

**WORKSHOP SERIES No. 5**

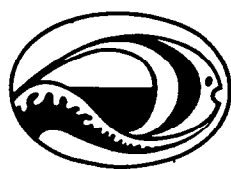
**WORKSHOP ON  
CONTAMINANTS IN  
WATERS OF THE GREAT  
BARRIER REEF**

Proceedings of a Workshop held at Griffith University,  
Brisbane, Australia, 26 May 1984

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## ACKNOWLEDGEMENTS

The Authority acknowledges the valuable contribution made by all workshop participants. The Authority would particularly like to recognise the guidance and expert assistance of the Session Chairmen; Dr. Barry Hart (Heavy Metals), Dr. Des Connell (PCBs and other Organochlorines) and Dr. David Smith (Hydrocarbons), and the Plenary Chairmen; Dr Joe Baker and Dr Alistair Gilmour; in conducting the workshop.

## PREFACE NOTE

This report outlines the proceedings of a workshop which was held at Griffith University on Saturday, 26 May 1984. The workshop was organised, and sponsored under the auspices of the Research and Monitoring program of the Great Barrier Reef Marine Park Authority. It was specifically concerned with the issue of contaminants in waters of the Great Barrier Reef (GBR).

This report sets out the information presented, and issues raised, during the workshop. The proposed follow-up actions by the Authority in relation to the matters raised are also defined.

Requests for further information on any aspect of this report, or the workshop generally, should be addressed to:

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## EXECUTIVE SUMMARY

This report outlines the proceedings and findings of a workshop on contaminants in waters of the Great Barrier Reef (henceforth GBR), held at Griffith University on Saturday, 26th May 1984. The workshop focussed on the three broad contaminant groups of heavy metals, polychlorinated biphenyls (PCBs) and other organochlorines and hydrocarbons.

Table 1 below summarises the broad findings of the workshop with respect to each of the three groups. It is based largely upon the plenary summary prepared by the session Chairman, Dr J. T. Baker.

The workshop participants noted that measured levels of substances within each contaminant group do not pose an immediate threat to human health, individual organisms or the GBR system as a whole. This finding was made subject to the recognition that only limited sampling has been undertaken in waters of the Great Barrier Reef. Measured levels of most contaminants within the reef waters proper are generally close to the lower limits of detection, although in some adjacent coastal waters (particularly harbours), concentrations indicative of low to moderate pollution levels equivalent to those found elsewhere in Australia and overseas, have been recorded.

In attempting to assign priorities to areas of further research, participants noted that other contaminants such as sediments and nutrients were more likely to be of greater concern than the three contaminant groups considered at this workshop. On that basis the five broad priority areas for further research were considered to be (in order):

- a) Sediments, particularly sediment export from mainland rivers and sediment movement within the GBR system and how both influence the GBR system.
- b) Methods for investigating and responding to accidental events and disasters, e.g.. oil spills, toxic chemical releases, and other leakages from grounded vessels.
- c) Effects of agricultural fertilisers and other nutrients exported to the GBR from the mainland.
- d) Effects of pesticides, especially organochlorines.
- e) Ecotoxicity of sub-lethal effects of heavy metals, PCBs and hydrocarbons.

From the workshop, a number of proposals for consideration by the Marine Park Authority have been derived. These include both short and long term actions, although it was noted that no priority response is required by the Great Barrier Reef Marine Park Authority in view of the generally low degree of threat posed by the contaminants considered at the workshop.

TABLE 1: SUMMARY OF WORKSHOP DISCUSSIONS

ISSUE	CONTAMINANT GROUP		
	HEAVY METALS	PCBs AND OTHER ORGANOCHLORINES	HYDROCARBONS
Current Knowledge	.some water sampling .clams are main source of data .some WQC information available	.sampling of diff-species - causes intercalibration problems	.methods used to date adequate
Available Information	.need to collate existing information .more information needed on tin	.Olafson results contrast with Waid/Smillie results .more information on pesticides needed	.generally adequate, but collation would be useful
International Standards	.no comment	.UNEP procedures should be adopted*	.no comment
Identification of Problem	.need for info. on sub-lethal effects .more study of bio-indicators required	.no problem at current levels	.no problem at current levels
Degree of Threat	.no threat to human health or individual organisms .insufficient information to predict effect on total ecosystem	.no problem at current levels .further study on sub-lethal effects desirable	.no problem at current measured levels .threat from oil spills potentially high
Sample Design /Methods	.agreement needed on size/age of specimens and types of organs to be used .stratified sampling recommended	.studies should be reproduceable	.stratification needed
Analytical Techniques	.generally adequate but problem with low levels .stressed need for pure solvents and clear apparatus	.adoption of UNEP procedures desirable .need for test laboratories	.current techniques adequate

Comparative Levels	.generally low	.at lower range of detection	.aliphatics lower than overseas .aromatics much lower but some coastal locations as high as overseas
Types of Pollutants of Concern	.copper, cadmium, zinc, lead, mercury and nickel studied .more information on tin needed	.PCB use declining .more research effort needed on Lindane and pesticides	.oil spills the major input threat
Source of Pollutants	.little reliable information .anthropogenic hard to distinguish from biogenic	.pesticides from mainland agriculture .PCBs from atmosphere (?)	.local sources - resorts, boats, etc
Level of Pollutants	.relatively high in some locations (e.g. Townsville Harbour), but seem low in main reef area	.no high levels, although limited reef-wide data	.no high levels reported, however concentrations elevated in some locations
Fate of Pollutants	.little information .nothing of predictive value	.some biodegradation .compounds persistent-monitoring required	.further study required-particularly in anoxic conditions
Potential Problems	.oil-shale mining on large scale	.inadequate supply of ecotoxicologists	.oil spills from tankers .oilshale mining
Current State of Problem	.localised, but more info on reef-wide distribution needed	.no significant problem, but concern about potential effects on reproduction and photosynthesis	.chronic low level pollution adjacent to resorts

