubidium	Protozoans	1700
	Algae	11-52
	Bivalves	4.2
	Gastropods	3.2
	Cephalopods	3.4
	Crustaceans	3.2-3.4
	Fish	0.13-5.8
	Mammals	2.2-4.3

(continued)

TABLE 6 (continued)

Samarium	Polychaetes	0.2-3.9
	Bivalves	0.1-4.7
Scandium	Bivalves	0.02-0.05
Selenium	Polychaetes	0.5-3.3
	Bivalves	0.32-16
	Crustaceans	0.05-7.1
	Fish	0.04-61
	Birds	0-89
	Mammals	0.06-480
Silver	Algae	0.01-20
	Plankton	0.5-1.4
	Polychaetes	0.1-5
	Bivalves	0.006-46
	Gastropods	0.01-9.9
	Cephalopods	4.4-84
	Crustaceans	0.01-5
	Echinoderms	0.001-0.02
	Fish	0.01-2
	Birds	0.03-44
	Mammals	0.1-39
Tin	Bivalves	0.3-600
Titanium	Bivalves	1.1-26
	Fish	0.5-1.7
Vanadium	Plankton	4.4-150
	Polychaetes	1.6-22
	Bivalves	0.03-140
	Gastropods	0.11-0.72
	Cephalopods	0.2-25
	Crustaceans	0.2-0.52
	Tunicates	0.12-27,000
	Fish	0.11-170
Zinc	Algae	1.2-6200
	Plankton	52-740
	Protozoans	620
	Coelenterates	280-290
	Polychaetes	22-35,000
	Bivalves	0.006-17,000
	Gastropods	2.6-4500
	Cephalopods	12-1500
	Crustaceans	1.7-3400
	Echinoderms	1-1500

(continued)

FATES OF CONTAMINANTS

TABLE 6 (continued)

Chaetognaths	76-90
Tunicates	10-14
Fish	0.003-7100
Birds	0.85-1100
Mammals	78-4200

*Some are wet weights, others are dry weights. No attempt has been made to provide a critical evaluation of these data: some values appear to be unreasonably high, and some concentration ranges are very broad (see text).

Levels of heavy metals in biota from the Buccaneer Field are given in TABLE 7. In most instances, these levels are toward the lower ends of the ranges of concentrations given in TABLE 6 for organisms sampled elsewhere. The exceptions are chromium in fish, cobalt in crustaceans and fish, and nickel in crustaceans. Comparisons with data from the South Texas Outer Continental Shelf (STOCS) study tend to allay concern over bioaccumulation of heavy metals: of these three metals, only chromium levels in fish are higher in the Buccaneer Study than in the STOCS study, and only by a factor of four (muscle) or three (livers) (ANDERSON et al., 1977; TILLERY, 1980b). Moreover, the burden of chromium tolerated by algae, plankton, bivalves, gastropods, crustaceans, and echinoderms is greater than that reported for fish (TABLE 6).

Bioaccumulation of heavy metals is not necessarily cause for concern. As BASCOM (1983) has pointed out, animals collected from the heavily polluted region associated with Los Angeles County sewage outfalls sequester heavy metals in metallothioneins, and he suggests that the metals are thus prevented from reaching the sites of toxic action in those animals. In contrast, animals exposed suddenly to high concentrations of heavy metals during acute toxicity bioassays are unable to bind the metals immediately, and toxic effects ensue. BASCOM (1983) concludes that "metals in the sea, even in regions of high concentration, are not a hazard to sea animals or to persons who eat those animals."

3.5.2b Biomagnification. The biomagnification of fat-soluble halogenated pesticides during transfer through the food web is well documented. Thus, it is not unreasonable to expect a similar phenomenon with the fat-soluble polynuclear aromatic hydrocarbons. Fortunately, this does not happen. Depuration of hydrocarbons from marine organisms is apparently quite efficient (see below): bioaccumulation (but not biomagnification) of these compounds takes place only during constant exposure to oil (LASDAY and MERTENS, 1976).

TABLE 7. Mean concentrations (ppm) of heavy metals in biota associated with Platform 296-B of the Buccaneer Field.