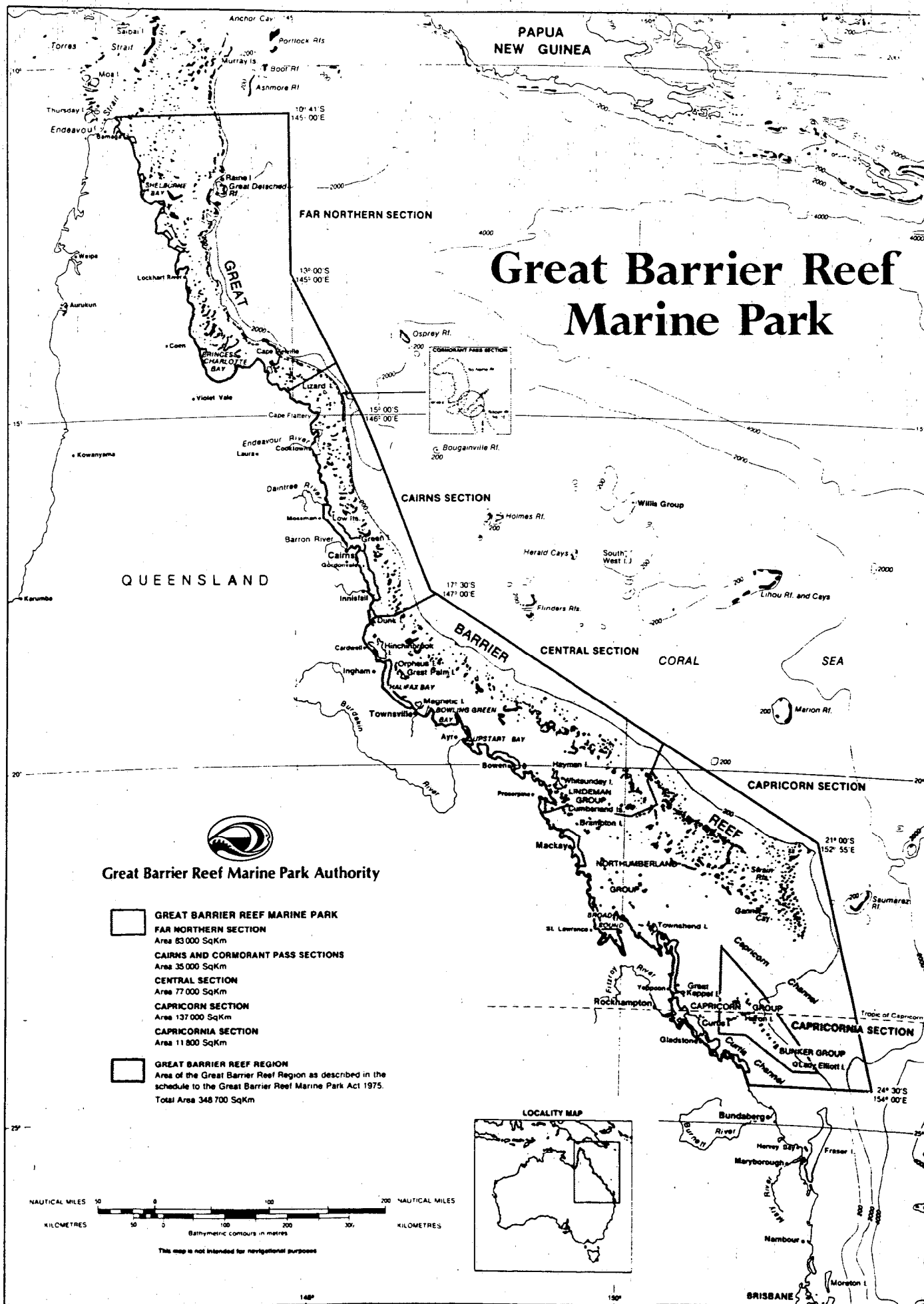
Future  
Directions

- |  |   |   |
|--|---|---|
| .systems approach preferred                            | .systems approach supported                                 | .coordinate chemical and microbiological approaches   |
| .interdisciplinary studies                             | .ecotoxicological training needed                           | .intercalibration exercises between laboratories beneficial   |
| .multi-institutional interaction                       | .standardise procedures using UNEP guidelines (or similar)* | .oil spill counter disaster plan needed   |
| .need to identify "hot spots" for more intensive study | .need M.S.coupled to G-C for analysis                       | .more research on toxic effects of hydrocarbons needed.   |
|  | .multiple analysis of samples more cost-effective           | .water-sediment interface a research need   |
|  | .link with DHAE national monitoring program recommended     | .capability to mobilise scientific effort needed in event of oil spill-post spill assessment also important |

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\* UNEP procedures are the preferred basis for standardisation.





## INTRODUCTION

The staging of a workshop on contaminants in waters of the Great Barrier Reef (GBR) was considered timely in view of both:

- a) reports (e.g. Mackay Mercury, 6/3/84; Age, 28/2/84; Latrobe University Record, February/March 1984) about the discovery of polychlorinated biphenyls (PCBs) in GBR organisms; and
- b) the wide range of contaminant research studies, either recently completed, or in progress, of which the Authority had only limited knowledge.

As a consequence of discussions with researchers engaged in contaminants studies in the GBR Region (outlined in Figure 1), the workshop was focussed on the following contaminant groups:

- a) heavy metals
- b) polychlorinated biphenyls and other organochlorines, and
- c) hydrocarbons

These groups broadly correspond with three of the four contaminant groups addressed in the Australian Musselwatch program (Baker, 1983), the exclusion being radionuclides, which have not been investigated in any detail in the GBR Region to date.

With respect to each of the three contaminant groups, the workshop objectives were defined as:

- 1) To receive and discuss the findings of recent contaminant research studies in the Great Barrier Reef Region, considering in particular:
  - a) sampling design and methods;
  - b) analytical techniques;
  - c) comparative national and international levels and their significance; and
  - d) an evaluation of the degree of threat which the measured levels are believed to pose to organisms and ecosystems of the GBR.
- 2) To determine what critical information deficiencies (if any) exist in relation to our understanding of the source, level and fate of marine contaminants in the GBR Region, and to identify how these could be overcome.

- 3) On the basis of (1) and 2) above, to determine priorities for further research in this field and how further research effort could best be coordinated. This should include consideration of parameter selection; design, techniques and frequency of sampling; analytical methods and intercalibration and how spatial and temporal variability may influence the design of cost-effective research.

Participants in the workshop included researchers who have had direct involvement in contaminant studies in the GBR Region and/or a comprehensive understanding of research issues and methods, and Commonwealth and State Government officers including staff of the Authority. A complete list of all participants is set out in Appendix A.

Appendix B outlines the workshop program. The format of the workshop was intended to enable discussion of each contaminant group and objective at a range of scales. The morning sessions comprised three concurrent small group presentations and discussions. They were followed by two Plenary sessions, the first of which involved outlines of small group discussions and summation of common findings and issues. The second Plenary session expanded to an 'open forum' discussion of broader issues such as monitoring design and research needs, information deficiencies and management priorities.

Throughout the workshop, participants were directed to keep in mind the management relevance and implications of matters under consideration. This control on workshop scope and direction was considered vital if the Authority, as the principal agency responsible for the care and development of the Great Barrier Reef Marine Park (Figure 1), was to receive practical guidance on matters such as the nature and degree of threat which contaminants pose to the ecosystems of the Great Barrier Reef.

Provision was also made, as appropriate, for consideration of broader scientific questions and concerns relating to sampling design and laboratory techniques and intercalibration. These were considered to be important influences on the applicability of research findings to management of the GBR.

## REVIEW OF CONTAMINANTS STATUS

### A: HEAVY METALS

#### Presentations

Two reports on heavy metals studies in the GBR Region were presented to this group.

The first of these was based on studies undertaken by C. Burdon-Jones and G. Denton of James Cook University since 1980. The studies involved the most comprehensive survey of heavy metals undertaken in the GBR Region to date. A copy of their report outline is enclosed in Appendix C (part a).

The second report was by M. Florence of the Division of Energy Chemistry, CSIRO. It focused on the possible effects of mainland oilshale mining in terms of heavy metal sources, levels and exports. An abstract of his report is enclosed in Appendix C (part b).

#### Review Discussions in Relation to Workshop Objectives

##### 1. Sampling Design and Methods

The group considered that the broad scale survey of the GBR Region by Burdon-Jones and Denton was appropriate to the establishment of "baseline" levels. The group noted that such an approach is necessary, at least initially, because of sampling problems such as access, scale and cost.

It was generally agreed that further surveys should move from the broad scale to specific sites. This will also need to involve event sampling rather than routine monitoring, because of the variability of environmental factors affecting metal export, pathways and release in the GBR Region. This approach has been adopted in studies done by Florence and needs to be extended to other areas of the Region if a comprehensive data base, suitable for detailed analysis of long-term trends is to be developed. The group was critical that event sampling was not undertaken at present by responsible agencies. It was noted that the one metal which has been rather neglected so far is tin. Speciation work is likely to be of importance in this respect as certain forms of tin would be precipitated in seawater. Of particular interest would be organic forms of tin, found in and around living organisms.

The possibility of using organisms such as giant clams, e.g. Tridacna crocea, T. maxima is being investigated by Burdon-Jones and Denton at present. This approach has parallels with the Musselwatch program and was supported by the group as a potentially valuable monitoring technique.

## 2. Analytical Techniques

Members suggested that there have traditionally been problems in achieving satisfactory intercalibration with respect to metals analyses. This problem was reported to have been discussed at a recent meeting at Deakin University, where it was observed that improved equipment and analytical methods have had a dramatic effect on the comparative metal levels recorded in some longer term studies. Examples of increasing metal levels recorded during some studies, suddenly declining, due to a change in laboratory analysis methods were quoted.

In GBR studies, problems associated with the accurate measurement of very low levels of metals have been noted. However, it was generally agreed that the laboratory methods and analytical techniques employed to date have been satisfactory. Analytical methods have been verified by reference to international (NBS) standards, and more recently, by participation in an IOC/GEMS intercalibration exercise.

## 3. Levels and Significance

The measured levels of various metals, as recorded by Burdon-Jones and Denton throughout the GBR Region, are reproduced in Appendix C.

Group members generally agreed that the levels recorded in waters of the GBR are low compared with concentrations recorded elsewhere in Australia and overseas. Higher levels of most metals were generally confined to the coastal areas visited. Not surprisingly, higher levels of zinc, copper, cadmium and lead were found in locations such as Townsville Harbour. Those levels are, however, only indicative of low to moderate pollution compared to levels recorded elsewhere in Australia and overseas.

Difficulties were noted with respect to separating naturally occurring levels of various metals, from those which may have been influenced by low level human activity. This problem is apparently most pronounced in and around "inshore" reef areas particularly those lying within close proximity to coastal towns and major estuaries.

Participants noted that there has been no sampling to date, north of Lizard Island. It was considered that more remote areas of the GBR are important bases for comparison, and thus further sampling is required. The group indicated a need to consider the OK Tedi project in New Guinea, and its possible effects on waters of the northern GBR.

#### 4. Threat

The group considered that the measured levels pose little threat to human health. In terms of the long-term health of the GBR system, members indicated that uncertainties associated with sub-lethal effects, bio-magnification and pathway processes make detailed assessment of the degree of threat difficult. Concern was expressed about the threat posed by a potential increase in industrial and mining projects which may involve metal discharges. A suggestion was made that any expansion of potential sources of metals in the coastal zone adjacent to the GBR should be monitored in view of this.

During the discussion on heavy metal pollution, some concern was expressed about the Ok Tedi project in New Guinea. The group noted that accidental discharges from this mine could represent a threat to the ecosystems of the northern section of the Great Barrier Reef.

#### 5. Information Deficiencies

As noted above, the group was particularly concerned about the lack of information on the processes of mobilisation and movement of metals within the GBR system and their fate. A need was seen for further studies which utilise a systems approach to ecotoxicological aspects of metals contamination.

Apart from these, data on specific sites and relevant to specific events (e.g. flood discharges from the Herbert River and the extent of metal export from tin mining areas) were seen as being a critical information gap at present. Such data would enhance the capacity for interpolation and assessment of trends derived from the existing information.

#### 6. Further Research

Apart from the research needs arising from the points raised in (5) above, the group considered it would be opportune to:

- . collate all existing data and information on metals within the GBR Region and estimate the total amount of metals entering the system presently; and
- . monitor land use activities in the coastal zone, seeking to identify existing or future possible metals sources; and
- . undertake further sampling in remote areas of the GBR (particularly north of Lizard Island).

The group also concluded that a "total system" approach be adopted in future studies of the GBR Region, thus reinforcing specific comments on sample design, methods and coverage.

#### B: PCBs AND OTHER ORGANOCHLORINES

##### Presentations

Four reports on PCBs and organochlorines studies relevant to the GBR Region, or to techniques for analysis, were presented to this group. Copies of each report outline are enclosed in Appendix D.

The first was by R. Smillie of Latrobe University who outlined recent research, undertaken in conjunction with J. Waid, into PCB levels in reef organisms. This study was part of a broader survey of PCB contamination of Australian marine biota. It also involved the incidental detection of other organochlorines.

This was followed by a report by D. Hawker of Griffith University who discussed the chemistry, characterisation and analysis of PCBs. The report was based largely on experiences with the use of GC and GC/MS facilities at Griffith University.

G. Shaw of the Queensland Government Chemical Laboratories outlined a range of important considerations in surveys of organochlorines, particularly sampling techniques and analysis procedures. The presentation concluded with a brief reiteration of results from an earlier study of PCBs in the Brisbane River which was considered an appropriate basis for comparison with GBR survey data, due to its comprehensive nature.

The final speaker in the group was D. Connell of Griffith University, who discussed aspects of the behaviour of lipophilic compounds in aquatic ecosystems. He stressed the importance of recognising environmental factors affecting uptake and the use of coefficient factors as a means of predicting uptake. His discussion was based on a range of studies, including hydrocarbon surveys in the GBR Region and the PCB survey of the Brisbane River. The outline of his report sets out the objectives of his recent research in this area.

## Review Discussions in Relation to Workshop Objectives

### 1. Sampling Design and Methods

It was generally agreed that despite the small number of samples obtained during the study by Smillie and Waid, the results obtained were an indication of the nature and degree of seriousness of PCB contamination in the GBR Region. A contrast pointed out by the researchers in this respect was that the earlier (1976) survey by Olafson was more comprehensive, and yet no PCBs were detected.

Group members drew attention to the problems associated with sampling in the GBR Region, such as difficulties associated with access, scale (the spatial extent of the reef), and cost. It was considered that these could, however, be at least partially resolved by improved coordination of scientific collecting activities and cooperative use of samples and collection facilities.

Group members agreed that two key elements of any future sampling design should be stratification and reproducibility. The former is important with respect to defining contaminant sources and an appropriate sample scale. It is especially intended to facilitate sampling in reef areas of contrasting characteristics. A suggestion was made that proximity to urban centres be one criterion for contrast with "baseline" levels (as obtained from measurements in remote, undisturbed areas of the GBR such as the Far Northern Section of the Swain Reef complex). The recent findings of Waid and Smillie suggest, however, that few "pristine" areas may exist in the GBR Region, because the influence of non-point sources derived from atmospheric and oceanic circulation on a global scale.

Survey reproducibility was considered to be of importance, in terms of measuring variations over time. Suggestions were made that GBR sampling should also form part of a national network, such as that being investigated at present by the Victoria Marine Science Laboratories, under contract to the Department of Home Affairs and Environment.

### 2. Analytical Techniques

Laboratory procedures and analytical techniques for the detection and measurement of PCBs and organochlorine substances generally were considered to be important questions, particularly in relation to sample intercalibration and reproducibility. Group members also questioned the interpretation of Gas Chromatograph (GC) peaks and the validity of GC use alone, as an analytical tool for PCB detection.



Members agreed with the suggestion of J. Baker that in accordance with UNEP (1982), GC not be considered an appropriate sole analytical tool in future studies. It was suggested that a Mass Spectrometer (MS) be used as the standardising analytical technique, although it was recognised that access to MS in Australia is limited in some areas at present.

### 3. Levels and Significance

The levels of PCBs detected in GBR organisms by Waid and Smillie are very low compared to surveys undertaken both in Australia (e.g. Shaw and Connell, 1980) and overseas. As shown in Appendix D, the highest concentrations were found to occur in sharks (range 6.5 to 85.8 ng PCB g<sup>-1</sup> WW, average 35.8 ng g<sup>-1</sup>).

Four main points of concern remain in relation to the findings, namely:

- . that there may have been a change in PCB levels since Olafson's survey in 1976;
- . PCBs may act synergistically with other chemicals;
- . although the measured levels are low, PCBs bioaccumulate through the food chain and as a consequence higher order organisms may be at risk; and (related to this)
- . global production of PCBs has been substantially reduced, but large quantities remain, and PCBs are very persistent

A further possible point of concern noted by Smillie was the suspected presence of photo-dieldrin in some of the samples he obtained from the GBR. This substance may have an adverse effect on photosynthesis. Dieldrin was also detected by Olafson (1978). Confirmation of its presence and current levels requires further study.

### 4. Threat

The group agreed that the measured levels of PCBs do not threaten the functioning or integrity of the GBR system at large. The group, was, however, concerned on the possible long-term risk to the GBR system of organochlorine pesticide used in mainland farming operations (see 5 below).

## 5. Information Deficiencies

Concern was expressed about the lack of knowledge of sources of PCBs, levels of use of organochlorine pesticides on the mainland, contaminant pathways in ecosystems of the GBR and possible sub-lethal effects of organochlorines on photosynthesis and reproduction.

## 6. Further Research

The need for further monitoring of PCBs and other organochlorines in the GBR Region was discussed at length. The group concluded that in view of the perceived low degree of threat from PCBs and the existence of baseline information from the Waid and Smillie study, only measurements which are incidental to other analyses be undertaken in the near future. The group did, however, agree that the Authority should seek information on the levels and areas of organochlorine usage. A suggestion was made that the Queensland Water Quality Council and the Bureau of Sugar and Experimental Stations could be valuable contacts in this regard.

It was suggested that the design and implementation of a monitoring system can remain a low priority while the objectives and program for a broader scale GBR Marine Park monitoring system are developed.

Group members did, however, consider that organochlorine pesticides should be given more attention. A desk-top study on the level of organochlorine/pesticide use in mainland agriculture was recommended as a priority for further study. The study should attempt to evaluate, on a region by region basis, trends in the useage of organochlorine pesticides in coastal areas adjacent to the Great Barrier Reef Marine Park. This may then necessitate a baseline survey of organochlorine levels in reef organisms coupled with a study of their ecotoxicological effects.

The group also expressed its concern about the lack of trained scientists in the area of ecotoxicology in Australia. A comparison with the other OECD countries by D. Connell indicated that Australia lags well behind in this respect.

## C: HYDROCARBONS

### Presentations

Four reports on hydrocarbon studies in the GBR Region were presented to this group. The first of these was by M. Coates from Griffith University. His studies in the GBR Region have involved analysis of alkane and mono-olefin hydrocarbons in GBR organisms and environment. A summary of his report is presented in Appendix E (part a).

The second report was by J. D. Smith of Melbourne University. His research in the GBR Region has been centred on the distribution of polycyclic aromatic hydrocarbons in reef ecosystems. A summary of his report is presented in Appendix E (part b).

B. Johns of Melbourne University outlined his work on surveys of hydrocarbons, which in the GBR Region have been mainly focussed on mangrove environments. N. Millis, also of Melbourne University, outlined her research in the field of quantification of oil-utilising bacteria. This research is of considerable relevance to understanding oil degradation processes.

### Review Discussions in Relation to Workshop Objectives

1. Despite the general problems of scale, access, cost and the like which are typically associated with GBR studies, the group agreed that the research undertaken to date has involved sufficient sampling to provide a reasonable assessment of the level of hydrocarbon contamination in key areas of the GBR.