Metal	Organisms	A	B	C	D
Barium	Barnacles		80	6.2	
	Fouling mat			520	
	Shrimp			2.9	
	Benthos		5.9*		
	Fish muscle		1.9*	1.5	
	Fish liver		1*		0.4
Cadmium	Barnacles		0.3	15	
	Fouling mat			1.7	
	Plankton	ND			
	Shrimp			1.9	
	Benthos		17*		
	Fish muscle	ND	0.6*	0.2	0.1
	Fish liver		10*		19
Chromium	Barnacles		ND	2.8	
	Fouling mat			85	
	Shrimp	ND		0.8	
	Benthos		35*		
	Fish muscle	12	4.7*	0.9	0.2
	Fish liver		8.0*		0.3
Cobalt	Barnacles		4.5	1.0	
	Fouling mat			4.6	
	Shrimp	1.5		0.5	
	Plankton	12			
	Benthos		15*		
	Fish muscle	0.5	1.1*	0.3	
	Fish liver		1.8*		
Copper	Barnacles		14	18	
	Fouling mat			22	
	Shrimp	26		30	
	Plankton	100			
	Benthos		38*		
	Fish muscle	3.0	3.5*	1.4	1.9
	Fish liver		24*		30
Iron	Barnacles		60	200	
	Fouling mat			6700	
	Shrimp	78		57	
	Benthos		70*		
	Fish muscle	60	18*	14	11
	Fish liver		910*		1300

(continued)



Documents

Document Sharing Hub

FATES OF CONTAMINANTS

TABLE 7 (continued)

Lead	Barnacles		28	0.8	
	Fouling mat			7.9	
	Shrimp	7.3		0.4	
	Plankton	470			
	Benthos		ND*		
	Fish muscle	3.0	4.4*	0.3	0.3
	Fish liver		3.8*		0.5
Manganese	Barnacles		13	15	
	Fouling mat			280	
	Shrimp			3.6	
	Plankton	100			
	Benthos		10*		
	Fish muscle	ND	2.3*	0.5	
	Fish liver		7.0*		6.0
Mercury	Barnacles		1.3	0.02	
	Fouling mat			ND	
	Shrimp			0.1	
	Benthos		0.2*		
	Fish muscle		0.3*	0.3	
	Fish liver		0.6*		0.2
Nickel	Barnacles		49	7.7	
	Fouling mat			15	
	Shrimp	17		1.6	
	Plankton	41			
	Benthos		15*		
	Fish muscle	3.0	2.1*	0.8	
	Fish liver		ND*		0.9
Strontium	Barnacles		200	550	
	Fouling mat			2200	
	Shrimp	17		34	
	Benthos		14*		
	Fish muscle	3.5	1.4*	7.5	
	Fish liver		1.5*		4.3
Zinc	Barnacles		160	370	
	Fouling mat			180	
	Shrimp	100		52	
	Plankton	230			
	Benthos		870*		
	Fish muscle	35	110*	18	
	Fish liver		150*		120

Footnotes to TABLE 7:

*Specimens from Platform 288-A, since no sample taken from Platform 296-B.

ND = not detected. Detection limits vary according to metal and are also different in each report. Absence of an entry for a metal indicates that no determination was performed.

References: A, ANDERSON et al. (1977); B, ANDERSON et al. (1979a); C, TILLERY (1980a); D, TILLERY (1980b).

SWARTZ and LEE (1980) have reviewed the somewhat conflicting data concerning the biomagnification of heavy metals. As in the case of studies relating to microbial degradation of hydrocarbons, there is some disparity between the results of laboratory and field experiments. Much valuable information has been gleaned from studies on radioactive zinc-65. Early experiments showed that this metal is taken up rapidly by crustaceans from both food and water but it was later demonstrated that much of it is lost during ecdysis (molting), reducing the potential for biomagnification. An opportunity for studying such processes in the field has been presented by the low-level discharge of radio-nuclides by nuclear reactors: zinc-65 has been traced through a portion of the food web off the Oregon coast (adjacent to the Hanford reactors on the Columbia River) but, again, no unequivocal evidence was obtained for biomagnification.

Studies of other heavy metals have almost invariably confirmed that bioaccumulation takes place, but not biomagnification (PHILLIPS, 1976a,b; GORDON et al., 1980; LOBEL et al., 1982; WINDOM et al., 1982; MURPHY and SPIEGEL, 1982). Evaluation of data for heavy metals in biota collected off the coast of southern California has indicated that only mercury has any propensity for biomagnification, but not to the same extent as DDT and polychlorinated biphenyls (SWARTZ and LEE, 1980). Mercury levels in seafood collected near the Los Angeles County municipal wastewater outfalls, however, were an order of magnitude below the 1-ppm limit set by the Food and Drug Administration for seafood (YOUNG et al., 1981).

3.5.2c Excretion/Depuration. A correlation was found between the accumulation of naphthalene by nine species of planktonic copepod and their dry weight and total lipid content, but there was an exponential loss of naphthalene after the animals were moved to uncontaminated water (HARRIS et al., 1977). In controlled ecosystem studies, naphthalenes were released from oysters (half-life, two days). For anthracene, fluoranthene, benz[a]anthracene, and benzo[a]pyrene, the half-lives for depuration were 3, 5, 9, and 18 days, respectively (LEE et al., 1978). Similar results were obtained for the uptake and depuration of