Most studies undertaken to date have sought to identify whether hydrocarbon compounds measured were of biogenic or anthropogenic origin. The studies have therefore yielded data on "baseline" hydrocarbon levels, and levels which have been raised or altered by human activity in the GBR Region.

#### 2. Analytical Techniques

These were generally considered to be adequate by the group, although intercalibration remains a problem. The group also noted that there was a need for closer integration of chemical and microbiological techniques and levels of analysis.

### 3. Levels and Significance

The studies by Coates and Smith indicated that only trace amounts of various hydrocarbon compounds occur in areas of the GBR which have not been directly influenced by human activities. Highest concentrations were found around harbours, areas visited by boats and in waters adjacent to tourist resorts.

Levels measured in Gladstone and Townsville harbour sediments were by far the highest, and they were comparable to levels reported in other harbours around the world. Hydrocarbon levels detected in reef areas were extremely low, as would be expected where the dominant source is biogenic.

### 4. Threat

The group identified two time frames of threat associated with hydrocarbons. The present level of threat is very low due to the low intensity of hydrocarbon use in the immediate environs of the GBR. The most common point source was identified as spillages from boats. Mainland sources are not considered to be a major threat because of the influence of prevailing wind and current patterns. These combine to keep possible mainland inputs away from the reef proper, although further knowledge of pathways may be necessary before the potential threat from this source can be completely discounted in all areas of the GBR.

Two possible future threats to the GBR in terms of hydrocarbon pollution are oil shale mining and oil spills. The group agreed that the former is of low concern because of the long lead time involved in oil shale production and the many uncertainties associated with, for example, possible levels and pathways of hydrocarbons from this source.

Members considered the possibility of an oil spill to be of high concern, and expressed concern that an oil spill contingency plan is not yet operational for the Great Barrier Reef Region. (At the time of preparation of this document, a contingency plan [REEFPLAN] was at an advanced stage of preparation, and was under review by staff of the Great Barrier Reef Marine Park Authority.)

### 5. Information Deficiencies

The group identified several information deficiencies in relation to hydrocarbon pollution. These include a need for:

- . further long-term data on hydrocarbon levels near point sources;
- . improved intercalibration capacity;

- . better understanding of the ecotoxicological effects of pure compounds on sensitive species;
- . greater understanding of the fate of hydrocarbons after an oil spill, such as the spatial extent of the effects of oil dispersion, degradation (including bacterial action) and transfer to the food chain; and
- . more knowledge of the fate of detergents (used in any oil spill clean-up action).

6. Further Research

The group considered that the priorities for further research in this area are (not in order):

- . improved intercalibration between test laboratories
- . hazard assessment, focussed on the risk of an oil spill and assessment of factors influencing response (e.g. how, when, where, oil type etc.);
- . development of an oil cleanup plan, including determination of the scale of monitoring needed for waters, biota and sediment after an oil spill; and
- . improved coordination of chemical and microbiological approaches to hydrocarbon analysis

## MAIN ISSUES AND CONCLUSIONS

Despite the separate and distinctive topics of discussion by each group, during the reports to the first plenary session by each small group discussion leader, and subsequent open-forum discussions a number of common issues and concerns became apparent. With respect to the workshop objectives, they may be categorised as:

### 1. Sampling Design and Methods

- . There are problems of sample design due to the scale of the GBR Region, access difficulties and cost (both time and funds).
- . There is scope for improved coordination of sampling effort.
- . There is a need for GBR contaminant sampling to be stratified (to detect human influences), and replicable (for monitoring change over time).
- . Areas of the GBR Region should be sampled as part of a national monitoring program if comparison of data obtained is to be meaningful.
- . Other than for scientific investigations into e.g. the presence or absence of specific compounds, any future routine sampling undertaken as part of a monitoring program will require the responsible agency to clearly identify its program objectives if a valid sample design is to be employed.
- . Because the goal of most data acquisition programs is to enhance system understanding and/or improve predictive capacity, sample data should be centrally collated, and, where practical linked to the needs and applications of "system models", such as those being developed at the Australian Institute of Marine Science.

### 2. Analytical Techniques

- . Problems of intercalibration are common, but are being overcome.
- . It is highly desirable to standardise field measurement and laboratory procedures (UNEP procedures seem to be applicable in many instances).

3. Levels and Significance

- . Levels of the three contaminant groups in the GBR proper are generally in the lower range of detection.
- . The highest levels have been recorded in coastal locations, particularly adjacent to major urban centres. In such cases, they are comparable to those found in similar locations elsewhere in Australia and overseas.

4. Threat

- . None of the measured levels of any of the three contaminant groups pose a known threat to the integrity or functioning of the GBR, nor to human health, in the short term.
- . Longer term threats which these contaminants may pose to the reef are considered to be low at this stage. However, participants agree that the situation with respect to each group needs to be monitored and supplementary research conducted on related matters such as the ecotoxicological effects of sub-lethal concentrations, bio-accumulation and pathway processes before any long-term threat to the stability or integrity of the GBR from local or global sources can be fully discounted.

5. Information deficiencies

- . The ecotoxicological effects of sub-lethal concentrations of compounds within each contaminant group require further investigation particularly in relation to major processes such as reproduction and photosynthesis.
- . Research into the processes of contaminant mobilisation, entry, movement and accumulation within the GBR system is also required.
- . While it is possible to define the likely origin of most contaminants in the GBR Region, further information is needed on the extent and location of contaminant use, amounts of contaminants used and pathways to the GBR (particularly less well understood processes, such as atmospheric entrainment and fallout).
- . Some further attention needs to be given to contaminant levels in more remote areas of the GBR such as the Far Northern Section of the GBRMP and the Swains Reef complex.

6. Further Research

Major areas for further research effort which were identified by participants with respect to the three contaminant groups considered are:

- . Ecotoxicological effects of sub-lethal concentrations.
- . A need to focus on "hot spots" (i.e. specific areas and/or events of pollutant concern) for monitoring purposes.
- . The potential for using agreed indicator species.
- . The use of organochlorine pesticides in mainland agriculture.
- . Microbiological processes in anoxic conditions.
- . Disaster control and containment (or other response, as appropriate in the event of e.g., an oil spill).

A number of more general points which were raised in the open-forum discussion which are relevant to further research needs included:

- . The possibility of using predictive models as an alternative to monitoring. This was debated, however, on the grounds that it would require more information than is currently available, and in addition, it would often not reveal a perturbation until after it had occurred (in which case a management response may be too late). An alternative proposal supported by most participants, is to link predictive models with a systems approach and monitor localities from where a change in the system may be induced and/or target species/systems which may rapidly indicate or respond to environmental change.
- . The potential for using selected organisms either for monitoring purposes or as stress indicators, or both. The potential use of clams (*Tridacna* spp.) is already under investigation, although further research into their suitability is considered necessary. There was also a suggestion that a much wider range of organisms (e.g. bacteria) could be used



- . In order to avoid reactive management of contaminant-related problems, the Authority was advised to anticipate likely problem areas ("hot spots"). Participants were told this is already done to a large extent, but could be improved through closer inter-agency cooperation.
- . A dichotomy between scientific information needs and management information needs in the GBR Region was drawn. While the different objectives of both were recognised by most participants, there was general agreement on the need for close coordination and integration of both, where possible.
- . The means of enforcing any necessary pollution controls were questioned. Participants noted that effective control requires close cooperation between Queensland agencies and the Authority.

## MANAGEMENT RESPONSE

### Short Term

On the basis of the information provided at the workshop, the following actions will be proposed to the Authority as priority short term response:

- 1) prepare, and circulate, a report of the proceedings of the workshop to all participants, and to place copies in the GBRMPA library and a description on the REEF database;
- 2) arrange to have undertaken, a study on the types of pesticides and other major organochlorine compounds in use in coastal areas adjacent to the GBR, and tabulate (if possible) the amounts of each compound used and where;
- 3) assist researchers involved in contaminant studies in the GBR with information on the GBR, and to assist in the coordination of their research activities and methods as appropriate;
- 4) incorporate the information and conclusions from this workshop into the background design information for the Great Barrier Reef Marine Park Authority monitoring network (in preparation); and
- 5) seek the completion of an oil spill cleanup plan for the GBR Region as a matter of urgency.

### Long-Term

While the measured levels of the contaminants discussed at this workshop do not appear to pose an immediate threat to the GBR system, it was noted that this situation could change over the longer term.

A range of possible options exist which would ensure that the Authority is kept informed of the status of contaminants in the GBR Region. They include:

- a) liaise with researchers engaged in contaminant studies in the GBR Region, monitoring of study results, and facilitate and coordinate research activities as appropriate;

- b) liaise with Queensland Government agencies in monitoring the establishment of new industries or facilities and changing land use activities in coastal and offshore zones of the GBR Region and evaluate their potential to affect/alter contaminant levels;
- c) undertake, or encourage (depending on the final design of the GBRMP Monitoring Network) periodic monitoring of contaminant levels in the GBR Region;
- d) encourage, and assist, as appropriate, further research into the ecotoxicological aspects of contaminants in the GBR area;
- e) support the proposal for a national contaminants monitoring network (currently being coordinated by the Commonwealth Department of Home Affairs and Environment); and
- f) facilitate the exchange of information between researchers and research users through mechanisms such as the REEF database, Australian Marine Research in Progress (AMRIP) and the Aquatic Research Electronic Bulletin (AQREB) (currently under development.)

These options will be submitted to the Marine Park Authority for evaluation and implementation consistent with the other long-term policies and procedures of the Authority.

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LIST OF PARTICIPANTS

<u>Name</u>	<u>Affiliation</u>	<u>Small Group</u>
AIREY, Dr D.	CSIRO	A
BAKER, Dr J.	GBRMPA and James Cook University	C
BECKMANN, Dr T.	Qld Gov Chem Lab	-
BOWEN, Dr R.	NSW Dept Agriculture	B
BREMNER, Dr A.	Marine Science Laboratories	A
BURDON-JONES, Prof C.	James Cook University	A
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CONNELL, Dr D.*	Griffith University	B
COSSER, Mr P.	Qld WQC	-
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DENTON, Dr G.*	James Cook University	A
DUTTON, Mr I.	GBRMPA (Workshop Secretary)	B
FLORENCE, Dr M.*	CSIRO	A
GAWNE, Dr K.	Deakin University	A
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SOLLY Mr W.	Brisbane City Council	B
SWAN, Dr J.	AMSTAC	-
THOMSON, Dr J.	Tasmanian Fisheries Authority	A
WAID, Prof J.	La Trobe University	B

\*denotes speaker in Small Group Session

PROGRAM

9.00-9.15	Registration (room 0.04, Science Building)
9.15-9.30	Workshop Opening by Mr G Kelleher, Chairman, GBRMPA
9.30-10.30	Small Group Discussion
10.30-11.00	MORNING TEA
11.00-12.30	Small Group Discussion
12.30-14.00	LUNCH
14.00-15.00	Plenary Session - Chairman, Dr J.T. Baker (including presentations by small group discussion leaders)
15.00-15.30	AFTERNOON TEA (Hub Dining Room)
15.30-17.00	Plenary Session - Chairman, Dr A.J. Gilmour
17.00-1730	Workshop Close
EVENING	DINNER

\* Small Group Discussions involved participants in review and discussion of marine contaminants according to the following group divisions:

GROUP A: Heavy Metals

- . Dr Barry Hart - discussion leader
- . Dr Wendy Craik - rapporteur

GROUP B: PCBs and Organochlorines

- . Dr Des Connell - discussion leader
- . Mr Ian Dutton - rapporteur

GROUP C: Hydrocarbons

- . Dr David Smith - Discussion Leader
- . Dr Peter Murphy - rapporteur

METALS IN MARINE ORGANISMS FROM  
THE GREAT BARRIER REEF

STUDY OUTLINE  
(1980-83)

---

C. BURDON-JONES  
&  
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METALS IN MARINE ORGANISMS FROM THE GREAT BARRIER REEF: STUDY OUTLINE

1. OBJECTIVES

- i. Establish base line levels of Zn, Cu, Cd, Ni, Pb & Hg in a wide range of marine organisms from within the Great Barrier Reef Province.
- ii. Establish regional and seasonal variations of the above metals in selected species showing high bio-indicator potential.

2. SAMPLING METHODS

1. Base line Survey

- a) Transect sampling in northern central and southern regions of the Great Barrier Reef (Fig. 1).
- b) Single visit to each location.
- c) Dominant species at various trophic levels collected (Table 1).
- d) Attention given to species of direct or potential economic value.
- e) Number collected dependent upon availability of species, time and manpower.
- f) Attention given to size of the organism, position on the shore or in the water column, and proximity to likely source of trace metal contamination.

2. Seasonal Survey

- a) Sampling sites visited at 3 monthly intervals.
- b) All stations visited within 3-4 weeks.
- c) All biota collected from subtidal sites thereby minimising variations in trace metals associated with temperature and salinity fluctuations.
- d) 2-3 kg/site of alga collected over wide area; bulk homogenised and subsampled.
- e) Bivalves selected within specific size ranges. Usually 10 individuals were sufficient to permit the detection of 50-100% change in mean metal levels<sup>1</sup>. Analysed individually.



- f) At least 20 fish/site were examined on each occasion. Sizes ranged from 17.5 - 37 cm. Analysed individually.
- g) Water samples (2/site) collected 48 hours apart. Each divided into 4 replicates for individual analysis.

### 3. ANALYTICAL METHODS

#### 1. Biota

- a) Hg analysis: approximately 1 g wet tissue weight/10 ml  $\text{HNO}_3:\text{H}_2\text{SO}_4$  (2:1). Boiling water bath (4 hr). Diluted to 100 ml  $\rightarrow$  flameless AAS<sup>2</sup> using the syringe technique<sup>3</sup>.
- b) Zn, Cu, Cd, Ni & Pb analysis: approximately 1 g dry weight/10 ml silica distilled  $\text{HNO}_3$ . Hot plate (2-3 days) at 135° maximum. Evaporated to dryness and further digested with  $\text{HNO}_3:\text{HClO}_4$  (1:1) made up to volume  $\rightarrow$  AAS.

#### 2. Water

- a) Hg analysis: Reduction of  $\text{Hg}^{2+} \rightarrow \text{Hg}^0$  with 20%  $\text{SnCl}_2$  in 50%  $\text{HCl}$  (25 ml/2 litre unfiltered sample) and subsequent trapping in 25 ml 2%  $\text{KMnO}_4$  + 50%  $\text{H}_2\text{SO}_4$  (1:1)<sup>4</sup>  $\rightarrow$  flameless AAS.
- b) Zn, Cu, Cd, Ni and Pb analysis: Preconcentrated from 0.45  $\mu\text{m}$  filtered, 3.5 litre samples on 3 x 1.5 column cm of Chelex 100 ( $\text{NH}_4^+$  form) at pH<sup>~</sup>8.0. Final volume for analysis - 5 ml.

### 4. STANDARDS AND INTERCALIBRATIONS

- a) Standards: from 1000 ppm stock solutions (BDH).
- b) Substandards for Hg in 20%  $\text{HNO}_3$  + 0.05%  $\text{K}_2\text{Cr}_2\text{O}_7$ .<sup>5</sup>
- c) For water analysis Hg standards in 2%  $\text{KMnO}_4$  + 50%  $\text{H}_2\text{SO}_4$ .
- d) Zn, Cu, Cd, Ni and Pb standards in 10%  $\text{HNO}_3$ .
- e) Instrument calibrated by standard additions (where matrix effects suspected) and by reference to standard solutions.
- f) Reagent blanks run with each batch of samples (1/25).
- g) N.B.S. reference materials run on a regular basis.
- h) Recoveries from new materials evaluated from spiked samples.
- i) Above methods varified by intercalibration exercise initiated by Dept. of Home Affairs & Environment and more recently by I.O.C.

5. PROBLEMS ASSOCIATED WITH:

- a) Confinement of samples to within a specific size range re. intersite variations in growth/size/age.
- b) Synchronous sampling re. weight changes associated with intersite variations in reproductive development.
- c) Statistics re. treatment of outliers, sample size estimates from non-normally distributed data.

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- <sup>3</sup> Stainton, M.P. Anal. Chem., 43, 625-7 (1971).
- <sup>4</sup> Topping, G. & J.M. Pirie. Anal. chim. Acta., 62, 200-3 (1972).
- <sup>5</sup> Feldman, C. Anal. Chem., 46, 99-102 (1974).

FIG. 1 SAMPLING LOCATIONS VISITED <sup>26</sup> ALONG THE GREAT BARRIER REEF

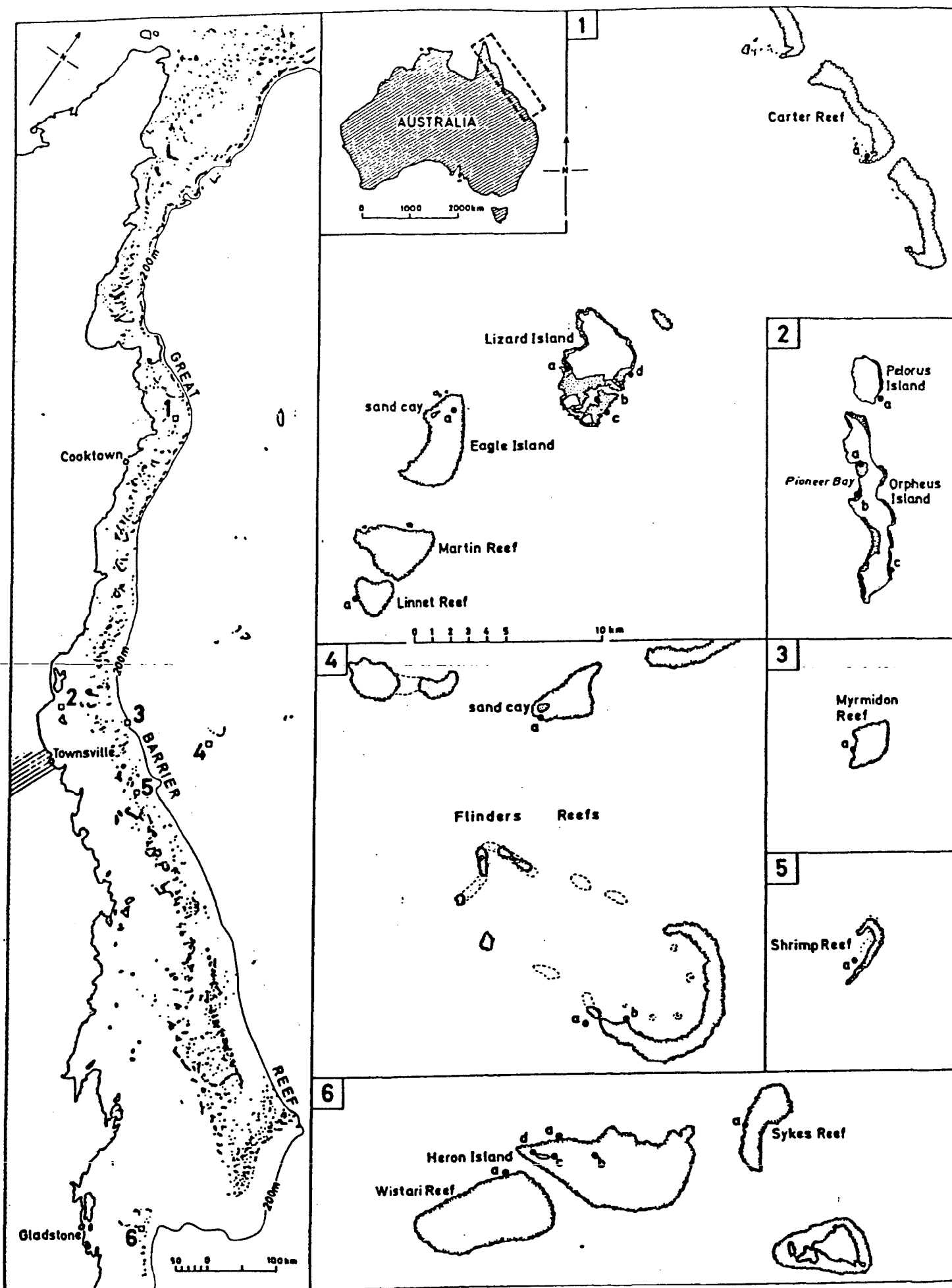


TABLE 1: RESEARCH SUMMARY

1. BASE LINE SURVEY (1980-81)

Three Stations selected in each of the northern central and southern sectors of the Great Barrier Reef. Wide range of marine organisms collected. Analyses for Zn, Cu, Cd, Ni, Pb, Hg.

BIOTIC COMPONENTS EXAMINED

ALGAE

Phaeophyceae	:	13 species
Rhodophyceae	:	15 species
Chlorophyceae	:	20 species
Cyanophyceae	:	1 species

COELENTERATES

Alcyonaria	:	4 species
Madrepora	:	3 species

ECHINODERMS

Holothuroidea	:	1 species
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MOLLUSCS

Bivalvia	:	17 species
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FISH

Osteichthys	:	47 species
Chondrichthys	:	3 species

ABIOTIC COMPONENTS EXAMINED

SEAWATER

Surface samples: top 10-20 cm

SEDIMENTS

Surface samples: top 1-2 cm

2. SEASONAL SURVEY (1982-83)

One Station selected in each of the northern, central and southern sectors of the Great Barrier Reef. Visited at 3 monthly intervals. Species showing high bioindicator potential selected for study. Metals examined as above.

BIOTIC COMPONENTS EXAMINED

ALGA

Chlorophyceae	:	<i>Chlorodesmis fastigiata</i> : whole plant less holdfast analysed
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TABLE 1: RESEARCH SUMMARY (CONTD.)

COELENTERATES

Alcyonaria : *Sarcophyton* sp. (soft coral): capitulum  
periphery analysed

MOLLUSCS

Bivalvia : *Tridacna maxima* (giant clam): individual tissues  
analysed  
: *Tridacna crocea* (giant clam): individual tissues  
analysed  
: *Septifer bilocularis* (deck mussel): whole flesh  
analysed  
: *Chama iostoma* (jewel box oyster): whole flesh  
analysed

FISH

Osteichthys : *Lutjanus carponotatus*\* (snapper): muscle & liver  
analysed

ABIOTIC COMPONENTS EXAMINED

SEAWATER

Surface samples: top 10-20 cm

\* Analysed for mercury only.

(RESULTS)

TABLE 2

COMPARATIVE ANALYSIS OF DATA

1. Surface Seawater (range of means: µg/l)

Study	Location	Zn	Cu	Cd	Ni	Pb	Hg
Present Study	Great Barrier Reef	0.03-0.35	0.12-0.18	<0.01-0.06	0.07-0.16	<0.06-<0.06	<0.001-0.005*
Present Study	Townsville Harbour	12.5-13.9	4.2-4.4	0.13-0.13	0.38-0.42	0.50-0.51	0.006-0.012
Literature (post 1975)	Open Ocean	0.006-0.030	0.05-0.21	<0.001-0.019	0.10-0.35	0.015	0.004-0.018
Literature " "	Nearshore waters	0.82-4.9	0.16-1.1	0.019-0.22	0.23-0.50	0.005-0.93	0.008-0.014
Literature " "	Polluted waters	6.7-285	1.5-16	0.43-3.0	1.91-11	1.4-9.0	0.030-0.034

\* inorganic Hg only; other data for total Hg

(RESULTS)      TABLE 3      COMPARATIVE ANALYSIS OF DATA

2. Algae (µg/g dry wt)

Study	Group	Location	Zn	Cu	Cd	Ni	Pb	Hg
Present study	Phaeophyta	Gt. Barrier Reef	1.27-10.32	0.74-3.50	0.21-0.60	0.61-4.80	<0.5-4.98	0.012-0.320
"	"	Rhodophyta	"	1.16-16.02	1.19-5.62	0.21-2.24	0.72-36.85	0.010-0.167
"	"	Chlorophyta	"	0.27-17.01	1.02-6.21	0.08-1.71	0.41-16.09	<0.006-0.246
"	"	Cyanophyta	"	2.01-17.06	1.32-7.17	0.16-1.08	12.31-19.60	0.036-0.170
Literature	Phaeophyta (related tropical sp)		3.7-210	1.4-49.74	<0.2-13.82	<0.3-32.0	<0.4-108	0.005-1.025
"	Rhodophyta		14.2-60.45	trace-80.41	ND-8.40	<0.5-13.62	0.59-16.04	0.078-0.125
"	Chlorophyta		3.73-71.97	1.20-12.6	<0.10-10.28	<0.5-18.33	ND-41.12	ND-0.282
"	Phaeophyta (temperate species)		2.5-3700	3.0-240	0.13-31.4	4.1-29.6	0.7-202	0.05-20.0
"	Rhodophyta		24-75	3.0-8.0	0.36-0.86	-	-	0.07-3.031
"	Chlorophyta		2.2-1820	5.5-110	0.10-13.0	0.24-33	4-1200	0.128-25.537

ND = not detectable

(RESULTS)

TABLE 4

COMPARATIVE ANALYSIS OF DATA

3. Fish Muscle ( $\mu\text{g/g}$  dry wt)

Study	Group	Location	Zn	Cu	Cd	Ni	Pb	Hg*
Present study	Osteichthys	Gt. Barrier Reef	4.27-41.76	0.47-2.39	<0.10-<0.10	<0.3-<0.3	<0.8-<0.8	<0.002-1.132
"	Chondrichthys	"	10.20-34.59	0.63-1.26	<0.06-0.33	<0.3-<0.3	<0.8-<0.8	0.09-1.941
Literature	Osteichthys (tropical species)		3.2-125	0.70-32.5	0.09-0.44	<0.2-1.2	0.13-2.4	0.003-5.70
"	Chondrichthys	"	17.6-18.0	15.8-23.2	-	-	-	0.03-4.92
"	Osteichthys (temperate species)		1.20-431	0.13-27.19	0.004-1.3	0.04-10.8	0.17-15.0	0.01-2.40
"	Chondrichthys	"	8-61	ND-6.1	<0.05-3.2	<0.9	ND-7.0	0.01-2.19

\*  $\mu\text{g/g}$  wet wt; ND = not detectable



(RESULTS)                      TABLE 5                      COMPARATIVE ANALYSIS OF DATA

4. Selected Species of Bivalves (µg/g dry wt)

Study	Group	Location	Zn	Cu	Cd	Ni	Pb	Hg*
<u>MUSSELS</u>								
Present	<i>Septifer bilocularis</i>	Gt. Barrier Reef	57.19-89.11	5.28-8.93	4.61-15.60	1.79-2.64	<0.81-<0.83	0.004-0.023
a	<i>S. virgatus</i>	Hong Kong waters	56.4-114	10.1-54.4	-	12-46	-	-
<u>OYSTERS</u>								
Present	<i>Saccostrea amasa</i>	Heron Is. (GBR)	54.42-130	33.10-189	2.64-5.47	0.49-1.74	<0.49-<0.71	0.015-0.019
b	"	T'ville Harbour	1916-9073	296-1775	0.90-3.90	<0.20-1.80	<0.20-1.30	-
b	<i>S. cucullata</i>	"	2577-8840	449-1423	1.00-3.50	<0.30-2.80	<0.30-2.30	-
c	"	NSW Estuaries	430-4716	19.7-326	0.54-7.09	-	1.6-10.0	-
<u>GIANT CLAMS**</u>								
Present	<i>T. maxima</i>	Lizard Island lagoon (GBR)	0.90-71.6	2.78-4.14	0.54-14.73	428-1700	8.49-21.59	0.179-0.521
"	"	Orpheus Is. (GBR)	51.63-454	1.71-39.67	6.22-70.15	629-1699	31.80-83.46	0.382-1.260
"	"	Heron Is. (GBR)	2.65-15.10	2.67-3.86	2.48-22.97	399-1353	9.03-26.76	0.305-0.503
"	<i>T. crocea</i>	Lizard Is. lagoon (GBR)	4.89-218	2.51-5.02	1.80-60.59	1176-3089	20.30-59.41	0.297-0.745
"	"	Orpheus Is. (GBR)	37.0-1287	3.10-6.08	9.34-100	799-2465	78.80-143	0.485-1.433

\* = µg/g wet wt.

\*\* = kidney tissue only

a Phillips & Yim. Mar. Ecol. Prog. Ser 6: 285-293 (1981)

b Burdon-Jones et al. unpublished data

c Mackay et al. Aust. J. mar. Freshwat. Res. 26: 31-46 (1975)

POTENTIAL ENVIRONMENTAL PROBLEMS FROM  
THE MINING AND PROCESSING OF OIL SHALE

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Australia possesses extensive oil shale deposits, many of them situated on the Queensland coast between Gladstone and Bowen. The Rundle deposit, near Gladstone has a total reserve of  $2 \times 10^9$  barrels of oil, while the Condor field, near Bowen has an estimated reserve of  $8.5 \times 10^9$  barrels. If fully utilized, oil from shale could supply Australia's liquid fuel needs for hundreds of years. The continuing fall in world oil prices, and its oversupply, has recently led to lessening of interest in the exploitation of oil shale. However, the continuous supply of petroleum depends on the fragile political stability of the Middle East, an interest in oil shale could re-kindle literally overnight. Experts believe that oil from shale would be Australia's cheapest alternative liquid fuel.

Producing oil from shale simply involves heating the crushed shale in a retort to decompose the organic matter ("kerogen"). A viscous oil then distils over together with the water in the shale. The oil is then hydrogenated before presentation to an oil refinery. To make the process economic, at least  $0.5 \times 10^6$  tonnes per day of shale will have to be processed and retorted. Because the shales on the Queensland coast contain 10-20% water, 50,000 to 100,000 tonnes of retort water will be produced each day. The retort waters contain a range of sulphur compounds, arsenic, selenium, mercury, phenols, amines, and polycyclic aromatic hydrocarbons. They would represent a serious environmental hazard if released to the environment. Other potential sources of water pollution are run-off waters from the huge piles of oil shale and spent (i.e. retorted) shale. These run-off waters contain leached heavy metals and a range of organic compounds.

Procedures are being planned to contain or process these oil shale waste waters, but it will be a formidable task because of the magnitude of the operation. The situation of some of the most important deposits on the coast, and opposite the centre of the Great Barrier Reef, will pose some very sensitive environmental problems for the industry.

POLYCHLORINATED BIPHENYLS AND ORGANOCHLORINE COMPOUNDS IN  
GREAT BARRIER REEF BIOTA

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With the support of MS and T funding we have been investigating PCB contamination of Australian marine biota sampled from various areas mainly in Port Phillip Bay, Bass Strait, the Great Barrier Reef and the Gulf of Carpentaria.

Samples from the GBR have included sharks, coral trout, sea cucumbers, small fish (Lutjanus spp), clams, soft corals and one dugong. After extraction using a high-speed blender and clean up on a florisil column samples are run through an HP 5880 g.c. equipped with a 30 m glass capillary column. The standards used include a range of PCBs (Aroclors) and common organochlorine pesticides such as DDT and Lindane. (In our earlier work, pre-1983, we used an extensive clean-up procedure using an acetic acid-chromic oxide digest to remove DDT and its derivatives).

Olafson surveyed corals, fish and molluscs in the GBR during 1976-1977 and did not detect PCBs but Lindane was present in some samples.

We have detected PCBs in all biota analysed from the GBR. We also find Lindane (thus confirming Olafson's results) and consistently detect pp' DDT, pp' DDE and many other organochlorines as yet not identified.

Apart from reef sharks the concentrations of PCBs in the GBR biota are similar to or less than the concentrations found in biota sampled from non-polluted environments in the northern hemisphere.

Sharks from the reef contain an average concentration of 35.8 ng PCB g<sup>-1</sup> wet weight of muscle tissue and the range of values is from 6.5 to 85.8 ng g<sup>-1</sup>. These values approach the range for biota sampled from more contaminated waters. Unfortunately we have not yet been able to sample for PCBs in sharks from such environments. The high concentrations we find in GBR sharks may not indicate pollution but rather bioaccumulation in carnivores at the top end of a food chain.

Recently we have sampled two groups of primary producers in the GBR - clams and soft corals. They accumulate PCBs and many pesticides not normally detected in fish.

The main factor now limiting our research is the lack of analytical resources, in particular unlimited access to a GC-MS, to identify the many unknown organochlorine compounds we have detected.

## CHEMISTRY AND CHARACTERISATION OF PCBs

D. Hawker - Griffith University

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Technical PCB samples invariably contain a complex mixture of some of the 209 theoretical chlorinated biphenyl isomers. The distribution of chlorine substituents is due to both chemical and statistical directive effects. Thus the commercial products with trade names such as "Aroclor" are graded mixtures of these chlorinated isomers. Contaminants in these materials, byproducts of the manufacturing process such as the chlorinated dibenzofurans, which are structurally related to the dibenzodioxins may in fact be more toxic than the PCBs themselves.

PCBs are most often detected by gas chromatographic or GC-MS techniques. GC-MS spectra are presented for several commercial PCB samples. The extent of chlorine incorporation is easily deduced for each GC peak, but the isomeric identity is somewhat more difficult to determine. The primary ion mass spectra of most PCB isomers are quite similar with successive losses of Cl from the molecular ion which in almost all cases is the base peak. (The isotopic cluster pattern of this ion is diagnostic with respect to chlorine content.) The similarity in mass spectra of isomers suggests randomization of chlorine over the phenyl rings in the molecular ion prior to fragmentation. Isomer identification is important in quantitative studies due to the variable detector responses of PCBs.

## BEHAVIOUR OF PCB's IN MARINE ECOSYSTEMS

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Polychlorinated biphenyls (PCB's) have been detected in both the abiotic and biotic components of the Brisbane River estuary (see Table 1). Maximum average concentrations were detected in the muscle tissue of pelican ( $8.2 \text{ mg kg}^{-1}$ ), gull ( $2.6 \text{ mg kg}^{-1}$ ) and catfish ( $2.1 \text{ mg kg}^{-1}$ ), while sediments and water had concentrations up to  $0.10$  and  $0.06 \text{ mg kg}^{-1}$  respectively. Biomagnification was shown not to be a significant factor controlling PCB concentrations in the organisms investigated, except in pelicans and gulls. In these cases, estimates of uptake from food sources indicated that biomagnification could be the major process involved. Metabolism or excretion was also found to influence the observed PCB composition of these organisms. Field and laboratory data indicated that, with some benthic organisms, sediment concentrations were the major influence on body concentrations of PCB's, and a direct relationship between body concentration and the log of sediment concentration was established. Further laboratory experiments indicated that the uptake of individual PCB's was influenced primarily by two factors: the partition coefficient of n-octanol to water ( $p$ ), and stereochemical effects. A direct relationship between uptake and the product of  $\log p$  and the steric effect coefficient was demonstrated. Thus, maximum uptake was found with penta- and hexachlorobiphenyls, predominant in Arochlor 1254. Comparatively less uptake was found with di-, tri- and tetrachlorobiphenyls (Arochlor 1242), which have lower values for  $\log p$ , and hepta- and octachlorobiphenyls, predominant in Arochlor 1260, which have lower steric effect coefficients.

Further work on the bioaccumulation of PCB's by mullet and polychaetes has shown that it is influenced by two factors: (i) partition behaviour, quantitatively measured by the partition coefficient between 1-octanol and water ( $p$ ), and (ii) the adsorption characteristics of the PCB's onto a surface, estimated by chromatographic elution time on carbon, and also by application of coefficients for chlorines in different substitution patterns giving a steric effect coefficient (SEC). The combination of these two factors, as  $\log p \times$  elution time or  $\log p \times$  SEC, gives a measure which is highly correlated with bioaccumulation.

Table 1. Total PCB concentrations and trophic data for organisms<sup>A</sup> from the Brisbane River

Species and No. analyses	Average concn of PCB corresponding to Arochlor 1260 (mg kg <sup>-1</sup> )	
	Wet basis	Lipid basis
Mussel, <i>Mytilus coruscus</i> Gould(2)	0.1	23
Sea Mullet, <i>Mugil cephalus</i> Linnaeus (15)	0.5	16
Polychaete, <i>Capitella capitata</i> Fabricius (20)	0.2	10
Sleepy crab, <i>Sesarma erythroductyla</i> Hess (19)	0.1	5
Fiddler crab, <i>Uca</i> sp (2)	0.2	46
Striped butterflyfish, <i>Selenotica multifasciata</i> Richardson (1)	0.04	4
Mud crab, <i>Heliograpsus haswellianus</i> Whitelegge (1)	0.1	38
Whiting, <i>Sillago ciliata</i> Cuvier (2)	0.5	25
Bony bream, <i>Menatolosa come</i> Richardson (2)	0.2	27
Oyster blennie, <i>Petroscirtes anolius</i> Cuvier & Valenciennes(5)	0.3	15
Catfish, <i>Neosaurus australis</i> Gunther (1)	0.3	15
Gull, <i>Larus novahollandiae</i> Stephens (3)	2.1	16
Stilt, <i>Himantopus himantopus</i> Linnaeus (1)	2.6	58
Flathead, <i>Platycephalus fuscus</i> Cuvier & Valenciennes(1)	0.3	9
Pelican, <i>Pelecanus conspicillatus</i> Temminck (6)	0.1	41
	8.2	170

<sup>A</sup>Identifications confirmed by the Queensland Museum.

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BEHAVIOUR OF LIPOPHILIC COMPOUNDS IN AQUATIC ECOSYSTEMS

by D. Connell - Griffith University

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The objectives of this investigation include:

1. To establish the physicochemical properties of lipophilic compounds which influence the bioaccumulation of lipophilic compounds by aquatic organisms, e.g. log p, stereochemistry,  $1/2$  life, etc.
2. To evaluate abiotic environmental factors which influence bioaccumulation, e.g. environmental concentration and form.
3. To evaluate the importance of ecological factors in bioaccumulation, e.g. biomagnification.



ALKANE AND MONO-OLEFIN HYDROCARBONS  
IN GREAT BARRIER REEF ORGANISMS AND ENVIRONMENT

by Mike Coates - Griffith University

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Hydrocarbons in surface sediments, water and the same suite of seven species from widely separated coral reefs in the Great Barrier Reef area were analysed by gas chromatography, and by gas chromatography coupled with mass spectrometry. The hydrocarbons found were substantially of biogenic origin. In nearly all samples, the concentrations of resolved hydrocarbons were low, in comparison with baseline studies in other regions. The major hydrocarbons were *n*-pentadecane, *n*-heptadecane, pristane and mono-olefins based on heptadecane and were believed to originate from benthic algae and phytoplankton. There was no evidence to suggest that lipid content, body weight and trophic level had any influence on hydrocarbon content. The organisms and sediments have characteristic patterns of hydrocarbons which would be altered by even small inputs of petroleum hydrocarbons. An unresolved complex mixture (UCM) in chromatograms, usually considered indicative of petroleum contamination, was found in greater than trace amounts only in Holothuria (sea cucumber), Acropora (coral) from the Capricorn Group and in some sediment samples from the Capricorn Group and Lizard Island area.

## OIL POLLUTION AND POLYCYCLIC AROMATIC HYDROCARBONS

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The work of this laboratory has been directed to studying the distribution of polycyclic aromatic hydrocarbons (PAH) in the reef ecosystem. On the global scale, PAH are introduced into the marine environment mainly as products of combustion of fossil fuels. The PAH are also minor components of crude oil, and are present at higher concentrations in oil products because of formation during high-temperature processing. On the local scale, input of PAH from oil and oil-products can exceed that from combustion products. In these conditions the PAH are useful as indicators of oil pollution. The PAH are important compounds as some are toxic or carcinogenic, and some are on the list of USEPA Priority Pollutants

We are developing methods for the measurement of aromatic hydrocarbons in natural waters with the aim of identifying the sources of oil, and allowing a quantitative assessment of levels of oil pollution.

### POLYCYCLIC AROMATIC HYDROCARBONS

#### 1. Tissues

PAH in tissues of the clam Tridacna maxima have been measured. Eight PAH compounds were detected and measured. Limits of detection ranged from 0.003 ug/kg for B(k)F to 0.1 ug/kg for B(ghi)P. Measurable concentrations of PAH were found only at locations frequently visited by boats.

#### 2. Sediments

PAH in sediments from Townsville and Gladstone harbours were shown to be present at concentrations similar to those reported in other harbours round the world. Despite the presence of high concentrations of PAH in these sediments, the sediments from the reef appear to be unaffected, with measurable PAH only in areas of boating activity. Seven PAH were found, with limits of detection ranging from 0.001 ug/kg for B(k)F to 0.1 ug/kg for fluoranthene. Levels of pyrene found range from 3000 ug/kg in Townsville Harbour to below the limit of detection on John Brewer Reef. Generally, John Brewer Reef sediments are at least five orders of magnitude lower in PAH than the Townsville Harbour sediments.

#### 3. Waters

PAH in waters from the busy resort of Green Island were measured. There are very few reports of PAH in marine waters, making assessment of the significance of these levels difficult, but there appears to be significant contribution from boating activity and possible from the sewage discharge.

## OIL POLLUTION

We have developed a technique for measuring the level of oil pollution in waters based on fluorescence analysis. Application to waters of Port Phillip Bay used emission spectra for quantitative measurements, with observed concentrations based on *m*-terphenyl equivalents, and synchronous fluorescence spectra for identification of the fluorescent material. The relative fluorescence intensity originating from compounds containing different numbers of fused aromatic rings is measured. Waters round Green Island were analysed using synchronous fluorescence spectra for quantification and identification. The waters round Green Island contained concentrations of fluorescent materials similar to those observed in Port Phillip Bay.

This method uses a sampler which minimises sample contamination but which is inexpensive. Solvent extraction using dichloroethane is simple, synchronous fluorescence is rapid, and the method is calibrated using the pure compound *m*-terphenyl. The procedure is suitable for extensive surveys and comparative studies, and is designed for use in determining the extent of the invisible halo of dissolved oil round the visible slick resulting from any oil spill.

GLOSSARY OF ABBREVIATIONS

DDT	Dichlorodiphenyl trichloroethane
FAO	Food and Agriculture Organisation (U.N.)
GC	Gas Chromatograph
GEMS	Global Environmental Monitoring System
GBR	Great Barrier Reef
GBRMPA	Great Barrier Reef Marine Park Authority
IOC	Intergovernmental Oceanographic Commission
IAEA	International Atomic Energy Agency
MS	Mass Spectrometer
NBS	National Bureau of (Biological) Standards
OECD	Organisation for Economic Cooperation and Development
PCB	Polychlorinated Biphenyl
PAH	Polycyclic Aromatic Hydrocarbons
WQC	Water Quality Council (of Queensland)
SEC	Steric Effect Coefficient
UCM	Unresolved Complex Mixture
UNEP	United Nations Environment Program
USEPA	United States Environmental Protection Agency